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## High resolution multi-annual riverine fluxes of organic carbon, nutrient and trace element from the largest European Arctic river, Severnaya Dvina

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2 **High resolution multi-annual riverine fluxes of organic carbon, nutrient and**  
3 **trace element from the largest European Arctic river, Severnaya Dvina.**

4

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15

16 *Novelty statement:* Historical and contemporary measurements of element fluxes in the largest  
17 European Arctic river did not reveal sizeable changes in discharge and DOC, DIC, Ca, Mg, Fe,  
18 Si, SO<sub>4</sub>, Cl concentrations and fluxes over past >60 years.

19

20 **Bullet points**

- 21 • High resolution export fluxes of DOC, major and trace element (TE) in the largest  
22 European Arctic river  
23 • Soluble highly mobile elements exhibited minimal concentrations in spring and  
24 maximal concentrations in winter  
25 • Trivalent and tetravalent TEs and organically bound metals showed a maximum at the  
26 spring flood peak  
27 • There is no statistically significant trend in element export fluxes since the beginning of  
28 observations (1930<sup>s</sup>)  
29 • Chemical runoff in the European Russian Arctic exhibits high inter-annual variability,  
30 which greatly exceeds any possible long-term trend  
31

32

33

34 **Abstract**

35 Assessing multi-annual riverine export fluxes of carbon, nutrients and metals from the continent to  
36 the Arctic Ocean is crucial for constraining the current status and foreseeing future changes in  
37 riverine export induced by climate change. Over 3 consecutive years (2012-2014), we measured  
38 daily to weekly concentrations of C, N, P, all major and 45 trace elements (TE) in filtered (< 0.45  
39  $\mu\text{m}$ ) river water at the terminal station of Severnaya Dvina, the largest European Arctic river,  
40 gauged since 1882. There were 3 main groups of elements according to their seasonal behavior,  
41 demonstrating distinct links between concentration and the discharge. Dissolved Inorganic Carbon  
42 (DIC), major anions (Cl,  $\text{SO}_4$ ), alkali and alkaline-earth elements (Li, Na, Mg, K, Ca, Rb, Sr, Ba),  
43 and oxyanions (B, Mo, Ge, As) and U exhibited minimum concentrations during spring flood and  
44 autumn high flow events, being significantly ( $p < 0.01$ ) negatively correlated with discharge and  
45 dissolved organic carbon (DOC) concentration. These elements reflected the dominant lithology  
46 of Severnaya Dvina watershed (carbonates, gypsum) and were controlled by dilution of  
47 underground (baseflow) influx by floods. The concentration of DOC, low-soluble trace elements  
48 (Al, Ti, Ga, Y, rare earth elements, Zr, Nb, Hf, Th) and organically-bound metals (V, Cr, Co, Ni,  
49 Cu, Cd, Pb) had the maximum at the spring flood peak. The input of these elements to the river  
50 occurred via surface flow and they were significantly ( $p < 0.01$ ) increasing with water discharge.  
51 Finally, N, P, Si, Mn and Fe originated from both surface and underground sources and were  
52 impacted by autochthonous biotic processes in the river channel; they exhibited a strong winter  
53 maximum and a summer minimum.

54 The spring flood (May and June) provided 50% of overall water and DOC, V, Cr, Mn, Fe,  
55 Co, Ni, Cu, Zn, Cd, Sb, and Pb flux and 60% of low-soluble TE (Al, Y, Nb, REEs, Ti, Zr, Hf and  
56 Th). The nutrients (K, Rb, Si, P, N) exhibited around 40% share of annual export during spring  
57 flood, whereas the export of soluble mobile elements (DIC,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , Li, B, Na, Mg, Ca, Sr, Mo  
58 and U) mainly occurred during winter (35-40%) with only 20-25% of annual flow provided by  
59 spring flood.

60 The 3-year mean export fluxes of dissolved components were 30 to 50% lower than (Ti,  
61 Cr, Mn, Fe, Co, Ni, Cu, Zn, Cu, Cd, and Pb) or comparable to ( $\pm 30\%$  for all other elements  
62 including DOC and for DIC) previous estimates of this river from 2007-2008 and the historic data  
63 of major components from 1930-1950. In particular, there was no trend in mean monthly seasonal  
64 and annual concentrations and export fluxes of DOC, DIC, SO<sub>4</sub>, Cl since the beginning of  
65 chemical analysis between 1929 and 1930 and in Ca, Mg, Si, and Fe since the 1950's through the  
66 duration of this study (2012-2014). The lack of seasonal and annual increases in discharge, carbon,  
67 and element concentrations in the permafrost-free Severnaya Dvina River for more than 120 years  
68 of discharge and over 60 years of chemical composition measurements is at odds with the reported  
69 short-term trend (based on measurements that began in 1970s) showing that element export fluxes  
70 increased in other Arctic rivers due to on-going climate warming and permafrost thaw.

71

## 72 **1. Introduction**

73 The importance of boreal and subarctic continental zones in regulating the carbon cycle on  
74 earth stems from the high storage of organic C in soils, the dominance of humid climate  
75 supporting abundant vegetation, and the presence of shallow soils and fresh rocks exposed to  
76 the surface that are capable of taking-up atmospheric CO<sub>2</sub> during weathering (Pokrovsky et al.,  
77 2012b; Olefeld and Roulet, 2014; Fabre et al., 2019). Altogether, these factors yield high  
78 riverine fluxes of both carbon and nutrients from the continent to the Arctic Ocean. Foreseeing  
79 the change of these fluxes from on-going climate warming is one of the major challenges of the  
80 scientific community currently working in the Arctic (Bring et al., 2016; McClelland et al.,  
81 2016). For this reason, major and trace element fluxes in large Arctic rivers have been and are  
82 being actively researched (Gordeev et al., 1996; Tank et al., 2016; O'Donnell et al., 2016;  
83 Kaiser et al., 2017; Griffin et al., 2018).

84 Extreme variations in discharge and chemical element concentration over the course of  
85 a year (Gordeev and Sidorov, 1993; Rember and Trefry, 2004; Yang et al., 2015) are strongly

86 specific to Arctic and subarctic zones. Thus, these zones require higher frequency sampling  
87 compared to temperate or tropical zones (e.g., daily versus weekly), notably during the spring  
88 flood or autumn high flow where sizeable changes in discharge and concentration may occur.  
89 The increase of ionic forms of major cations and anions during winter, under the ice, also  
90 requires regular monitoring (Bagard et al., 2011; Walvoord and Striegl, 2007). This is  
91 especially important given the increase in winter discharge of the Arctic rivers and the decrease  
92 in ice coverage period are well documented over past decades (Brabets and Walvoord, 2009;  
93 Yang et al., 2015).

94 As a result of the difficulties in conducting high-resolution geochemical studies in space  
95 and time for these remote regions, the majority of available geochemical information have been  
96 acquired during the summer-autumn low flow period, which is the easiest time to collect (cf.,  
97 Huh et al., 1998; Huh and Edmond, 1999; Gebhardt et al., 2004; Guieu et al., 1996). Recently,  
98 the fluxes of suspended and dissolved major components of the Arctic rivers became available  
99 thanks to Arctic Great River Observatory program (Cooper et al., 2008; Holmes et al., 2012;  
100 Mann et al., 2016; McClelland et al., 2016). In each watershed, the flux was calculated from  
101 year-round chemical measurements based on regular (weekly or monthly) sampling of river  
102 water; discharges are available either from direct gauging station measurements or via  
103 extrapolation from adjacent gauging stations. However, the sub-Arctic permafrost-free rivers of  
104 Northern Eurasia have not been assessed within the Arctic GRO program  
105 (<https://arcticgreatrivers.org/>).

106 The purpose of this work was to use the largest European Arctic river, Severnaya Dvina,  
107 to elaborate the methodology of seasonal and spatial sampling for rigorous evaluation of annual  
108 carbon, major and trace element flux. Severnaya Dvina represents an unregulated pristine river  
109 draining southern and northern taiga forest of non-permafrost zone. A secondary objective was  
110 to assess climate-change induced long-term variation in discharge and major element fluxes in  
111 this river based on multi-annual observations. One can hypothesize that lack of permafrost thaw

112 and absence of change in groundwater regime in the Severnaya Dvina watershed provide  
113 sizable differences in element export flux trends between Severnaya Dvina and other Arctic  
114 rivers. The Russian Hydrological Survey (RHS) has been collecting data in this river since the  
115 end of of 19<sup>th</sup> century (Derugin et al., 1940; Gordeev et al., 1996; Nikanorov et al., 2010a, b)  
116 and more recently our group collected data 10 years ago (Pokrovsky et al., 2010). The  
117 extremely long time span of physical (discharge, from 1882) and chemical (total dissolved  
118 solids (TDS), total organic carbon (TOC), HCO<sub>3</sub>, SO<sub>4</sub>, Cl, from 1929 and dissolved organic  
119 and inorganic carbon (DOC and DIC, respectively), Ca, Mg, Si, Fe since 1950's) parameters  
120 available for the Severnaya Dvina River makes it unique among all other Arctic rivers by  
121 allowing the ability to examine temporal changes in discharge and hydrochemical fluxes to the  
122 ocean.

123

## 124 **2. Methods**

### 125 *2.1. Study site*

126 The Severnaya Dvina River (watershed area = 357,000 km<sup>2</sup>) is the largest river in the  
127 north of European Russia (**Fig. 1 A**), formed by the confluence of Sukhona and Yug Rivers  
128 (watershed of 50,300 and 35,600 km<sup>2</sup>, respectively), and its largest tributary is the Vychegda  
129 River (watershed = 121,000 km<sup>2</sup>). The basin is located between 58.5°N and 65°N latitude (Fig.  
130 1 A) and has no permafrost development. The discharge of Severnaya Dvina is 110 km<sup>3</sup>/year  
131 which is about 1/3 of the total river flow into the Barents and White Seas. The watershed area  
132 is covered with a thick layer of glacial deposits and is underlain by sedimentary rocks of P-C  
133 age, represented by limestone, dolomite, marl, clays and sandstones. The Pinega tributary  
134 drains through gypsum deposits, subjected to strong karst processes (Malov, 2013). The whole  
135 watershed is located within a taiga biome comprised of spruce, pine, and larch (with forested  
136 area percentages between 80 and 85%, while bog coverage is about 8.5%). The hydrographic  
137 network is well developed; there are 61,900 rivers and streams which combine to a total length

138 of 206,000 km. Given its medium size, low runoff (300 mm y<sup>-1</sup>) and peatland with boreal taiga  
139 landscapes, Severnaya Dvina is representative to other Eurasian Arctic rivers not encompassed  
140 by the Arctic GRO program (Onega, Mezen, and Pechora of European Russia, and, in a lesser  
141 extent, Pur, Taz and Nadym of western Siberia). However, unlike other, permafrost-affected  
142 Arctic Rivers, Severnaya Dvina exhibits two baseflow periods: December to April and July to  
143 August. Two high-water periods include spring flood in May-June and autumn rains occurring  
144 in September-October.

145         Among approximately 1,000 active river discharge monitoring stations in the Russian  
146 Arctic (McClelland et al., 2015) maintained by RHS, the Ust-Pinega gauging station at the  
147 Severnaya Dvina River is one of the oldest one dating back to 1882. Available data include  
148 daily discharges and 5 to 15 analyses per year of TDS, DIC, TOC, Ca, Mg, SO<sub>4</sub>, and Cl (since  
149 1929) as well as more complete chemical data sets including major cations and anions, TOC,  
150 Si, and Fe (since 1950).

151         The mouth zone of the Severnaya Dvina River includes the low reaches of the main  
152 streams from the Pinega River inlet until the sea edge of the delta and SE part of the Dvinskoi  
153 Bay of the White Sea (**Fig. 1B**). The tide-ebb water level fluctuations are not pronounced at the  
154 Pinega River mouth. Based on morphological features of the Severnaya Dvina River mouth  
155 zone, the main observation point was at the border between the near-mouth zone and the delta,  
156 located entirely in the freshwater zone (**Fig. 1C**). To choose this monitoring point for high  
157 frequency hydrochemical measurements in this study, we used the criteria of easy accessibility  
158 from the laboratory and its ability to represent a terminal gauged station of the river. For this,  
159 extensive sampling of the low reaches of the Severnaya Dvina River at the beginning of its  
160 delta till the Dvina Bay was conducted at the end of summer baseflow (**Fig. 1C**). It is expected  
161 that spatial differences in element concentrations will be mostly pronounced during low water  
162 level, when there is sufficient underground feeding and maximal biotic activity. According to  
163 the results of three-year surveys, variations in DOC, DIC, and all major element concentrations

164 in waters within the Northern Dvina River area did not exceed 5%. The normality of element  
165 concentrations distribution was tested using histogram construction and a Shapiro-Wilk test  
166 (SW-W test). The  $p$  criterion of significance for chloride (most indicative for seawater and  
167 underground water influence) were equal to 0.0045, 0.0554 and 0.1955, in 2012, 2013, and  
168 2014, respectively. The analyses demonstrated that  $p(\text{SW-W test}) > 0.01$  and as such, for  
169 normal data distribution, the parametric statistics could be used. The t-test demonstrated that 38  
170 parameters of water chemistry, obtained from the monitoring point, can be used for calculating  
171 annual fluxes of the whole delta of the Severnaya Dvina. Note that there is no impact of the city  
172 of Arkhangelsk on trace element concentrations at the monitoring station which is 500 m  
173 offshore (Pokrovsky et al., 2010).

174 The seasonal patterns of temperature (T) and precipitation (P) at the mouth zone of the  
175 Severnaya Dvina River are given in **Fig. 2 A**, whereas the comparison of T and P in 2012,  
176 2013, and 2014 with mean multi-annual values of two periods—1892 to 1978 and 2001 to  
177 2011—is illustrated in **Fig. 2 B**. Over 3 years of observations, both temperature and  
178 precipitation were similar to the long-term average values, although inter-annual variations  
179 sizably exceeded any long-term systematic differences, especially during summer periods.

180

## 181 *2.2. Sampling and analyses*

182 Between 2012 and 2014, during the spring flood (May) we sampled the river every 1-2  
183 days, whereas during summer, autumn and winter baseflow we sampled weekly. Altogether, 65  
184 samples during spring flood and 40 samples during baseflow were collected. Additionally, at  
185 the chosen monitoring station, we sampled every three hours in order to assess diurnal variation  
186 of dissolved components during spring flood (12 samples during 2 days) and summer baseflow  
187 (13 samples during 1.5 days) under stable anticyclone conditions (no rain for 5 precedent days).  
188 For baseflow, we have chosen the end of summer (1-2 September 2013) because this is the  
189 period of most contrasting day/night pattern at 64°N due to the daylight cycle and high



190 productivity of planktonic biota. Water samples were collected 200 m offshore from 0.5 m  
191 depth in pre-cleaned polypropylene bottles and were immediately filtered through sterile, single  
192 use Minisart® filter units (Sartorius, acetate cellulose filter) with a pore size of 0.45 µm.  
193 Dissolved O<sub>2</sub> level and temperature were measured in situ with the Oxi 197i oximeter (WTW,  
194 Germany) with a Cellox 325 submersible sensor (WTW, Germany; ± 0.5% and ± 0.2 °C  
195 uncertainty, respectively). The conductivity and pH were measured on site using a Hanna  
196 HI991300 conductivity meter and a WTW portable pH meter with combined electrode. Filtered  
197 water samples for nutrient (N, P) analyses were frozen (−20 °C) within 1–3 hours of collection  
198 and analysed within 1 week after sampling.

199         DOC and DIC concentrations were measured using methods used in the Géosciences  
200 Environment Toulouse (GET) laboratory to analyze boreal water samples (Pokrovsky et al.,  
201 2012a, Shirokova et al., 2013). Note that high DOC concentration in the Severnaya Dvina  
202 River did not allow freezing and acidification of filtrates as it could have caused flocculation.  
203 Pyrolyzed (2.5 h at 550 °C) glassware was used for sample collection and storage. In winter,  
204 the DIC concentration was obtained from alkalinity following a standard HCl titration  
205 procedure using an automatic Titro-Line alpha TA10plus titrator (Schott®, Germany) with an  
206 uncertainty of ±2% and a detection limit of  $5 \times 10^{-5}$  M. During spring flood and summer, when  
207 DOC is higher than 10 mg L<sup>-1</sup>, DIC was measured by a Shimadzu® TOC-VCSN (acid addition  
208 without combustion), with a detection limit of 0.01 mM and uncertainty of 5%. The agreement  
209 between the two methods of DIC analysis was within 10%. Major anion concentrations (Cl and  
210 SO<sub>4</sub>) were measured by ion chromatography (Dionex ICS 2000) with an uncertainty of 2%.  
211 Internationally certified water samples (ION-915, MISSISSIPPI-03, RAIN-97, DES, 2018)  
212 were used to check the validity and reproducibility of of analysis. Good agreement between our  
213 replicated measurements and the certified values was obtained (relative difference < 10%).  
214 DOC was measured using a Shimadzu TOC-VCSN with an uncertainty of 5% and a detection

215 limit of 0.1 mg L<sup>-1</sup>. The DOC blanks of filtrate never exceeded 0.1 mg/L which is quite low for  
216 the organic-rich river waters sampled in this study (i.e., 5–30 mg/L DOC).

217 Nutrient (N, P) analyses were based on colorimetric assays (Koroleff, 1983a, b). Total  
218 dissolved organic nitrogen (DON) was measured from the difference between the total  
219 dissolved nitrogen (persulfate oxidation) and the total dissolved inorganic nitrogen (DIN, or the  
220 sum of NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>). Uncertainties of DON and DIN analyses were between 10 and  
221 20 % and detection limits were between 10 and 50 µg/l. Filtered solutions for cation analyses  
222 were acidified (pH ~ 2) with ultrapure double-distilled HNO<sub>3</sub> and were stored in pre-washed  
223 high-density polyethylene (HDPE) bottles. The preparation of bottles for sample storage was  
224 performed in a clean bench room (International Organization for Standardization (ISO), A  
225 10,000). Blanks were performed to control the level of pollution induced by sampling and  
226 filtration. Major cations (Ca, Mg, Na, K), Si, and trace elements were determined with an  
227 inductively coupled plasma mass spectrometry (ICP-MS) Agilent ce 7500 with In and Re as  
228 internal standards. We used 3 external in-house standards, which were placed after each 10  
229 river water samples. The Riverine Water Reference Material for Trace Metals (SLRS-5,  
230 certified by the National Research Council of Canada) was used to check the accuracy and  
231 reproducibility of analyses (Yeghicheyan et al., 2014). Further details of trace element analysis  
232 in the Severnaya Dvina river water are given elsewhere (Pokrovsky et al., 2013).

233

### 234 *2.3. Historical data on discharges and element concentration in the Severnaya Dvina River*

235 The main source of historical information for calculating riverine fluxes of dissolved  
236 and suspended material to the Arctic Ocean are data of the Russian Hydrological Survey,  
237 collected at the Ust-Pinega gauging station by standard procedures (Gordeev et al., 1996;  
238 Nikanorov et al., 2010a,b; Magritsky, 2010). These data comprise the daily discharge (water  
239 level) and several (typically 5 to 15 measurements per year) of dissolved load. Since both  
240 sample handling procedure and chemical analysis adopted by RHS differ from those used for

241 river water sample processing in this study, a calibration of RHS data with independent  
242 sampling, filtration, and analysis is often required. Examples include assessment of nutrient  
243 transport to the Arctic Ocean by Siberian (Gordeev et al., 1996; Holmes et al., 2000) and  
244 European rivers (Leonov and Chicherina, 2004), and major elements and organic carbon flux  
245 measurements in both permafrost-free (Pokrovsky et al., 2010) and permafrost-bearing regions  
246 (Pokrovsky et al., 2005; Cooper et al., 2005; Frey et al., 2007; Drake et al., 2018). While for the  
247 nutrients (N, P), rigorous procedure of sampling, filtration, storage and analysis is mandatory,  
248 the major cations and anions (Ca, Mg, Cl, SO<sub>4</sub>, HCO<sub>3</sub>), Si and organic carbon can be  
249 adequately (i.e., within 10-20%) approximated by available RHS data.

250 Water sampling and analysis methods of RHS used for assessing long-term trends in  
251 this study are described elsewhere (Semenov, 1977; Gordeev and Sidorov, 1993; Zakharova et  
252 al., 2005, 2007; Pokrovsky et al., 2005). Briefly, the RHS water samples were filtered through  
253 0.8 µm paper filters. Si, Fe, and SO<sub>4</sub> were determined by spectrophotometry with molybdenum  
254 blue with a detection limit of 3 µg/L, oxiquinoline with a detection limit is 5 µg/L, and BaCl<sub>2</sub>  
255 with a detection limit of 100 µg/L, respectively. The uncertainty in these Si, Fe, and SO<sub>4</sub>  
256 measurements are ±5%. Dissolved organic matter concentration was determined via  
257 permanganate oxidation (PO) in an acidic medium (Semenov, 1977) and expressed as grams of  
258 oxygen per liter. An average conversion coefficient of 1.05±0.05 was used to relate PO and  
259 Total Organic Carbon (TOC) in the river water of the boreal tundra and taiga zone (Maltzeva et  
260 al., 1977). This conversion is comparable to that used in Finland Hydrochemical surveys  
261 (Lepistö et al., 2008). The agreement between the “traditional” chemical analyses used by RHS  
262 and modern “certified” methods used in this study was shown to be within ±10% for major  
263 anions (Cl, SO<sub>4</sub>), cations (Ca, Mg), DIC (alkalinity), Si and organic carbon as demonstrated in  
264 previous works of our group (Zakharova et al., 2005, 2007; Pokrovsky et al., 2005, 2010,  
265 2012b; Prokushkin et al., 2011; Kolosov et al., 2016) and other researchers (Drake et al., 2018).

266 Daily discharges for Severnaya Dvina River were obtained from the ROSHYDROMET  
267 for 2006–2015. Long-term (1939–1995) monthly discharges are available from the R-ArcticNet  
268 Database ([www.r-arcticnet.sr.unh.edu/v4.0/main.html](http://www.r-arcticnet.sr.unh.edu/v4.0/main.html)). Historic data for discharges are  
269 available since 1882, where as TDS, DIC, TOC, Ca, Mg, SO<sub>4</sub>, and Cl concentrations in the  
270 Severnaya Dvina River were collected by the State Service of Hydrometeorology and  
271 Environment Monitoring (then USSR) from 1929.

272

#### 273 *2.4. Statistical treatment of original and historical data and methods of flux calculation*

274 Element export fluxes were calculated based on measured discharge and concentrations  
275 from 2012-2014. This included daily sampling during spring flood and weekly sampling during  
276 the remainder of the year. We used measured discharge (41 measurements over 2012-2014) and  
277 daily water level measured at the Ust-Pinega station. A linear dependence between discharges  
278 at the Ust-Pinega station and Arkhangelsk mouth zone allowed calculation of mean daily  
279 discharges at the sampling point where average uncertainty was 1.3%. Daily concentrations  
280 were either measured directly, during high water period (frequency of 1 to 3 days) or calculated  
281 via linear interpolation (in case of missing values for certain periods). Based on these data, we  
282 first estimated daily load (mass of component day<sup>-1</sup>) obtained from a time series of paired river  
283 flow and constituent concentration data. Then, the area-normalized element exports were  
284 expressed per watershed area (g component km<sup>-2</sup> y<sup>-1</sup>). The ratio of the number of measured and  
285 calculated daily loads was on average 3:1.

286 Comparison of element concentration in river during summer/fall/winter/spring and  
287 different time intervals for which the hydrochemical data were available (1929, 1950-1952,  
288 1963-1972, 1973-1983, 2000-2010, 2012-2014) was conducted using non-parametric H-  
289 criterium Kraskal-Wallis test, which is suitable for analysis of such data (Grimvall et al.,  
290 1991). For this, we used median and interquartile intervals (25-75%). The use of non-  
291 parametric criteria was necessary because the historical data set obtained from diferent sources

292 is nonuniform and restricted in size. Concentrations of certain elements were lacking during  
293 certain periods (e.g., Ca, Mg, Fe and Si in 1929-1930). To avoid bias linked to non-  
294 homogeneity of sampling over seasons, we used 10-year mean multi-annual (10 year-interval)  
295 seasonal concentration values. A multivariate extension of the nonparametric Mann-Kendall  
296 rank test was used for detecting trends of element concentration and discharge. Because of the  
297 high seasonal variation in water chemistry - time series, trend tests were performed separately  
298 for each season (winter, December-April; spring, May-June; summer, July-September, and  
299 autumn, October-November).

300 Mean monthly and annual discharges were available from 1882 through July 2015,  
301 which allowed for testing the trends and/or changes over 132 years of monitoring. For this, we  
302 used Mann-Kendall statistic (HydroGeoLogic, Inc). Annual element fluxes were estimated  
303 similar to LOADEST method (<https://water.usgs.gov/software/loadest/>, Holmes et al., 2012)  
304 from calculated daily element loads. The latter were obtained from a calibration regression,  
305 applied to daily discharge from RHS. The calibration regression was constructed from time  
306 series of paired streamflow and measured element concentration data for 2012-2014. According  
307 to available historical data, the concentrations of Ca, Mg, SO<sub>4</sub>, HCO<sub>3</sub>, Cl and TOC demonstrate  
308 a strong power dependence on water discharge. Because this dependence was valid over the  
309 full period of observations, it was used for the estimation of mean multi-annual concentrations.  
310 For this purpose, measured data for a given period of observation were used to generate the  
311 coefficients  $k$  and  $n$  in equation 1

$$C_i = k \cdot Q_i^n \quad (1)$$

312 where  $C_i$  represents measured ion concentration for a given day of the year,  $Q_i$  is water  
313 discharge for this day,  $k$  and  $n$  are empirical constants for each element. Examples of  $C$  vs  $Q$   
314 dependence for dissolved components over full period of observation are given in **Fig. S1 of**  
315 **Supplement**, where data spanning 1929 to 2014 are presented. Based on Eqn. 1, mean multi-  
316 annual concentration were calculated for considered periods. A similar method was used for

317 estimation of mean monthly and annual concentrations of dissolved elements in rivers of the  
318 Lena Basin (Gordeev and Sidorov, 1993), the Karelian rivers of the White Sea basin  
319 (Zakharova et al., 2007), and the Transbaikal region (Zakharova et al., 2005).

320

### 321 **3. Results**

#### 322 *3.1. High-frequency seasonal and annual fluxes*

323 Diurnal variations of main hydrochemical parameters of the Severnaya Dvina River  
324 were conducted in spring and summer baseflow. The spring flood period sampling did not  
325 demonstrate any sizeable (< 10%) variations on all major and trace components whereas the  
326 summer basflow sampling yielded  $\leq 10\%$  variations of all components including DIC, DOC,  
327 major and trace elements, except Fe, Si (ca. 20-25% difference between day and night) and Mn  
328 (up to 40% difference) as shown in **Fig. S2** of the **Supplement**. These variations were not  
329 linked to O<sub>2</sub>, temperature, pH, and specific conductivity regime. Only concentrations of Fe and  
330 Mn anti-correlated with river water level (significant at  $p < 0.005$ ) due to ebb-tide alterations  
331 (not shown). The change in water level controls the extent of groundwater/riparian zone  
332 discharge to the main stream from the coastal waterlogged areas where sizeable reduction of Fe  
333 and Mn may occur. Overall, our results demonstrate that snapshot sampling during any time of  
334 the day in such a big river is representative for at least a 1-2 day interval in high flow and a 3  
335 day period in base flow. Accordingly, we designed the frequency of sampling depending on the  
336 water level stage.

337 The 3-year average monthly and annual discharges, concentrations, and fluxes of all  
338 dissolved components are listed in **Table S1** of the Supplement. According to element  
339 correlation with DOC over full period of our observations, 3 groups could be distinguished  
340 based on the Kendall Tau correlation coefficients (**Table S2** of the Supplement). The 1<sup>st</sup> group  
341 exhibited strongly negative correlations with DOC (and discharge) and comprised S.C., DIC,  
342 Cl, SO<sub>4</sub>, B, Ca, Mg, Sr, Ba, Li, Na, K, Rb, Ge, Mo and U as illustrated in **Fig. 3** for SO<sub>4</sub> and B.

343 The components of 2<sup>nd</sup> group positively correlated with DOC and included Al, Ga, Y, REEs,  
344 Ti, Zr, Hf, Th, Be, Cr, Cu, Ni, Pb, V and Nb, illustrated in **Fig. 3** for Al and Th. The 3<sup>rd</sup> group  
345 of components (As, Cd, Co, Cs, Fe, Mn, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>tot</sub>, NH<sub>4</sub>, pH, PO<sub>4</sub>, P<sub>tot</sub>, Sb, Si, Sn, Te, W  
346 and Zn) exhibited either weak or no relationship with DOC; the nutrients (N, P, Si, Fe, Mn) had  
347 weak negative or positive correlations with DOC and were strongly enriched in winter and  
348 depleted in summer, as shown in **Fig. 3** for Fe and N-NO<sub>3</sub>.

349 The variations in DOC and DIC concentrations were in opposition (**Fig. 4**). The  
350 average annual concentration of DOC and DIC were equal to 12±3 and 23±5 mg/L,  
351 respectively. The annual riverine load into the White Sea was equal to 1.50±0.34 and 1.52±0.08  
352 Tg of DOC and DIC, respectively. Based on three year continuous monitoring, we calculated  
353 mean multi-annual export fluxes of all major and trace dissolved components of the Severnaya  
354 Dvina River during the period of observation from 2012 to 2014 as listed in **Table 1**. The 3-  
355 year mean annual distribution of export fluxes among four hydrological seasons in percent of  
356 annual flow was also calculated (**Table 2**).

357 The spring flood (May-June) provided 50% of overall discharge and flux of DOC and  
358 organically-bound metals (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, Sb, and Pb) and 60% flux of  
359 low soluble TE (Al, Y, REEs, Nb, Ti, Zr, Hf, and Th). The nutrients (K, Si, PO<sub>4</sub>, P<sub>tot</sub>, NO<sub>3</sub><sup>-</sup>, and  
360 NH<sub>4</sub><sup>+</sup>) and trace elements - analogous of macronutrients (Rb and Ge) exhibited around 40% share  
361 of annual export during spring flood, whereas the export of soluble highly mobile elements (DIC,  
362 Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Li, B, Na, Mg, Ca, Sr, Mo, and U) mainly occurred during winter (35-40%) with only  
363 20-25% of annual flow occurring in spring.

364 The dependence of element concentration on river discharge allowed to distinguish  
365 three main groups of elements. First, the DIC, major anions (Cl, SO<sub>4</sub>), alkali and alkaline-earth  
366 elements (Li, Na, Mg, K, Ca, Rb, Sr, Ba), oxyanions (B, Mo, Ge, As) and UO<sub>2</sub><sup>2+</sup> exhibited  
367 minimum concentrations during spring flood and autumn high flow and maximal concentrations  
368 during winter and summer baseflow, being negatively correlated with discharge (**Fig. 5**). Second,

369 the DOC, low-soluble TE (Al, Ti, Ga, Y, Be, Nb, Zr, REEs, Hf, and Th) and some metals having  
370 high affinity to organic matter (V, Cr, Co, Ni, Cu, Cd and Pb) exhibited maximal concentrations  
371 during peak of spring and autumn flood, and they positively correlated with river discharge (**Fig.**  
372 **6**). Finally, small number of elements, essentially nutrients, exhibited features of the 1<sup>st</sup> and 2<sup>nd</sup>  
373 group but did not show statistically significant linkage to discharge on the annual scale. For  
374 example, Si, NO<sub>3</sub>, and Mn demonstrated one maximum at the end of winter and one minimum in  
375 summer (July-August), **Fig. 7 A-C**. The Fe showed two maxima of concentration, one at the end  
376 of spring flood in June and another at the end of winter (March to April) at the minimal flow under  
377 ice (**Fig. 7 D**).

378

### 379 *3.2. Historical trends in the Severnaya Dvina River discharge and hydrochemistry*

380 Historical data for discharge in Severnaya Dvina were collected since 1882 which is  
381 unique for Arctic rivers. We used mean monthly values of river discharge at the Ust-Pinega  
382 gauging station to calculate the dependence of mean monthly discharge for the year of  
383 observation (**Fig. 8 A**). We then calculated the slope of the Q - year dependences in m<sup>3</sup> s<sup>-1</sup> y<sup>-1</sup>  
384 (**Fig. 8 B**). Based on Mann Kendallll statistical trend over full data set, the monthly trends in  
385 discharge of Severnaya Dvina were either absent or located within the uncertainty range (**Table**  
386 **S3**). Only spring flood and summer baseflow demonstrated statistically significant decrease in  
387 discharge (negative values). Other seasons did not show any sizeable trend or the trend was  
388 within the uncertainty.

389 Mean seasonal decadal and multi-annual concentrations of Ca, Mg, HCO<sub>3</sub>, SO<sub>4</sub>, Cl,  
390 TOC, Si, and Fe between 1929 and 2014 in the Severnaya Dvina River are illustrated in **Fig. 9**.  
391 The mean fluxes of dissolved components over the historical period of observation are shown  
392 in **Fig. 10**. Note that the Mann-Kendall statistical test such as that used for analyzing the long-  
393 term discharge data (**Table S3**) is not suitable for chemical composition data due to too few  
394 measurements and sizeable gaps of observations during some periods. Nevertheless, it can be



395 seen that, within  $\pm 30\%$  variation, there is no change in DOC, DIC, Ca, Mg, Si, Fe, SO<sub>4</sub>, and Cl  
396 concentrations and fluxes when comparing the 10-years average values from 1950 through 2002  
397 made by RHS and those from 2013 through 2015 collected by our group for this study.

398 The winter-time concentrations of all dissolved components of Severnaya Dvina were also  
399 very stable over the past 65 years without any significant trend over time. Furthermore, several  
400 inorganic components of the river water measured since 1929 such as DIC, Ca, Mg, SO<sub>4</sub>, and Cl  
401 did not demonstrate any sizeable change in average annual concentrations and/or in the pattern of  
402 dependence between the concentration and the discharge. However this conclusion is based on  $p <$   
403  $0.99$  criteria. At weaker probability level ( $p \leq 0.95$ ), there is an increase in export fluxes during  
404 winter and a decrease in overall annual fluxes. The non-systematic variations of mean values  
405 seen in both **Figs. 9-10 and Table S3** are due to an insufficient number of measurements, non-  
406 homogeneity of data, and, less likely, different methods of analyses used by the RHS and our  
407 group in this study. Given changes in analytical methods (between RHS measurements and our  
408 analyses) and sparse sampling over historical period, weaker probability trends can be  
409 considered significant. This strongly suggests a possibility of overall decreasing trend on  
410 discharges (**Table S3**) and element export fluxes by the Severnaya Dvina River to the Arctic  
411 Ocean, occurring during spring, summer, autumn, as well as over the annual scale.

412

## 413 **4. Discussion**

### 414 *4.1. Seasonality of dissolved element export and mechanism of element mobilization*

415 The annual flux of DIC and soluble, highly mobile elements exhibited the largest  
416 contribution from summer and winter baseflow in agreement with general knowledge of Ca,  
417 Mg, DIC, and other soluble element seasonality in boreal rivers, including Russian subarctic  
418 zone (Gordeev et al., 1996; Frey et al., 2007; Bagard et al., 2011; Pokrovsky et al., 2012b) and  
419 the Severnaya Dvina itself (Pokrovsky et al., 2010). These elements were negatively correlated  
420 to DOC and discharge (**Table S2**). Presumably, the enrichment of river water in these elements

421 occurs due to their input from deep groundwaters which are progressively diluted by surface  
422 waters during the open-water period (Johnson et al., 1969; Pokrovsky et al., 2012a). The  
423 mother rocks of the Severnaya Dvina watershed are carbonates and gypsum which explains the  
424 enrichment of groundwaters in these soluble, highly mobile elements (Malov, 2013; Petrov and  
425 Semenchuk, 2017).

426         The DOC flux of the Severnaya Dvina River is dominated by spring flood (~50%  
427 during May-June, **Table 2**), which is consistent with other large and small high-latitude  
428 watersheds (Finlay et al., 2006; Raymond et al., 2007; Striegl et al., 2007; Griffin et al., 2018).  
429 Further, the majority (c.a. > 50%) of annual flux of insoluble trace metals in the Severnaya  
430 Dvina River occurs during spring flood, following the maximal DOC export (**Table 2**). The  
431 peak of DOC in the stream with rising discharge during storm events known from small  
432 catchments of N. America (McGlynn and McDonnell, 2003; Herndon et al., 2015) also occurs  
433 in the Severnaya Dvina River, when DOC is released from soil organic matter, both in the  
434 riparian zone and forested subcatchments. A number of solutes that are stored preferentially in  
435 the riparian zone, such as divalent metals (Be, Cu, Pb), follow this C - Q pattern (compare **Fig.**  
436 **4 A** and **6**), being strongly correlated with DOC (**Fig. 3, Table S2**). Indeed, riverine transport  
437 of insoluble trace elements, notably trivalent and tetravalent TE is controlled by organo-ferric  
438 colloids whereas V, Cr and divalent metals (Co, Ni, Cu, Cd, and Pb) are bound to organic  
439 complexes of fulvic nature in the Severnaya Dvina River (Pokrovsky et al., 2010). These  
440 elements are also associated with organo-mineral (Fe, Al) colloids in permafrost-free European  
441 subarctic (Pokrovsky and Schott, 2002; Vasyukova et al., 2010; Ilina et al., 2016) and Siberian  
442 (Pokrovsky et al., 2006; Bagard et al., 2011) watersheds as well as those in Canada (Cuss et al.,  
443 2018) and Alaska (Stolpe et al., 2013). Note that divalent metals (Be, Cu, Pb), insoluble  
444 trivalent (Al, Ga, Y, REE) and tetravalent (Ti, Zr, Hf, Th) element association with DOC,  
445 observed in the Severnaya Dvina River over full period of our observations (**Table S2**) is fully  
446 consistent with the dominance of organic and organo-mineral colloids as main vectors of metal

447 transport in the Severnaya Dvina River, established in previous study of this riverine system  
448 (Pokrovsky et al., 2010).

449         Given that the organic colloid flux is mainly formed at the beginning of the active  
450 season, when the majority of the soil profile in the Severnaya Dvina watershed is still frozen,  
451 the importance of plant litter in providing sizeable part of dissolved metals is incontestable.  
452 This is also supported by mass balance calculations in other regions (Pokrovsky et al., 2006,  
453 2012b; Soper et al., 2018). Note that a number of autochthonous processes occurring in the river  
454 channel may impact temporal and discharge-dependent patterns of elements. Exceptional events  
455 can strongly enrich river water in DOM and related elements, leading to a deviation from element  
456 – discharge dependence, as for example, the autumn flood in 2012 that occurred after massive  
457 litterfall or the summer bloom of phytoplankton (see **Fig. 4 A**). Both events yielded strong  
458 enrichment of riverwater in DOC that occurred at rather low discharges. A number of nutrients (N,  
459 PO<sub>4</sub>, Si, Fe, Mn, Zn) demonstrated pronounced depletion during summer time detectable at the  
460 element – DOC relationship plot (**Fig. 3**) which was presumably induced by plankton and  
461 periphyton uptake.

462         Noteworthy that strong spatial heterogeneity leading to dissimilarity in concentration -  
463 discharge behaviors of soluble elements (Ca, K, Mn), DOC and organically-complexed Fe and Al  
464 as reported in small headwater catchments of temperate zone (i.e., Herndon et al., 2015a), was not  
465 pronounced at the scale of the Severnaya Dvina River in this study. Presumably, large river basin  
466 integrates the local heterogeneity of soil organic matter and vegetation distribution across small  
467 subcatchments. Another important difference between small streams and large river is that there  
468 were no chemostatic elements (i.e., elements exhibiting little variation in concentration over a  
469 wide range of discharge values) in the Severnaya Dvina River (**Fig. 5** and **6**). In contrast, the  
470 behavior of most major weathering elements (Na, K, Mg, Mn) in temperate headwater streams  
471 was largely chemostatic (Henderson et al., 2015a).

472           The maximal export of divalent metals and trivalent and tetravalent TE during the spring  
473 flood period, documented in this study for the Severnaya Dvina River, is consistent with seasonal  
474 observations on other Arctic rivers such as those in Alaska (Rember and Trefry, 2004), Siberia  
475 (Bagard et al., 2011) and Sweden (Porcelli et al., 1997; Ingri et al., 2000; Andersson et al., 2006).  
476 Dissolved Fe showed a spring flood maximum (**Fig. 7 D**) when Fe was transported in the form of  
477 organic colloids (i.e., Pokrovsky et al., 2010), and a winter maximum, which was linked to an  
478 increase in underground feeding by Fe(II)-rich anoxic waters. During the latter period, Fe was  
479 strongly decoupled of DOC as illustrated in **Fig. 3**. The summer minimum of Fe might be linked  
480 to Fe removal by a number of biological (bio-degradation, uptake by plankton and periphyton  
481 (Shirokova et al., 2017), and physico-chemical (photodegradation) processes of organo-ferric  
482 colloids (Oleinikova et al., 2017b; Chupakova et al 2018). Similar summer minimums in dissolved  
483 N and P forms, when these nutrients are decoupled of DOC (**Fig. 3**) could be linked to biological  
484 uptake by river plankton and peryphyton as is known for other rivers in temperate and boreal  
485 zones (Vorobyev e al., 2017). In addition to instream autochthonous processes, it is well known  
486 that seasonal uptake by vegetation regulates concentrations of nutrient elements in stream water  
487 (e.g., Johnson et al., 1969; Vitousek, 1977; Mulholland, 1992). It is remarkable that these  
488 processes, identified at the scale of small headwater streams, are also pronounced within large  
489 boreal river, with diverse sub-catchments and lithology of the basin.

490           Dissolved Mn demonstrated a single peak at the beginning of spring flood (**Fig. 7 C**) that  
491 was likely linked to its leaching from plant litter (i.e., Herndon et al., 2015b) and desorption from  
492 river suspended matter (i.e., Pokrovsky et al., 2013). Ni, Cu, Cd, and Sb yielded maximal  
493 concentrations at the end of spring flood in the beginning of June. This may be linked to their  
494 leaching from top soil and lichens as these elements strongly accumulate in lichen cover of the  
495 Severnaya Dvina River watershed (Shevchenko et al., 2013). Arsenic had a minimum at the spring  
496 flood followed by a maximum in summer (July-September) and a minimum in winter (November-

497 January). It is possible that this behavior is controlled by both groundwater dilution and  
498 mobilization from bed river or riparian zone sediments under biotic activity.

499  
500 *4.2. High-resolution versus low-resolution sampling strategy for flux evaluation and*  
501 *comparison with other data*

502 A comparison of high-resolution (daily to weekly sampling, this study) and medium-  
503 resolution (biweekly to monthly sampling, Pokrovsky et al., 2010) measurements of dissolved  
504 component fluxes in the Severnaya Dvina River demonstrated that both studies yielded similar  
505 (within  $\pm 30\%$  of the uncertainty in previous work) annual fluxes of DOC, DIC, Ca, Na, Mg, Si,  
506 K, and Sr. The high-resolution study provided ca. 20 to 50% lower fluxes of Fe, Cr, Co, Ni, Cu,  
507 Mo, Zn, and REEs, and obtained 2 to 3 times lower annual export fluxes of Mn, Ti, Cr, and Pb.  
508 The largest difference between high and medium resolution flux estimations was observed for  
509 Pb and Cd (factor of 3.4 to 3.7), Ni and Cu (factor of 5.9 to 8.7). It is possible that on average  
510 the 1.5 to 3.0 times overestimation of fluxes based on medium-resolution observations is due to  
511 overestimation of summer and autumn baseflow period export. This is because in our previous  
512 study (Pokrovsky et al., 2010), July-November fluxes were represented by quite a low number  
513 of samplings.

514 The DIC yield for the Severnaya Dvina River ( $4.3 \pm 0.2$  t/km<sup>2</sup>/y, this study) is much  
515 higher than that of other Russian Arctic Rivers (Gordeev et al., 1996) and comparable to values  
516 of Yukon and Mackenzie ( $5.4 \pm 0.3$  and  $3.7 \pm 0.3$  t/km<sup>2</sup>/y, respectively, see Tank et al., 2012).  
517 This is due to the strong contribution of carbonate rocks to the lithology of Severnaya Dvina  
518 watershed. The DOC export flux by the Severnaya Dvina River is comparable with available  
519 literature data. The value of  $1.5 \pm 0.3$  Tg yr<sup>-1</sup> of DOC obtained in this work is between the recent  
520 estimations of Johnson et al. (2018) and Pokrovsky et al. (2010) (1.19 and 1.86 Tg yr<sup>-1</sup>,  
521 respectively). In this regard, the overall role of Severnaya Dvina in DOC export to the Arctic

522 Ocean exceeds that of large rivers like the Kolyma and the Mackenzie (0.86 and 1.15 Tg yr<sup>-1</sup>,  
523 respectively Kaiser et al., 2017).

524 It is pertinent to note that other Arctic rivers such as Ob (Vorobyev et al., 2019), or  
525 Yukon (Guo et al., 2012) exhibit similar response in DOC and DIC variations with discharge,  
526 although the ratio between DOC and DIC export in major Arctic rivers does not follow any  
527 specific pattern, which could be directly linked to first-order climate (temperature and  
528 precipitation), landscape (forest versus wetlands) and lithological parameters of river watershed  
529 (Prokushkin et al., 2012). The latter authors demonstrated a declining DIC concentration in  
530 Siberian rivers in both northward and eastward directions yielding an overall decrease in total C  
531 export with latitude.

532 The average watershed area-normalized DOC yield of the Severnaya River is equal to  
533  $4.2 \pm 0.8 \text{ t C}_{\text{org}} \text{ km}^{-2} \text{ y}^{-1}$  which is the highest among all known rivers flowing to the Arctic Ocean.  
534 This was first noted by Gordeev et al (1996) and later confirmed by Raymond et al (2007);  
535 thus, the Ob, Yukon, Lena, Yenisey, and Mackenzie rivers exhibit a DOC yield from 0.5 to 2.5  
536 t C/km<sup>2</sup>/y. We suggest that the main factor responsible for such high DOC yield in Severnaya  
537 Dvina is the high proportion of peatlands on its watershed (ca., around 20% of bogs in its lower  
538 reaches according to Sokolov (1952)). For example, a high latitude peat-rich watershed of the  
539 Lena River basin exported  $4.75 \text{ t C}_{\text{org}} \text{ km}^{-2} \text{ y}^{-1}$  (Suzuki et al., 2006). Similarly, high values were  
540 also reported for the high-peat Koyukuk River in the Yukon basin (Striegl et al., 2007). The  
541 peatland-draining Taz (watershed = 150,000 km<sup>2</sup>), Pur (112,000 km<sup>2</sup>), and Nadym (64,000  
542 km<sup>2</sup>) rivers of the Western Siberia Lowland (WSL), located entirely in the discontinuous  
543 permafrost zone, also have a DOC flux of 1.9, 2.1, and 4.4 t C<sub>org</sub> km<sup>-2</sup> y<sup>-1</sup>, respectively  
544 (Gordeev et al., 1996 and calculations based on data from the RHS), and in general, the WSL  
545 rivers draining frozen and thawed peatlands export between 1.5 and 3.5 t C<sub>org</sub> km<sup>-2</sup> y<sup>-1</sup>  
546 (Pokrovsky et al., 2015).

547           It is likely that high DOC yield of the Severnaya Dvina River is also due to a sizeable  
548 contribution of the low-water periods to the overall annual yield (18% in winter, December to  
549 April and the same amount in autumn, October and November, see **Table 2**). For all major  
550 Arctic rivers, the contribution of these low-water periods is much smaller (cf., Raymond et al.,  
551 2007). Consistent with our data, the Severnaya Dvina River demonstrates an unusually high  
552 winter flux of DOM and chromophoric DOM (CDOM) as documented in recent work of  
553 Johnson et al. (2018). We hypothesize that this flux, which strongly exceeds that for large  
554 permafrost-affected Arctic rivers, is due to the presence of unfrozen mires and wetlands in the  
555 watershed of the Severnaya Dvina and its tributaries. The bogs remain an active supplier of  
556 allochthonous chromophoric DOM in winter. This is not the case in other permafrost-affected  
557 northern rivers where the organic matter supplies available for leaching are low in winter and  
558 water entering the streams may bypass frozen organic soil horizons (i.e., Mann et al., 2016;  
559 O'Donnell et al., 2016).

560           Another important difference between the Severnaya Dvina River and other Arctic  
561 Rivers is the low biolability of DOC transported by Severnaya Dvina to the Arctic Ocean. In  
562 contrast to Alaskan rivers, which exhibited substantial losses (20-40%) of DOC in spring flood  
563 samples (Holmes et al., 2008), the biodegradability of spring-time DOM in the Severnaya  
564 Dvina River and its estuary is almost negligible when compared to that of summer baseflow-  
565 period (Shirokova et al., 2017). Furthermore, the biodegradable DOC yield in the Severnaya  
566 Dvina (10-20%, Shirokova et al., 2017) is much lower than that in the Ob River which drains  
567 similar taiga and peat bog regions but of the permafrost zone (20% annual, 45% in winter, cited  
568 from Wickland et al., 2012). As a result, the losses and DOC in the Severnaya Dvina main  
569 channel due to bio- and photodegradation may be smaller than those observed in other Arctic  
570 rivers having sizeably higher runoff, and the overall DOC yield in the former is the highest.

571

572           4.3. *The lack of long-term trends and consequences of climate warming for the*  
573 *Severnaya Dvina River*

574           A Mann-Kendall statistical test for the discharge data between 1882 and 2015  
575 demonstrated no sizeable increase in winter discharge (**Table S3**) in contrast to what is reported  
576 for Siberian (Smith et al., 2007; Shiklomanov et al., 2006, 2007; Kolosov et al., 2016) and  
577 North American (Spence et al., 2014; Yang et al., 2015; Walvoord and Striegl, 2007; Tank et  
578 al., 2016) permafrost-affected rivers after the 1970's. It is important to note that across the  
579 Russian Arctic drainage basin, however, there is no widespread significant changes in trends of  
580 spring discharge from 1940 to 2001 (Shiklomanov et al., 2007). In fact, Severnaya Dvina is the  
581 only Russian Arctic river that shows negative change in runoff from 1980 to 2007  
582 (Shiklomanov and Lammers, 2009). Furthermore, decreases in river discharge have been noted  
583 for some small North American rivers (Déry et al., 2005; McClelland et al., 2006) and the Ob  
584 River annual discharge did not change significantly over the past 40 years (Drake et al., 2018).  
585 The decrease of Severnaya Dvina's discharge during open-water period (**Fig. 8 B**) may be due  
586 to changes at the watershed (such as forest clear-cut and/or bank abrasion) although a  
587 straightforward explanation is lacking. Another important note is that there was no major  
588 change in human activity on the watershed of the Severnaya Dvina river in terms of water  
589 management (no dams, no water used for irrigation or housing, etc.). The flood time (May)  
590 discharges generally decreased, despite the fact that daily snow depth and coverage was  
591 reported to increase in the western half of Russia between 1966 and 2007 (Bulygina et al.,  
592 2009). On the other hand, a decreasing extent and duration of snow coverage was reported in  
593 the Arctic (Callaghan et al., 2011). However, only a smaller period of snow records is available  
594 for analysis and it does not allow straightforward comparison between snow depth and spring  
595 period discharge.

596           Regarding chemical fluxes, our findings demonstrate that the continental chemical runoff  
597 in the European Russian Arctic exhibits high inter-annual variability, which greatly exceeds any



598 possible long-term trend (**Fig. 10**). There is no measurable annual trend in element fluxes for at  
599 least the past 65 years, and for some components it can be traced back to the first decades of 20<sup>th</sup>  
600 century. Moreover, because the discharge decreases (at  $p = 0.97$ , **Table S3** and **Fig. 8 A**) and  
601 concentrations generally stay the same (**Fig. 9**), the overall export flux likely decreases although  
602 the significance of this decrease cannot be quantified (**Fig. 10**). Note that the element loads are  
603 less subjected to long-term variations, due to their large inter-annual variances as it was  
604 recently shown for water constituents of Swiss rivers over a period of 39 years (Zobrist et al.,  
605 2018).

606 Overall, the Severnaya Dvina River presents a prominent exception among other Arctic  
607 rivers whose discharge and concentrations are known to increase since the 1970's (Peterson et al.,  
608 2002). Regardless of biases linked to the different durations of observation (~40 years in N.  
609 America, Siberia, and Europe vs ~80 years in Severnaya Dvina), we suggest the main reason for  
610 the non-increase of dissolved element fluxes in this river is the lack of permafrost in its watershed.  
611 Further, Nikanorov et al. (2010b) demonstrated that over 20 years of RHS observation (from  
612 1981 to 2000), there was no detectable change ( $\leq 10\%$ ) of discharge and export fluxes of DOC,  
613 Fe, and Si by the Severnaya Dvina River. They also reported the lack of sizeable change in  
614 riverine fluxes of C, Fe, and Si in European Arctic rivers not subjected to permafrost thaw such  
615 as Onega (watershed = 55,700 km<sup>2</sup>), Mezen (56,400 km<sup>2</sup>), and Pechora (312,000 km<sup>2</sup>). This  
616 contrasts with the medium-size rivers of the Kara Sea basin such as Taz (150,000 km<sup>2</sup>), Pur  
617 (112,000 km<sup>2</sup>), Nadym (64,000 km<sup>2</sup>) and rivers of the Laptev Sea basin (Anabar, 78,800 km<sup>2</sup>  
618 and Olenek, 198,000 km<sup>2</sup>) where there was about a 1.5-3.0 times increase in fluxes of DOC, Fe,  
619 and Si between 1981 and 2000 while annual discharge increased only 1.5-2 times (Nikanorov  
620 et al., 2010b). These comparisons qualitatively confirm the hypothesis that the lack of  
621 permafrost thaw and absence of change in groundwater regime are responsible for the  
622 difference in export flux trends between Severnaya Dvina and other Arctic rivers.

623           Although numerous studies have been devoted to analyzing the temporal trends of  
624 dissolved river constituents, most databases include relatively short (first decades, typically  
625 from 1970's) time interval (Lettenmaier et al., 1991; Foster and Charlesworth, 1996; Worrall  
626 et al., 2004; Monteith et al., 2007; Lepistö et al., 2008; Huser et al., 2011; Toohey et al.,  
627 2016; Zobrist et al., 2018). The lack of trend in discharge, DOC, DIC, and major cations (Ca,  
628 Mg, etc.) concentration and export fluxes in the Severnaya Dvina River over the past 60-80  
629 years of low-resolution RHS observation combined with medium-resolution data from 2007-  
630 2009 (Pokrovsky et al., 2010) and high-resolution data from 2013-2015 in this study  
631 demonstrate the lack of ability to detect a decadal scale climate change impact on the river  
632 water chemistry and export flux of major inorganic dissolved components. Therefore, unlike  
633 the large increases in DOC concentrations observed over 20-30 years periods in small  
634 catchments of Northern England (Worrall et al., 2004) and across the European and North  
635 American Freshwaters (Björnerås et al., 2017), or the "browning" of Nordic lakes, attributed  
636 to the reduction in sulphate deposition during the last 2 to 3 decades (Finstad et al., 2016), the  
637 Severnaya Dvina River seems to behave differently from other European aquatic systems  
638 because it does not show any sizeable increase in DOC concentration for over 80 years of  
639 observation. Additionally, discharges, element concentrations and fluxes during winter did  
640 not demonstrate any trend over the period of observation. This contrasts with the dominant  
641 paradigm in other large Arctic rivers, that are subjected to permafrost coverage, where  
642 sizeable increase in winter-time fluxes is evidenced. This increase is linked to thawing of  
643 frozen soil and increase of hydrological connectivity via taliks leading to an increasing  
644 contribution of groundwater to streamflow as suggested in Siberia (Kolosov et al., 2016) and  
645 the Yukon basin (Walvoord and Striegl, 2007; Toohey et al., 2016). Thus, the Yukon and its  
646 small tributary demonstrate significant increases of Ca, Mg as well as Na, SO<sub>4</sub>, and P annual  
647 fluxes between 1982 and 2014 (Toohey et al., 2016). These observations are consistent with  
648 the general view that permafrost thaw is the main factor responsible for change of

649 hydrological regime, through altered surface and subsurface interactions (Bring et al., 2016;  
650 Connon et al., 2014). However, for all Arctic rivers except the Severnaya Dvina, the period  
651 of observation is rather short, starting only since the 1970's so the long-term changes can not  
652 be fully quantified.

653

## 654 **5. Conclusions**

655 We conclude that high frequency (daily to weekly) sampling is mandatory for Arctic rivers  
656 if precise (i.e.,  $\leq 30\%$  uncertainty) fluxes are required. At the same time, high resolution diel  
657 sampling (every 3 hours over 2 days) did not evidence any sizeable ( $> 10\%$ ) variation of DOC or  
658 major and trace element concentration. This allows considering single sampling as representative  
659 for the day of observation. Overall, the exact geographic position of the sampling point and the  
660 period of day/night have subordinate influence on the representability of element concentration as  
661 compared to period of the year and proper matching of the sampling date with the most significant  
662 discharge variation. The watershed-specific DOC and DIC export fluxes of the Severnaya Dvina  
663 River ( $4.2\pm 0.8$  and  $4.3\pm 0.2$  t km<sup>-2</sup> yr<sup>-1</sup>, respectively) are much higher than those of many other  
664 large Arctic rivers. This is linked to the dominance of unfrozen bogs and carbonate rocks at the  
665 watershed of Severnaya Dvina. Furthermore, the annual DOC export by this river to the Arctic  
666 Ocean is higher than that of Mackenzie and Kolyma Rivers and thus requires detailed  
667 investigation in terms of C molecular structure and biodegradability.

668 The maximal dissolved fluxes of low-mobile elements occurred during spring flood,  
669 whereas the soluble major (DIC, Ca, and Mg) elements and some nutrients (Si, Mn, NO<sub>3</sub><sup>-</sup>, Sr,  
670 and Mo) were sizeably ( $\geq 30\%$ ) transported during winter baseflow. Dissolved Fe showed both  
671 spring maximum, when Fe was transported in the form of organic complexes, and winter  
672 maximum, linked to an increase of underground feeding.

673 Results of this study and available RHS data on the Severnaya Dvina River demonstrate a  
674 decrease, rather than increase, of open-water period discharges but a lack of significant trend in

675 winter discharges. The data did not reveal any sizeable trend in mean seasonal and annual  
676 concentrations and export fluxes for DIC, DOC, SO<sub>4</sub><sup>2-</sup>, and Cl<sup>-</sup> between 1929 and 2014 and for Ca,  
677 Mg, Si, and Fe between 1950 and 2014. Therefore, the ongoing climate warming is unlikely to  
678 change the magnitude of C and major and trace element fluxes of this river to the Arctic Ocean.  
679 Furthermore, the major changes in the chemical nature of riverine fluxes to the Arctic Ocean from  
680 European Russia under a climate warming scenario are likely to be linked to the change of  
681 vegetation (species, biomass, and geographical extension), and peatland hydrological regime,  
682 rather than to rising of temperature and changing of river hydrology. For this, further studies of  
683 terrestrial biomes incorporating long-term monitoring and archive data are clearly needed.

684

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689

## 690 **References**

- 691 Andersson K., Dahlgvist R., Turner D., Stolpe B., Larsson T., Ingri J. and Andersson P. (2006)  
692 Colloidal rare earth elements in a boreal river: Changing sources and distributions during the  
693 spring flood. *Geochim. Cosmochim. Acta* **70**(13), 3261-3274.
- 694 Bagard M.L., Chabaux F., Pokrovsky O.S., Prokushkin A.S., Viers J, Dupré B. and Stille P.  
695 (2011) Seasonal variability of element fluxes in two Central Siberian rivers draining high  
696 latitude permafrost dominated areas. *Geochim. Cosmochim. Acta* **75**, 3335–3357.
- 697 Björnerås C., Weyhenmeyer G.A., Evans C.D., Gessner M.O., Grossart H.-P., Kangur K., ...  
698 Kritzberg, E.S. (2017). Widespread increases in iron concentration in European and North  
699 American freshwaters. *Global Biogeochemical Cycles*, **31**, 1488–1500.
- 700 Brabets T.P. and Walvoord M.A. (2009) Trends in streamflow in the Yukon River Basin from  
701 1944 to 2005 and the influence of the Pacific Decadal Oscillation. *J. Hydrology* **371**, 108-  
702 119.
- 703 Bring A., Fedorova I., Dibike Y., Hinzman L., Mard J., Mernild S.H., Prowse T., Semenova O.,  
704 Stuefer S.L. and Woo M.-K. (2016) Arctic terrestrial hydrology: A synthesis of processes,  
705 regional effects, and research challenges. *J. Geophys. Res.: Biogeosci.*, **121**, 621-649.
- 706 Bring A., Shiklomanov A. and Lammers R.B. (2017) Pan-Arctic river discharge: Prioritizing  
707 monitoring of future climate change hot spots. *Earth's Future*, **5**, 72–92,  
708 doi:10.1002/2016EF000434.
- 709 Bulygina O.N., Razuvaev V.N. and Korshunova N.N. (2009) Changes in snow cover over  
710 Northern Eurasia in the last few decades. *Environ. Res. Lett.* **4**, 045026.
- 711 Callaghan T.V., Johansson M., Brown R.D., Groisman P.Y., Labba N., Radionov V., et al.  
712 (2011) The changing face of Arctic snow cover: A synthesis of observed and projected  
713 changes. *Ambio*, **40**(1), 17-31.

714 Connon R.F., Quinton W.L., Craig J.R. and Hayashi M. (2014) Changing hydrological  
715 connectivity du eto permafrost thaw in the lower Liard River valley, NWT, Canada. *Hydrol.*  
716 *Processes*, **28**(14), 4163-4178.

717 Cooper L.W., Benner R., McClelland J.W., Peterson B.J., Holmes R.M. et al. (2005) Linkages  
718 among runoff, dissolved organic carbon, and the stable oxygen isotope composition of  
719 seawater and other water mass indicators in the Arctic Ocean. *J. Geophys. Res.* **110**,  
720 G02013, doi: 10.1029/20058JG000031.

721 Cooper L.W., McClelland J.W., Holmes R.M., Raymond P.A., Gibson J.J., Guay C.K.,  
722 Peterson B.J. (2008) Flow-weighted values of runoff tracers ( $\delta^{18}\text{O}$ , DOC, Ba, alkalinity)  
723 from the six largest Arctic rivers. *Geophys. Res. Lett.* **35**, L18606,  
724 doi:10.1029/2008GL035007.

725 Derugin K.M., Marutin, TP. and Protopopov I.D. (1940) Severnaya Dvina Delta, mouth of  
726 Onega and Pechora, in Marutin, T.P., Protopopov I.D., eds. Hydrologicla handbook of seas  
727 of USSR, vol. 5. The White Sea, Issue No 3. Glavnoe upr. Gidromet. Sluzhby, State  
728 Hydrological Institute, Moscow-Leningrda, Gidrometeoizdat, vol. 5 Issue 3, 170 pp.

729 Déry S.J., Stieglitz M., McKenna E.C. and Wood E.F. (2005) Characteristics and trends of  
730 river discharge into Hudson, James, and Ungava Bays, 1964-2000. *J. Clim.* **18**(14), 2540-  
731 2557.

732 DES (2018) Monitoring and Sampling Manual: Environmental Protection (Water) Policy. .  
733 Brisbane: Department of Environment and Science Government.  
734 [https://environment.des.qld.gov.au/water/monitoring/sampling-manual/pdf/monitoring-](https://environment.des.qld.gov.au/water/monitoring/sampling-manual/pdf/monitoring-sampling-manual-2018.pdf)  
735 [sampling-manual-2018.pdf](https://environment.des.qld.gov.au/water/monitoring/sampling-manual/pdf/monitoring-sampling-manual-2018.pdf), assessed 28.01.2019.

736 Drake T.W., Tank S.E., Zhulidov A.V., Holmes R.M., Gurtovaya T. and Spencer R.G.M.  
737 (2018) Increasing alkalinity export from large Russian Arctic River. *Environ. Sci.*  
738 *Technol.* **52**, 8302-8308.

739 Shver Ts.A., Egorova A.C. (1982) The climate of Arkhangelsk. Gidrometeoizdat, Leningrad,  
740 208 pp.

741 Fabre C., Sauvage S., Tananaev N., Espitalier Noël G., Teisserenc R., Probst J.L., Sanchez  
742 Pérez J.M. (2019) Assessment of sediment and organic carbon exports into the Arctic  
743 Ocean: The case of the Yenisey River basin. *Water Res.*, 158, 118-135.

744 Finlay J., Neff J., Zimov S., Davydova A. and Davydov S. (2006) Snow-melt dominance of  
745 dissolved organic carbon in high-latitude watersheds: Implications for characterization and  
746 flux of river DOC. *Geophys. Res. Lett.*, **33**, L10401, doi: 10.1029/2006GL025754

747 Finstad A.G., Andersen T., Tominaga K., Blumentrath S., de Wit H.A., Tommervik H. and  
748 Hessen D.O. (2016) From greening to browning: Catchment vegetation development and  
749 reduced S-deposition promote organic carbon load on decadal time scales in Nordic lakes.  
750 *Scientific Rep.*, **6**, Art No 31944, doi: 10.1038/srep31944.

751 Fraysse F., Pokrovsky O.S. and Meunier J.-D. (2010) Experimental study of terrestrial plant  
752 litter interaction with aqueous solutions. *Geochim. Cosmochim. Acta* **74**, 70–84.

753 Frey K.E., Siegel D.I. and Smith L.C. (2007) Geochemistry of west Siberian streams and their  
754 potential response to permafrost degradation. *Water Resources Research* **43**, W03406, doi:  
755 10.1029/2006WR004902.

756 Foster I.D.L. and Charlesworth, S.M. (1996) Heavy metals in the hydrological cycle: Trends  
757 and explanation. *Hydrol. Process.*, **10**, 227–261.

758 Gebhardt A.C., Gaye-Haake B., Unger D., Lahajnar N. and Ittekkot V. (2004) Racent  
759 particulate organic carbon and total suspended matter fluxes from the Ob and Yenisei Rivers  
760 into the Kara Sea (Siberia). *Marine Geol.* **207**, 225-245.

761 Gordeev V.V. and Sidorov I.S. (1993) Concentration of major elements and their outflow into  
762 the Laptev Sea by the Lena River. *Marine Chemistry* **43**, 33-45.

763 Gordeev V.V., Martin J.M., Sidorov I.S. and Sidorova M.V. (1996) A reassessment of the  
764 Eurasian river input of water, sediment, major elements, and nutrients to the Arctic ocean.  
765 *Amer. J. Sci.* **296**, 664-691.

766 Griffin C.G., McClelland J.W., Frey K.E. and Holmes R.M. (2018) Quantifying CDOM and  
767 DOC in major Arctic rivers during ice-free conditions using Landsat TM and ETM+ data.  
768 *Remote Sen. Environ.* **209**, 395-409.

769 Guieu C., Huang W.W., Martin J.-M. and Yong Y.Y. (1996) Outflow of trace metals into the  
770 Laptev Sea by the Lena River. *Marine Chem.* **53**, 255-267.

771 Guo L., Cai Y., Belzile C., Macdonald R.W. (2012) Sources and export fluxes of inorganic and  
772 organic carbon and nutrient species from the seasonally ice-covered Yukon River.  
773 *Biogeochemistry*, **107**, 187–206, doi: 10.1007/s10533-10010-19545-z

774 Herndon E.M., Dere A.L., Sullivan P.L., Norris D., Reynolds B., and Brantley S.L. (2015a)  
775 Landscape heterogeneity drives contrasting concentration - discharge relationships in shale  
776 headwater catchments. *Hydrol. Earth Syst. Sci.*, **19**, 3333-3347.

777 Herndon E.M., Jin L., Andrews D.M., Eissenstat D.M., and Brantley S.L. (2015b) Importance  
778 of vegetation for manganese cycling in temperate forested watersheds. *Global Biogeochem.*  
779 *Cycles*, **29**, 160–174, doi:10.1002/2014GB004858.

780 Holmes R.M., Peterson B.J., Gordeev V.V., Zhulidov A.V., Meybeck M., Lammers R.B. and  
781 Vörösmarty C.J. (2000) Flux of nutrients from Russian rivers to the Arctic Ocean: Can we  
782 establish a baseline against which to judge future changes? *Water Resources Res.* **36**(8),  
783 2309-2320.

784 Holmes R.M., McClelland J.W., Peterson B.J., Tank S.E. et al. (2012) Seasonal and annual  
785 fluxes of nutrients and organic matter from large rivers to the Arctic Ocean and surrounding  
786 seas. *Estuaries and Coasts* **35**, 369-382, doi: 10.1007/s12237-011-9386-6.

787 Holmes R.M., McClelland J.W., Raymond P.A., Frazer B.B., Peterson B.J. and Stieglitz M.  
788 (2008) Lability of DOC transported by Alaskan rivers to the Arctic Ocean. *Geophys. Res.*  
789 *Letters* **35**, L03402, doi:10.1029/2007GL032837

790 Huh Y., Panteleyev G., Babich D., Zaitsev A. and Edmond J.M. (1998) The fluvial  
791 geochemistry of the rivers of Eastern Siberia: II. Tributaries of the Lena, Omoloy, Yana,  
792 Indigirka, Kolyma, and Anadyr draining collisional/accretionary zone of the Verkhoyansk  
793 and Cherskiy ranges. *Geochim. Cosmochim. Acta* **62**, 2053-2075.

794 Huh Y. and Edmond J.M. (1999) The fluvial geochemistry of the rivers of Eastern Siberia: III.  
795 Tributaries of the Lena and Anabar draining the basement terrain of the Siberian Craton and  
796 the Trans-Baikal Highlands. *Geochim. Cosmochim. Acta* **63**, 967-987.

797 Huser B.J., Kohler S.J., Wilander A., Johansson K. and Folster J. (2011) Temporal and spatial  
798 trends for trace metals in streams and rivers across Sweden (1996-2009). *Biogeosciences* **8**,  
799 1813-1823.

800 Ilina S.M., Lapitsky S.A., Alekhin Y.V., Viers J., Benedetti M. and Pokrovsky O.S. (2016)  
801 Speciation, size fractionation and transport of trace element in the continuum soil water – mire  
802 – lake – river – large oligotrophic lake of a subarctic watershed. *Aquatic Geochem.*, **22**(1), 65-  
803 95.

804 Ingri J., Widerlund A., Land M., Gustafsson O., Andersson P. and Ohlander B. (2000)  
805 Temporal variations in the fractionation of the rare earth elements in a boreal river; the role  
806 of colloidal particles. *Chem. Geol.*, **166**, 23–45.

807 Johnson N.M., Likens G.E., Bormann F.H., Fisher D.W. and Pierce R.S. (1969) A working  
808 model for the variation in stream water chemistry at the Hubbard Brook Experimental  
809 Forest, New Hampshire. *Water Resources Res.*, **5**, 1353-1363.

810 Johnston S.E., Shorina N., Bulygina E., Vorobjeva T., Chupakova A., Klimov S.I. et al (2018).  
811 Flux and seasonality of dissolved organic matter from the Northern Dvina (Severnaya  
812 Dvina) River, Russia. *J. Geophys. Research: Biogeosciences*, **123**,  
813 <https://doi.org/10.1002/2017JG004337>.

814 Kaiser K., Canedo-Oropeza M., McMahon R. and Amon R.M.W. (2017) Origins and  
815 transformations of dissolved organic matter in large Arctic rivers. *Sci. Reports* **7**, 13064 |  
816 DOI:10.1038/s41598-017-12729-1.

817 Kolosov R.R., Prokushkin A.S., Pokrovsky O.S. (2016) Major anion and cation fluxes from the  
818 Central Siberian Plateau watersheds with underlying permafrost. *IOP Conf. Series: Earth  
819 and Environ. Sci.*, **48**, 012018, doi:10.1088/1755-1315/48/1/012018.

820 Koroleff F. (1983a) Total and organic nitrogen. In: Grasshoff K., Ehrhardt M. and Kremling K.  
821 (eds.), *Methods for seawater analysis*. Verlag Chemie Weinheim, pp. 162–168.

822 Koroleff F. (1983b) Determination of phosphorus. In: Grasshoff K., Ehrhardt M. & Kremling K.  
823 (eds.), *Methods for seawater analysis*, Verlag Chemie, Weinheim, pp. 125–136.

824 Leonov A.B. and Chicherina O.V. (2004) Export of biogenic components of the riverine flux to  
825 the White Sea. *Water Resources* **31**(2), 170-192.

826 Lepistö A., Kortelainen P. and Mattsson T. (2008) Increased organic C and N leaching in a  
827 northern boreal river basin in Finland. *Global Biogeochem. Cycles*, **22**, GB3029,  
828 doi:10.1029/2007GB003175.

829 Lettenmaier D.P., Hooper E.R., Wagoner C. and Faris K.B. (1991) Trends in stream quality in  
830 the continental United-States, 1978-1987. *Water Resour. Res.*, **27**, 327–339.

831 Magritsky D.V. (2010) Annual suspended matter flow of the Russian rivers belonging to the  
832 Arctic Ocean basin and its anthropogenic transformation. *Vestnik Moscow State Unive. Ser.  
833 Geography* **5**(6), 17-24.

834 Maltzeva A.V., Tarasov M.N. and Smirnov M.P. (1977) Ratio between the permanganate  
835 oxidation value and total organic carbon content in river waters of the USSR. *Hydrochem.  
836 Mater. (Gidrokhimicheskie Materialy)* **66**, 56–61.

837 Malov A.I. (2013) The use of the geological benchmarks to assess the residence time of  
838 groundwater in the aquifer using uranium isotopes on the example of the Northern Dvina  
839 basin. *Lithol. Mineral Resour.*, **48**, 254-265, <https://doi.org/10.1134/S002449021303005X>.

840 Mann P.J., Spencer R.G.M., Hernes P.J., Six J., Aiken G.R., Tank S.E., McClelland J.W., Butler  
841 K.D., Dyda R.Y. and Holmes R.M. (2016) Pan-Arctic Trends in Terrestrial Dissolved  
842 Organic Matter from Optical Measurements. *Front. Earth Sci.* **4**, Art No 25, doi:  
843 10.3389/feart.2016.00025.

844 McClelland J.W., Holmes R.M., Peterson B.J. and Stieglitz M. (2004) Increasing river  
845 discharge in the Eurasian Arctic: Consideration of dams, permafrost thaw, and fires as  
846 potential agents of change. *J. Geophys. Res.*, **109**, D18102, doi:10.1029/2004JD004583

847 McClelland J., Déry S., Peterson B.J., Holmes R. and Wood E (2006) A pan-Arctic evaluation  
848 of changes in river discharge during the latter half of the 20th century. *Geophys Res. Letters*  
849 **33**, L06715.

850 McClelland J.W., Tank, S.E., Spencer, R.G.M. and Shiklomanov A.I. (2015) Coordination and  
851 sustainability of river observing activities in the Arctic. *Arctic*, **68**, Suppl 1, 59-68.

852 McClelland J.W., Holmes R.M., Raymond P.A., Striegl R.G., Zhulidov A.V., Zimov S.A., Zimov  
853 N., Tank S.E., Spencer R.G.M., Staples R., Gurtovaya T.Y. and Grif C.G. (2016) Particulate  
854 organic carbon and nitrogen export from major Arctic rivers. *Global Biogeochem. Cycles*, **30**,  
855 629-643, doi:10.1002/2015GB005351.

856 McGlynn B.L. and McDonnell J.J. (2003) Quantifying the relative contributions of riparian and  
857 hillslope zones to catchment runoff. *Water Resour. Res.*, **30**, 1310-1330.

858 Monteith D.T., Stoddard J.L., Evans C.D., de Wit H.A., Forsius M., Hogasen T., Wilander A.,  
859 Skjelkvale B.L., Jeffries D.S., Vuorenmaa J., Keller B., Kopacek J. and Vesely J. (2007)  
860 Dissolved organic carbon trends resulting from changes in atmospheric deposition  
861 chemistry. *Nature*, **450**, 537–U539.

862 Mulholland P.J. (1992) Regulation of nutrient concentrations in a temperate forest stream: roles  
863 of upland, riparian, and instream processes. *Limnol. Oceanogr.*, **37**, 1512-1520.

- 864 Nikanorov A.M., Bryzgalov V.A., Kosmenko L.S. and Reshetnyak O.S. (2010a) The role of  
865 chemical river runoff in the anthropogenic transformation of the state of the aquatic  
866 environment in the Enisei mouth area. *Water Resources* **37**(4), 471-480.
- 867 Nikanorov A.M., Smirnov M.P. and Klimenko O.A. (2010b) Long-term trends in total and  
868 anthropogenic discharge of organic and biogenic substances by Russian rivers into the  
869 Arctic and Pacific Seas. *Water Resources* **37**(3), 361-371.
- 870 O'Donnell J.A., Aiken G.R., Swanson D.K., Panda S., Butler K.D. and Baltensperger A.P. (2016)  
871 Dissolved organic matter composition of Arctic rivers: Linking permafrost and parent material  
872 to riverine carbon. *Global Biogeochem. Cycles*, **30**, 1811–1826.
- 873 Olefeldt D., Roulet N. (2014) Permafrost conditions in peatlands regulate magnitude, timing,  
874 and chemical composition of catchment dissolved organic carbon export. *Global Change*  
875 *Biol.*, **20**, 3122-3136.
- 876 Peterson B.J., Holmes R.M., McClelland J.W., Vorosmarty C.J., Lammers R.B., Shiklomanov  
877 A.I., Shiklomanov I.A. and Rahmstorf S. (2002) Increasing river discharge to the Arctic  
878 Ocean. *Science* **298**, 2171–2173.
- 879 Petrov V.V. and Semenchuk A. (2017) Ecological-hydrogeochemical conditions of the  
880 North-Dvina basin groundwater. *Regional Geology and Metallogenia* **71**, 84-92 (in  
881 Russian)
- 882 Pokrovsky O.S., Schott J., Kudryavtzev D.I. and Dupré B. (2005) Basalts weathering in Central  
883 Siberia under permafrost conditions. *Geochim. Cosmochim. Acta* **69**, 5659-5680.
- 884 Pokrovsky O. S., Schott J. and Dupré B. (2006) Trace element fractionation and transport in  
885 boreal rivers and soil porewaters of permafrost-dominated basic terrain in Central Siberia.  
886 *Geochim. Cosmochim. Acta*, **70**, 3239-3260.
- 887 Pokrovsky O.S., Viers J., Shirokova L.S., Shevchenko V.P., Filipov A.S. and Dupré B. (2010)  
888 Dissolved, suspended, and colloidal fluxes of organic carbon, major and trace elements in  
889 Severnaya Dvina River and its tributary. *Chem. Geol.*, **273**, 136–149.
- 890 Pokrovsky O.S., Shirokova L.S., Zabelina S.A., Vorobieva T.Y., Moreva O.Y., Klimov S.I.,  
891 Chupakov A.V., Shorina N.V. et al. (2012a) Size fractionation of trace elements in a seasonally  
892 stratified boreal lake: control of organic matter and iron colloids. *Aquatic Geochemistry*, **18**,  
893 115–139.
- 894 Pokrovsky O.S., Viers J., Dupré B., Chabaux F., Gaillardet J., S. Audry, Prokushkin A.S.,  
895 Shirokova L.S., Kirpotin S.N., Lapitsky S.A. and Shevchenko V.P. (2012b) Biogeochemistry  
896 of carbon, major and trace elements in watersheds of Northern Eurasia drained to the Arctic  
897 Ocean: The change of fluxes, sources and mechanisms under the climate warming  
898 prospective. *C.R. Geoscience*, **344**, 663-677.
- 899 Pokrovsky O.S., Shirokova L.S., Gordeev V.V., Shevchenko V.P., Viers J., Chupakov A.,  
900 Vorobieva T.Y., Candadaup F., Casseraund C., Lanzanova A., Zouiten C. (2013) Fate of  
901 colloids in the Arctic estuary. *Ocean Science* **10**, 107–125.
- 902 Pokrovsky O.S., Manasypov R.M., Shirokova L.S., Loiko S.V., Krickov I.V., Kopysov S., and  
903 Kirpotin S.N. (2015) Permafrost coverage, watershed area and season control of dissolved  
904 carbon and major elements in western Siberia rivers. *Biogeosciences Disc.*, **12**, 10621-  
905 10677, doi:10.5194/bgd-12-10621-2015.
- 906 Porcelli D., Andersson P.S., Wasserburg G.J., Ingri J. and Baskaran M. (1997) The importance  
907 of colloids and mires for the transport of uranium isotopes through the Kalix River  
908 watershed and Baltic Sea. *Geochim. Cosmochim. Acta* **61**(19), 4095–4113.
- 909 Prokushkin A.S., Pokrovsky O.S., Shirokova L.S., Korets M.A., Viers J., Prokushkin S.G.,  
910 Amon R., Guggenberger G. and McDowell W.H. (2011) Sources and export fluxes of  
911 dissolved carbon in rivers draining larch-dominated basins of the Central Siberian Plateau.  
912 *Environ. Res. Letters* **6**, 045212 (14pp), doi:10.1088/1748-9326/6/4/045212.
- 913 Raymond P.A., McClelland J.W., Holmes R.M., Zhulidov A.V., Mull K., Peterson B.J., Striegl  
914 R.G., Aiken G.R. and Gurtovaya T.Y. (2007) Flux and age of dissolved organic carbon



915 exported to the Arctic Ocean: a carbon isotopic study of the five largest arctic rivers. *Global*  
916 *Biogeochem. Cycles* **21**, GB4011, doi: 10.1029/2007GB002934.

917 Rember R.D. and Trefry J.H. (2004) Increased concentrations of dissolved trace metals and  
918 organic carbon during snowmelt in rivers of the Alaskan Arctic. *Geochim. Cosmochim. Acta*  
919 **68(3)**, 477-489.

920 Semenov, A.D., editor (1977) Guide on the Chemical Analysis of Continental Surface Waters,  
921 Gidrometeoizdat, Leningrad, 344 pp. (In Russian)

922 Shevchenko V.P., Pokrovsky O.S., Starodymova, D.P., Vasyukova E.V., Lisitzin, A.P.,  
923 Drovkina S.I., Zamber N.S., Makhnovich N.M., Savvichev A.S. and Sonke J. (2013)  
924 Geochemistry of terricolous lichens in the White Sea catchment area. *Doklady Earth*  
925 *Sciences Russ. Acad. Sci.* **450(1)**, 514–520, doi: 10.1134/S1028334X13050073

926 Shiklomanov A.I. and Lammers R.B. (2009) Record Russian river discharge in 2007 and the  
927 limits of analysis. *Environ. Res. Lett.*, **4(4)**, 045015, doi: 10.1088/1748-9326/4/4/045015.

928 Shiklomanov A.I., Yakovleva T.I., Lammers R.B., Karasev I.Ph., Vörösmarty C.J. and Linder  
929 E. (2006) Cold region river discharge uncertainty—estimates from large Russian rivers. *J.*  
930 *Hydrol.* **326**, 231–256.

931 Shiklomanov A.I., Lammers R.B., Rawlins M.A., Smith L.C. and Pavelsky T.M. (2007)  
932 Temporal and spatial variations in maximum river discharge from a new Russian data set. *J.*  
933 *Geophys. Res.*, **112**, G04S53, doi:10.1029/2006JG000352.

934 Shirokova L.S., Pokrovsky O.S., Moreva O.Y., Chupakov A.V., Zabelina S.A., Klimov S.I.,  
935 Shorina N.V. and Vorobieva T.Y. (2013) Decrease of concentration and colloidal fraction of  
936 organic carbon and trace elements in response to the anomalously hot summer 2010 in a  
937 humic boreal lake. *Science Total Environ.*, **463–464**, 78–90.

938 Shirokova L.S., Chupakova A.A., Chupakov A.V. and Pokrovsky O.S. (2017) Transformation  
939 of dissolved organic matter and related trace element in the mouth zone of the largest  
940 European Arctic river: experimental modeling. *Inland Waters* **7(3)**, 272-282.

941 Smith L.C., Pavelsky T.M., MacDonald G.M., Shiklomanov A.I. and Lammers R.B. (2007)  
942 Rising minimum daily flows in northern Eurasia: A growing influence of groundwater in the  
943 high-latitude hydrologic cycle. *J. Geophys. Res.* **112**, G04S47, doi:10.1029/2006JG000327.

944 Sokolov A.A. (1952) Hydrography of USSR. Gidrometeoizdat, Leningrad (in Russian)

945 Soper F.M., Chamberlain S.D., Crumsey J.M., Gregor S., Derry L.A., Sparks J.P. (2018)  
946 Biological cycling of mineral nutrients in a temperate forested shale catchment. *J. Geophys.*  
947 *Res.: Biogeosciences* **123**, 3204-3215.

948 Spence C., Kokelj S.V., Kokelj S.A., McKluskie M. and Hedstrom N. (2014) Evidence of a  
949 change in water chemistry in Canada's subarctic associated with enhanced winter  
950 streamflow. *J. Geophys. Res. Biogeosci.*, **120**, 113-127.

951 Stolpe B., Guo L., Shiller A.M. and Aiken G.R. (2013) Abundance, size distributions and trace-  
952 element binding of organic and iron-rich nanocolloids in Alaskan rivers, as revealed by  
953 field-flow fractionation and ICP-MS. *Geochim. Cosmochim. Acta*, **105**, 221-239.

954 Striegl R.G., Dornblaser M.M., Aiken G.R., Wickland K.P. and Raymond P.A. (2007) Carbon  
955 export and cycling by the Yukon, Tanana, and Porcupine rivers, Alaska, 2001-2005. *Water*  
956 *Resour. Res.*, **43**, W02411, doi:10.1029/2006WR005201.

957 Suzuki K., Konohira E., Yamazaki Y., Kubota J., Ohata T. and Vuglinsky V. (2006) Transport  
958 of organic carbon from the Mogot Experimental Watershed in the southern mountainous  
959 taiga of eastern Siberia. *Nord. Hydrol.*, **37**, 303-312.

960 Tank S.E., Raymond P.A., Striegl R.G., McClelland J.W., Holmes R.M., Fiske G.J. and  
961 Peterson B.J. (2012) A land-to-ocean perspective on the magnitude, source and implication  
962 of DIC flux from major Arctic rivers to the Arctic Ocean. *Global Biogeochem. Cy.*, **26**,  
963 GB4018, doi:10.1029/2011GB004192.

- 964 Tank S.E., Striegl R.G., McClelland J.W. and Kokelj S.V. (2016) Multi-decadal increases in  
965 dissolved organic carbon and alkalinity flux from the Mackenzie drainage basin to the Arctic  
966 Ocean. *Environ. Res. Lett.* **11**, 054015. doi:10.1088/1748-9326/11/5/054015.
- 967 Toohey R.C., Herman-Mercer N.M., Schuster P.F., Mutter E.A. and Koch J.C. (2016) Multi-  
968 decadal increases in the Yukon River Basin of chemical fluxes as indicators of changing  
969 flowpaths, groundwater, and permafrost. *Geophys. Res. Lett.*, **43**, doi:10.1002/2016GL070817.
- 970 Vasyukova E.V., Pokrovsky O.S., Viers J., Oliva P., Dupre B., Martin F. and Candaudap F.  
971 (2010) Trace elements in organic- and iron-rich surficial fluids of the boreal zone: Assessing  
972 colloidal forms via dialysis and ultrafiltration. *Geochim. Cosmochim. Acta* **74**(2), 449-468.
- 973 Vitousek P.M. (1977) The regulation of element concentrations in mountain streams in the  
974 northeastern United States. *Ecol. Monogr.*, **47**, 65-87.
- 975 Vorobyev S.N., Pokrovsky O.S., Serikova S., Manasypov R.M., Krickov I.V., Shirokova L.S.,  
976 et al. (2017) Permafrost boundary shift in western Siberia may not modify dissolved nutrient  
977 concentrations in rivers. *Water*, **9**, 985, [https://doi:10.3390/w9120985](https://doi.org/10.3390/w9120985)
- 978 Vorobyev S.N., Pokrovsky O.S., Kolesnichenko L.G., Manasypov R.M., Shirokova L.S.,  
979 Karlsson J., Kirpotin S.N. (2019) Biogeochemistry of dissolved carbon, major and trace  
980 elements during spring flood periods on the Ob River. *Hydrological Processes*, **33**(11),  
981 1579-1594.
- 982 Walvoord M.A. and Striegl R.G. (2007) Increased groundwater to stream discharge from  
983 permafrost thawing in the Yukon River basin: Potential impacts on lateral export of carbon  
984 and nitrogen. *J. Geophys. Res.*, **34**, L12402, doi:10.1029/2007GL030216.
- 985 Wickland K.P., Aiken G.R., Butler K., Dornblaser M.M., Spencer R.G.M. and Striegl R.G.  
986 (2012) Biodegradability of dissolved organic carbon in the Yukon River and its tributaries:  
987 seasonality and importance of inorganic nitrogen. *Glob. Biogeochem. Cycles* **26**,  
988 2012gb004342.
- 989 Worrall F., Harriman R., Evans C.D., Watts C.D., Adamson J., Neal C., Tipping E., Burt  
990 T., Grieve I., Monteith D., Naden P.S., Nisbet T., Reynolds B. and Stevens P. (2004) Trends  
991 in dissolved organic carbon in UK rivers and lakes. *Biogeochemistry*, **70**, 369–402.
- 992 Yang D., Shi X. and Marsh P. (2015) Variability and extreme of Mackenzie River daily  
993 discharge during 1973-2011. *Quarter. Internat.* **380-381**, 159-168.
- 994 Zakharova E.A., Pokrovsky O.S., Dupré B. and Zaslavskaya M.B. (2005) Chemical weathering  
995 of silicate rocks in Aldan Shield and Baikal Uplift: insights from long-term seasonal  
996 measurements of solute fluxes in rivers. *Chem. Geol.* **214**, 223-248.
- 997 Zakharova E.A., Pokrovsky O.S., Dupré B., Gaillardet J. and Efimova L. (2007) Chemical  
998 weathering of silicate rocks in Karelia region and Kola peninsula, NW Russia: Assessing the  
999 effect of rock composition, wetlands and vegetation. *Chem. Geol.* **242**, 255-277.
- 1000 Zobrist J., Schoenenberger U., Figura S., and Hug S.J. (2018). Long-term trends in Swiss rivers  
1001 sampled continuously over 39 years reflect changes in geochemical processes and pollution.  
1002 *Environ. Sci. Pollution Res.*, **25**(17), 16788-16809, doi: 10.1007/s11356-018-1679-x.

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1011 **Table 1.** Mean annual fluxes (ton year<sup>-1</sup>) and annual yields per 1 km<sup>2</sup> of catchment area (ton  
 1012 year<sup>-1</sup> km<sup>-2</sup>) of substances/elements in the fraction <0.45 μm of the Northern Dvina River.  
 1013 Fluxes of PO<sub>4</sub><sup>3-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> are given as P-PO<sub>4</sub>, N-NO<sub>2</sub>, N-NO<sub>3</sub> and N-NH<sub>4</sub>,  
 1014 respectively. The uncertainty reflects the standard deviation of mean of 3 years (2012-2014).

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I.D.	Flux, t year <sup>-1</sup>	Yield, t km <sup>-2</sup> year <sup>-1</sup>	I.D.	Flux, t year <sup>-1</sup>	Yield, t km <sup>-2</sup> year <sup>-1</sup>
DOC	1498000±340000	4±1	Rb	84±12	(2.3±0.3)×10 <sup>-4</sup>
DIC	1522000±86800	4.3±0.2	Sr	30200±3100	0.085±0.009
Cl <sup>-</sup>	445000±17800	1.25±0.05	Y	24±4	(7±1)×10 <sup>-5</sup>
SO <sub>4</sub> <sup>2-</sup>	3463000±145000	9.7±0.4	Zr	24±5	(7±1)×10 <sup>-5</sup>
P-PO <sub>4</sub> <sup>3-</sup>	3810±935	0.011±0.003	Nb	1.4±0.8	(4.0±0.2)×10 <sup>-6</sup>
P <sub>tot</sub>	8346±2161	0.023±0.006	Mo	27±4	(8±1)×10 <sup>-5</sup>
N-NO <sub>2</sub> <sup>-</sup>	266±100	(7±3)×10 <sup>-4</sup>	Ag	0.10±0.01	(2.7±0.3)×10 <sup>-7</sup>
N-NO <sub>3</sub> <sup>-</sup>	19800±2550	0.056±0.007	Cd	0.7±0.1	(1.9±0.3)×10 <sup>-6</sup>
N-NH <sub>4</sub> <sup>+</sup>	7954±1699	0.022±0.005	Sb	4.2±0.8	(1.2±0.2)×10 <sup>-5</sup>
N <sub>tot</sub>	67796±19457	0.19±0.05	Cs	0.4±0.2	(1.0±0.5)×10 <sup>-6</sup>
Si	306800±35370	0.9±0.1	Ba	2765±375	0.008±0.001
Li	293±22	(8.2±0.6)×10 <sup>-4</sup>	La	22±6	(6±2)×10 <sup>-5</sup>
B	1737±257	0.0049±0.0007	Ce	40±11	(1.1±0.3)×10 <sup>-4</sup>
Na	616510±58679	1.7±0.2	Pr	6±1	(1.7±0.3)×10 <sup>-5</sup>
Mg	586000±71900	1.6±0.2	Nd	25±8	(7±2)×10 <sup>-5</sup>
Al	8471±1319	0.024±0.004	Sm	6±2	(1.6±0.4)×10 <sup>-5</sup>
K	96167±18028	0.27±0.05	Eu	1.5±0.3	(4.3±0.9)×10 <sup>-6</sup>
Ca	2099000±260000	5.9±0.7	Gd	6±1	(1.6±0.4)×10 <sup>-5</sup>
Ti	191±110	(5±3)×10 <sup>-4</sup>	Tb	4.6±0.9	(1.3±0.3)×10 <sup>-5</sup>
V	74±10	(2.1±0.3)×10 <sup>-4</sup>	Dy	4.4±0.9	(1.2±0.3)×10 <sup>-5</sup>
Cr	35±6	(1.0±0.2)×10 <sup>-4</sup>	Ho	0.9±0.2	(2.4±0.6)×10 <sup>-6</sup>
Mn	3558±1075	0.010±0.003	Er	2.5±0.6	(7±2)×10 <sup>-6</sup>
Fe	27300±8800	0.08±0.02	Tm	0.31±0.08	(0.9±0.2)×10 <sup>-6</sup>
Co	8±2	(2.3±0.5)×10 <sup>-5</sup>	Yb	2.0±0.5	(6±1)×10 <sup>-6</sup>
Ni	80±26	(2.2±0.7)×10 <sup>-4</sup>	Lu	0.32±0.07	(9±2)×10 <sup>-7</sup>
Cu	81±15	(2.3±0.4)×10 <sup>-4</sup>	Hf	0.9±0.5	(3±1)×10 <sup>-6</sup>
Zn	722±449	0.002±0.001	W	1.3±0.8	(4±2)×10 <sup>-6</sup>
Ga	1.9±0.5	(5±1)×10 <sup>-6</sup>	Pb	10.1±2.4	(2.8±0.7)×10 <sup>-5</sup>
Ge	0.7±0.2	(2.0±0.4)×10 <sup>-6</sup>	Th	2.4±0.8	(7±2)×10 <sup>-6</sup>
As	64±15	(1.8±0.4)×10 <sup>-4</sup>	U	20±1	(5.7±0.4)×10 <sup>-5</sup>

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1023 **Table 2.** The annual distribution of water and element fluxes in the Severnaya Dvina River  
 1024 (mean of 3 years (2012-2014) with 1 SD uncertainties). Winter: January, February, March,  
 1025 April and December; spring flood: May and June; summer: July, August and September;  
 1026 autumn: October and November.  
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% of annual flow	winter (Dec-Apr)	spring flood (May-Jun)	summer (Jul-Sep)	autumn (Oct-Nov)
Discharge	24±10	46±6	14±4	17±11
DOC	18±12	52±9	12±6	18±16
DIC	37±5	24±2	22±3	17±4
Cl <sup>-</sup>	39±4	21±5	23±2	18±2
SO <sub>4</sub> <sup>2-</sup>	40±7	20±3	22±3	17±3
PO <sub>4</sub> <sup>3-</sup>	20±8	41±14	9±2	30±28
P <sub>tot</sub>	19±13	38±7	10±3	33±32
NO <sub>2</sub> <sup>-</sup>	18±6	55±36	15±3	12±5
NO <sub>3</sub> <sup>-</sup>	43±13	36±8	6±2	16±7
NH <sub>4</sub> <sup>+</sup>	22±11	33±3	11±3	34±19
N <sub>tot</sub>	21±9	46±13	8±3	25±21
Si	34±12	39±6	10±5	17±12
Li	35±4	28±3	20±3	17±4
B	35±5	27±10	21±3	17±3
Na	38±5	22±6	22±2	18±2
Mg	36±5	26±7	21±3	18±4
Al	15±13	59±7	9±5	17±16
K	28±7	40±11	16±3	16±7
Ca	37±8	25±6	20±5	18±3
Ti	14±8	59±33	4±3	23±20
V	22±15	48±9	14±4	17±17
Cr	20±14	54±8	9±4	18±17
Mn	39±9	42±19	8±5	11±7
Fe	26±7	46±13	7±5	21±21
Co	25±14	50±16	8±4	17±12
Ni	16±6	54±13	13±6	16±15
Cu	20±12	52±10	12±5	16±12
Zn	18±10	47±35	18±17	18±15
Ga	19±13	49±10	14±4	18±17
Ge	30±9	41±12	14±5	15±10
As	20±7	42±9	20±6	18±13
Rb	28±6	38±6	18±3	16±8
Sr	39±5	23±6	21±3	17±3
Y	14±12	62±8	9±5	16±15
Zr	17±13	56±9	10±6	17±15
Nb	11±9	67±46	12±11	9±7
Mo	35±4	26±7	23±3	17±4
Ag	28±5	48±8	13±2	10±2

Cd	25±16	47±9	8±3	20±19
Sb	24±7	52±10	15±6	9±4
Cs	24±8	42±3	11±9	22±21
Ba	33±6	32±7	19±2	17±6
La	13±12	62±12	7±5	18±17
Ce	12±11	65±16	6±5	17±15
Pr	13±12	64±12	7±5	16±14
Nd	14±14	64±16	6±5	16±16
Sm	13±12	63±15	7±6	16±15
Eu	15±12	59±10	9±5	18±17
Gd	13±12	63±15	7±5	17±17
Tb	13±13	64±10	7±5	16±15
Dy	14±12	62±8	8±6	17±17
Ho	13±12	62±11	7±6	17±17
Er	14±12	61±13	8±6	17±17
Tm	14±10	65±14	6±4	15±14
Yb	14±12	62±13	8±6	17±17
Lu	17±11	56±11	9±5	18±17
Hf	11±6	65±36	11±8	13±13
W	18±5	47±46	22±16	13±3
Pb	21±12	50±11	10±5	18±17
Th	11±10	65±16	6±5	18±17
U	39±3	22±4	22±2	17±2

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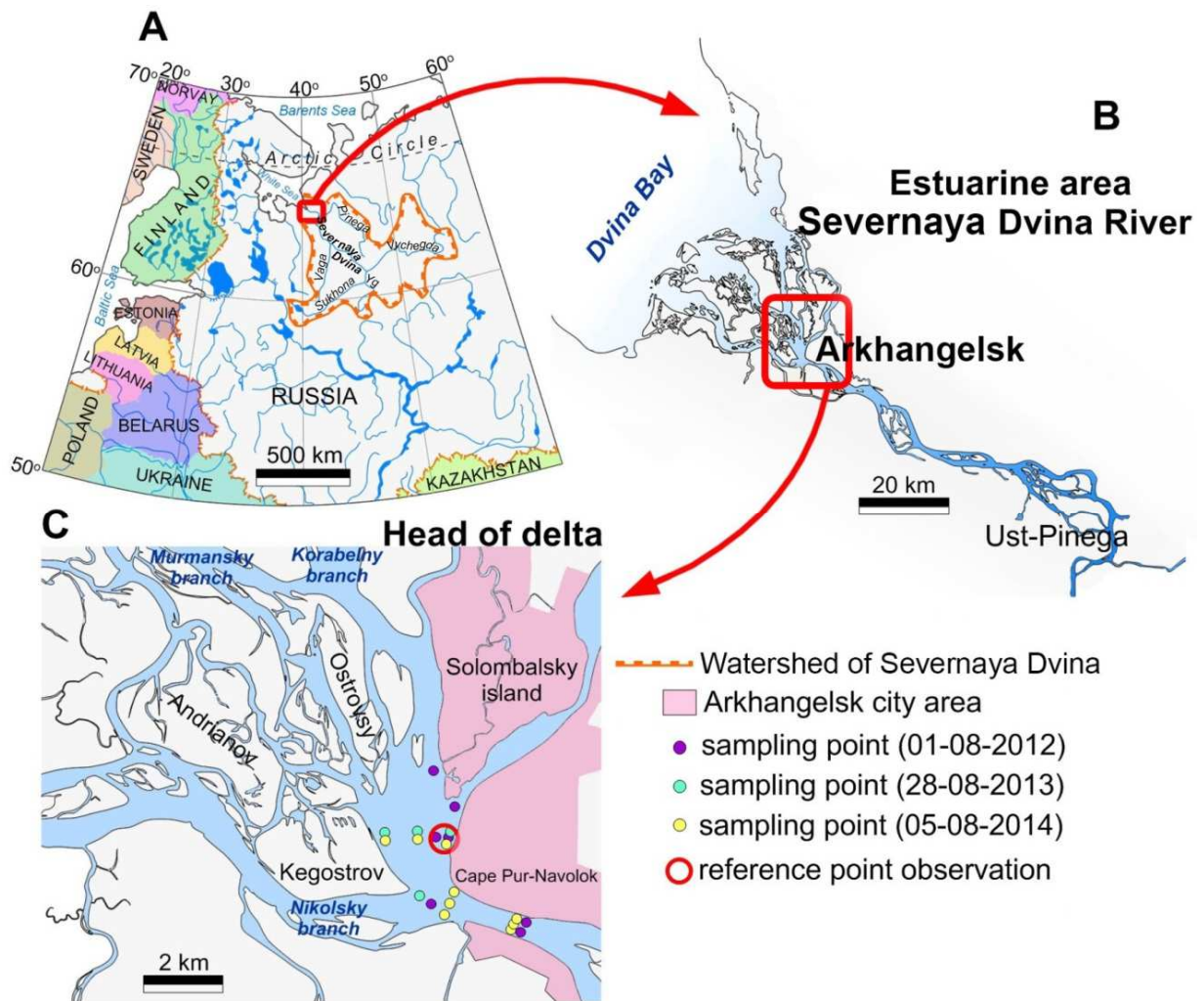
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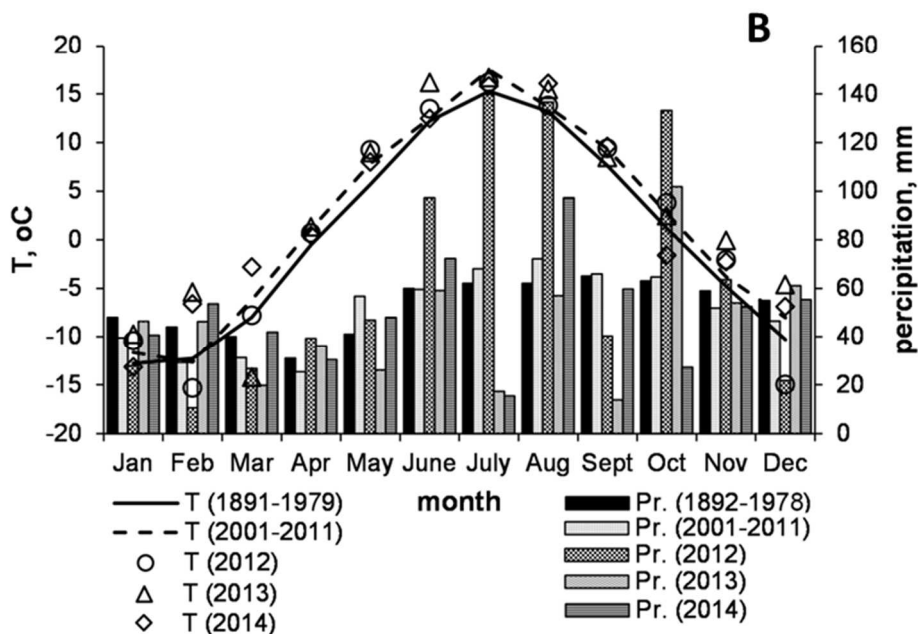
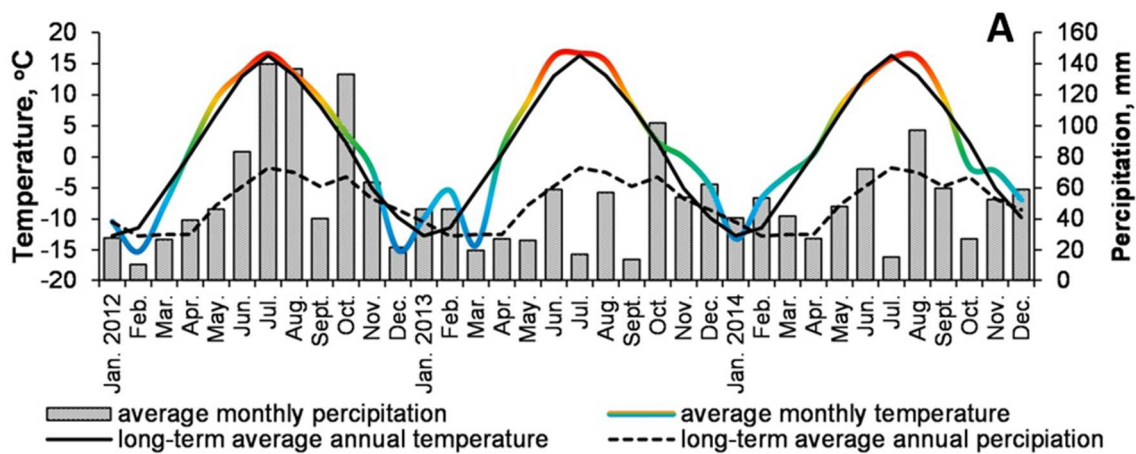
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**Fig. 1.** Scheme of the study site including the watershed of the Severnaya Dvina River (A), its mouth zone (B), and the monitoring site located at the beginning of the river delta (C). All sampling points shown in (C) are located in the freshwater zone.

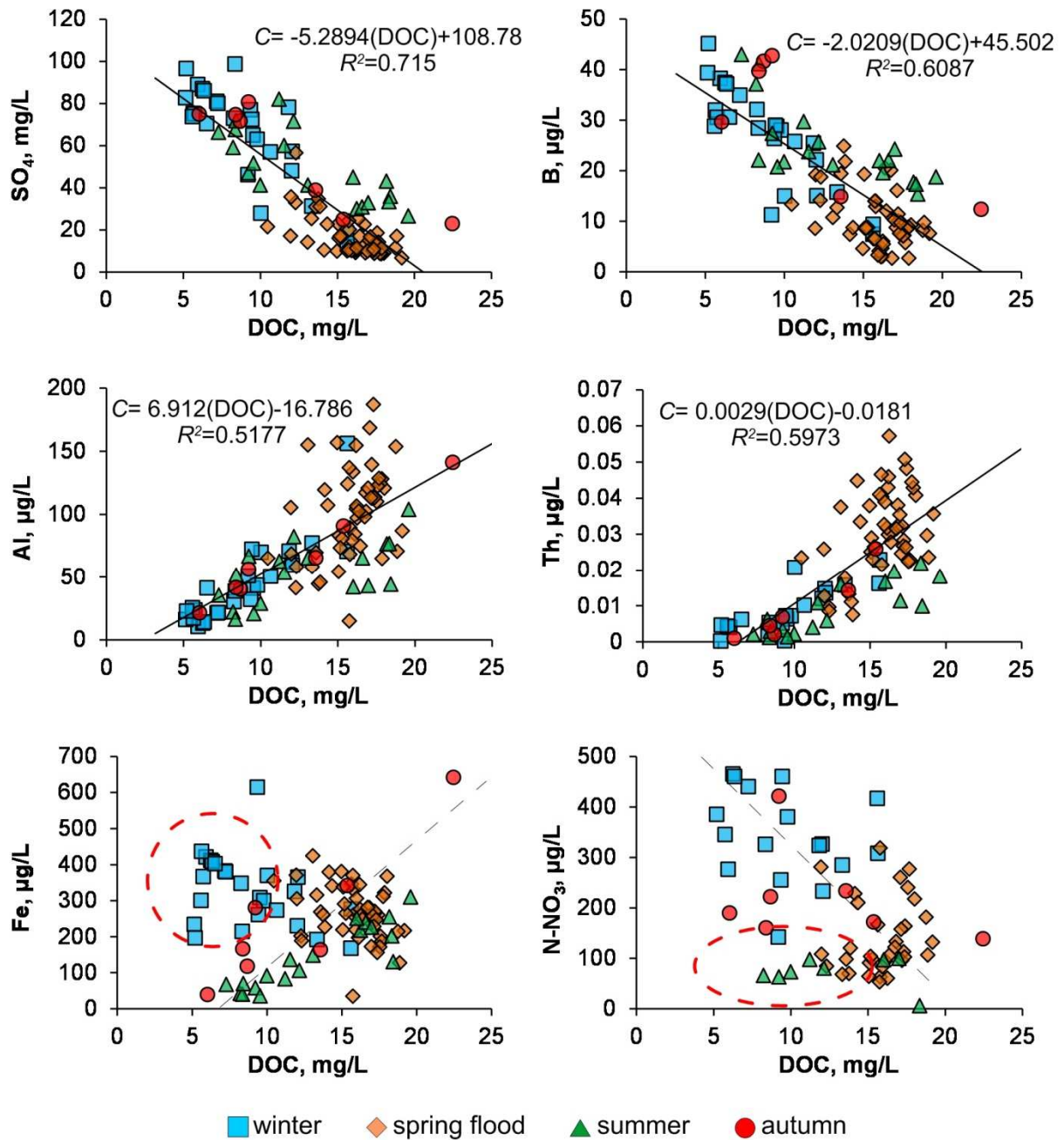
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**Fig. 2. A**, Seasonal pattern of temperature and precipitation at the mouth zone of the Severnaya Dvina River (A), and **B**, temperature and precipitation during three years of river sampling (2012-2014) plotted together with mean historical data (1891-1979 and 2001-2011). The mean monthly data for the period between 1892 and 1969 are from Shver and Egorova (1982). The mean monthly data for 2001-2011 are from RosGidromet portal ([www.pogodaiklimat.ru](http://www.pogodaiklimat.ru))

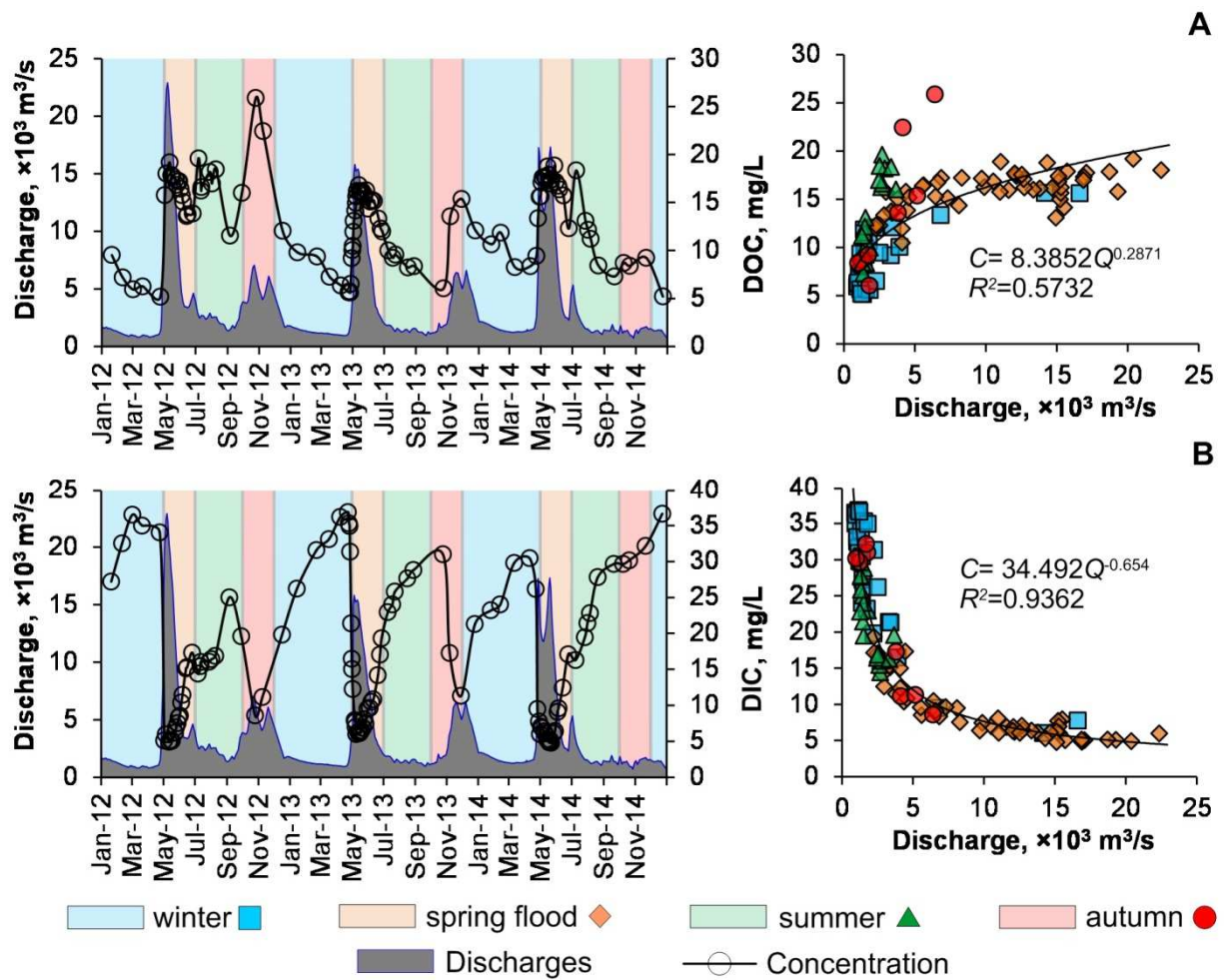
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**Fig. 3.** Relationships between DOC and trace element concentrations illustrating 3 main group of elements - strong negative (SO<sub>4</sub>, B), strong positive (Al, Th) relationships and weak positive or negative relationships with pronounced element depletion during summer time (which is induced by plankton and periphyton activity), and element enrichment during winter baseflow, as illustrated for Fe and NO<sub>3</sub> (encircled in red).





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1086 **Fig. 4.** The annual variations and concentration -discharge relationships of DOC (A) and DIC  
 1087 (B) in 2012-2014. An autumn flood and a summer phytoplankton produced high DOC  
 1088 concentration that deviate from the general trend. Note that Chl *a* was an order of magnitude  
 1089 higher for summer phytoplankton bloom event (not shown).

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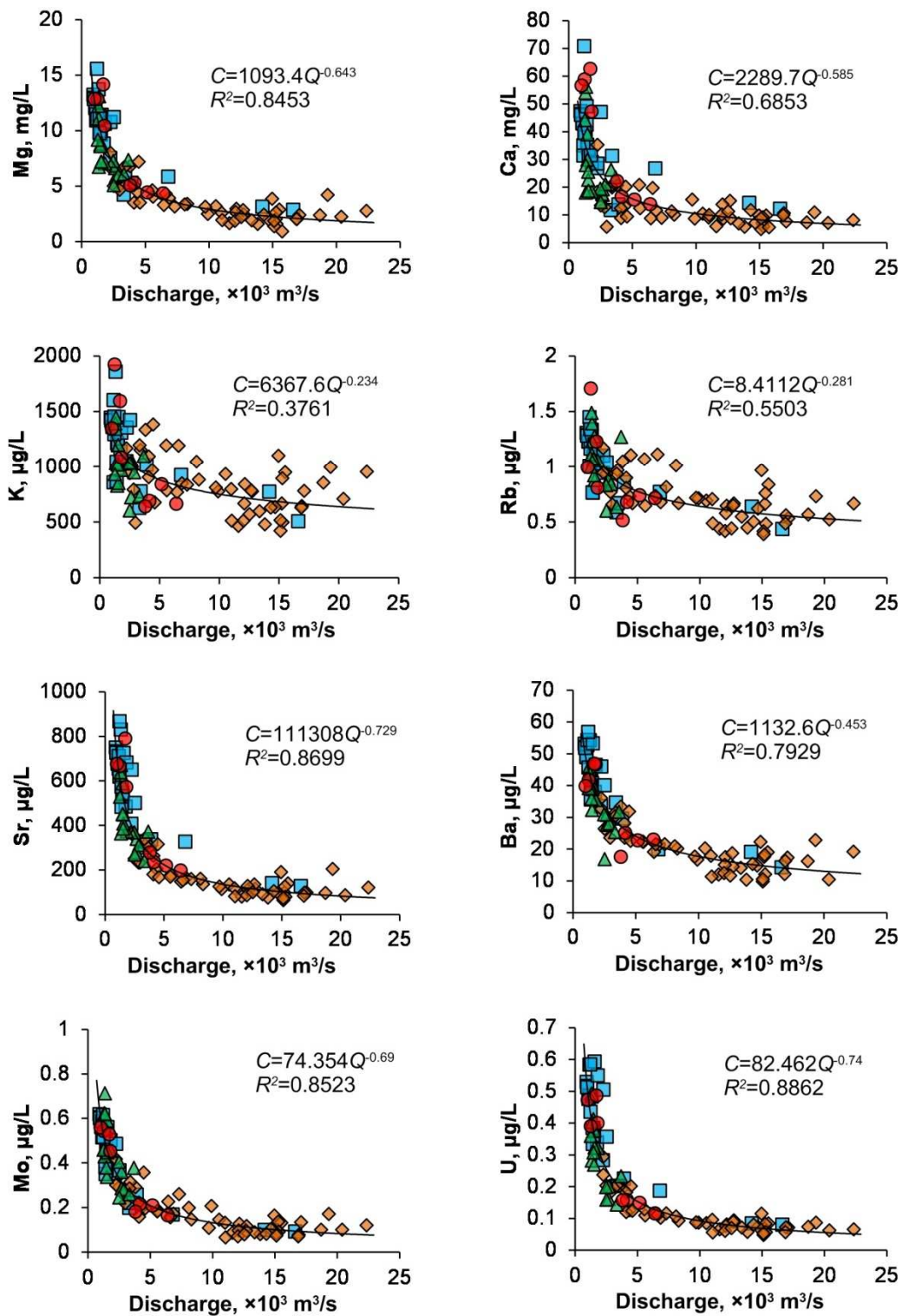
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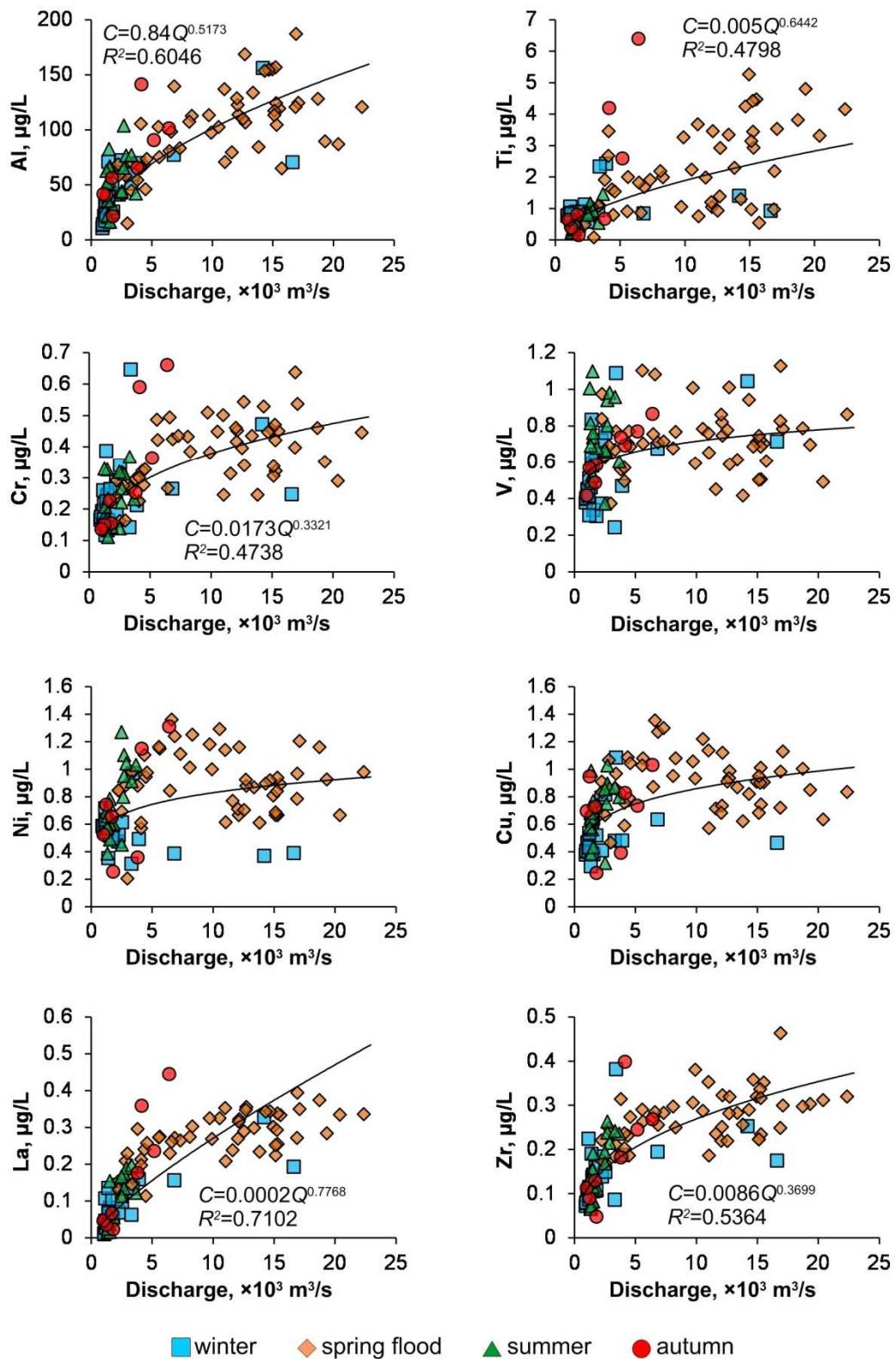
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■ winter    ◆ spring flood    ▲ summer    ● autumn

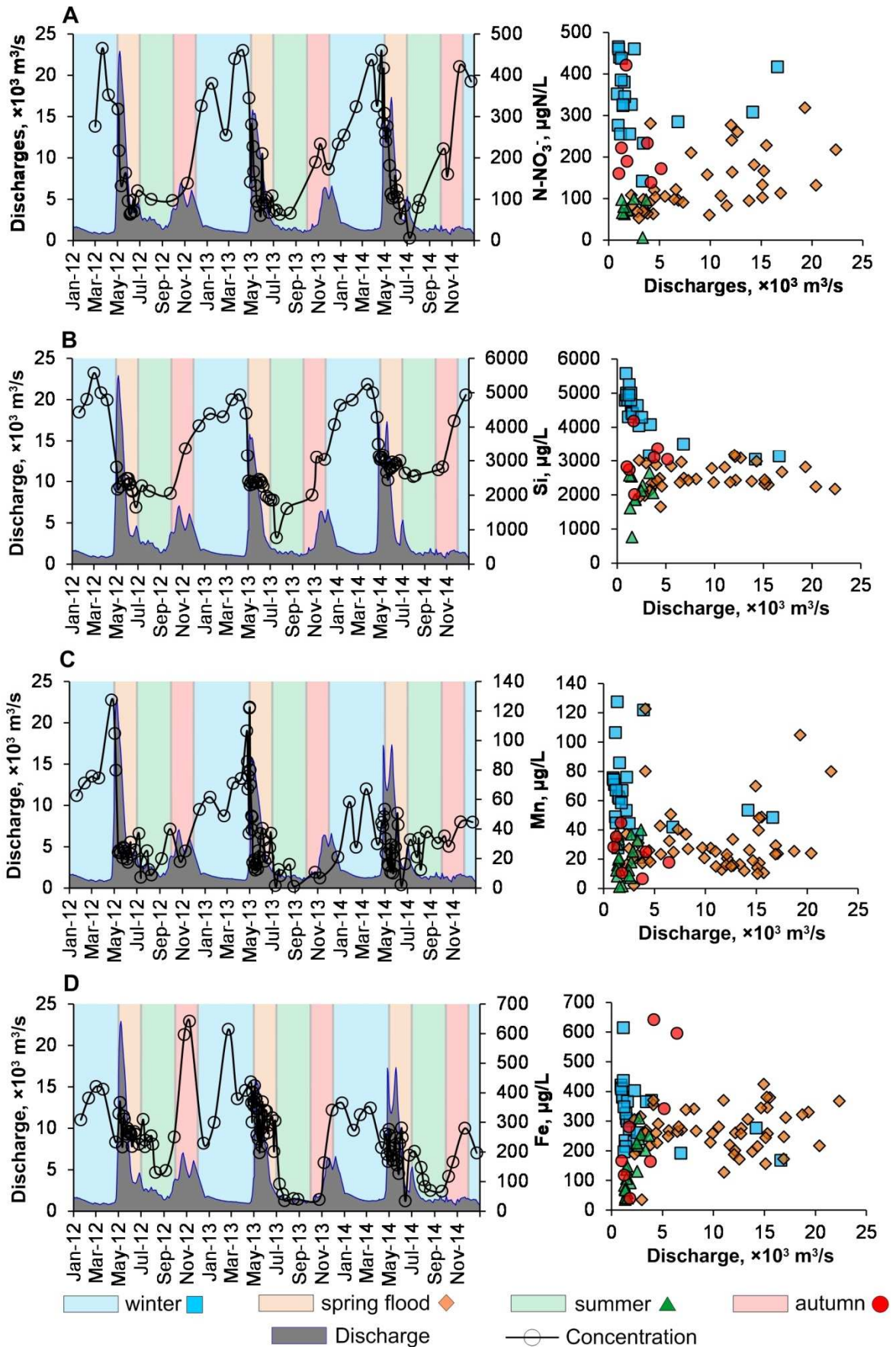
1097 **Fig. 5.** Soluble, highly mobile element concentration versus discharge over 3 year observation  
 1098 period (2012-2014). Examples are shown for major river water solutes (Mg, Ca, K), oxyanions  
 1099 (Mo), metal cations (Rb, Sr, Ba) and uranyl(VI) ion. These are most representative elements of  
 1100 the first group of river constituents. All the power relationships between element concentration  
 1101 (y) and discharge (x) are significant at  $p < 0.01$ . Winter, squares; spring, diamonds; summer,  
 1102 triangles; autumn, circles.



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1104 **Fig. 6.** Concentration – discharge relationships for representative low-mobility elements  
 1105 associated with organic and organo-ferric colloids over a three-year observation period (2012-  
 1106 2014). Examples are shown for Al, Ti, Cr, V, Ni, Cu, La, and Zr. All the power relationships  
 1107 between element concentration (y) and discharge (x) are significant at  $p < 0.01$ . Winter,  
 1108 squares; spring, diamonds; summer, triangles; autumn, circles.

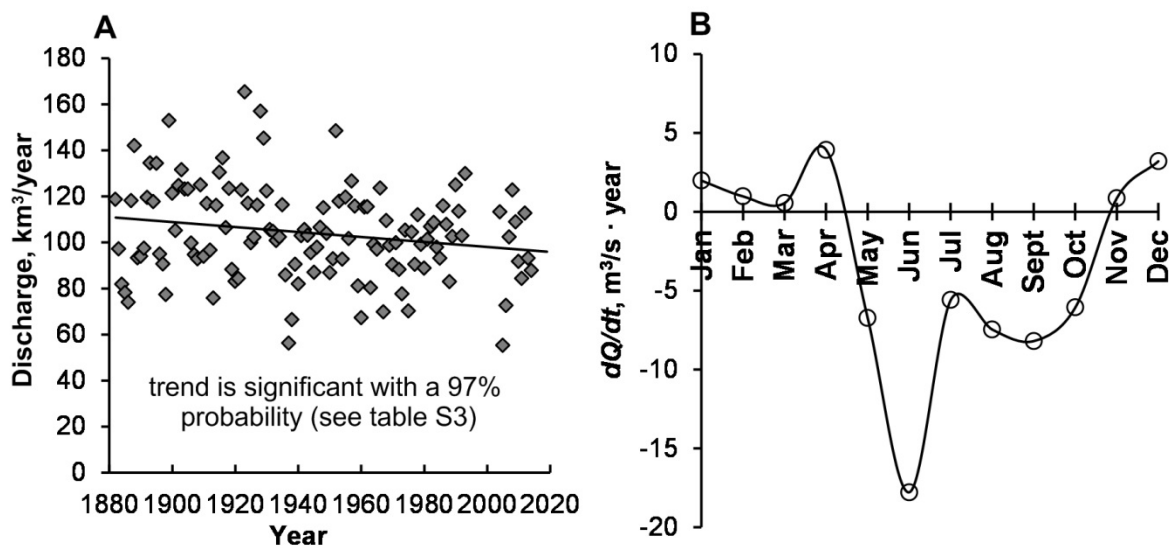
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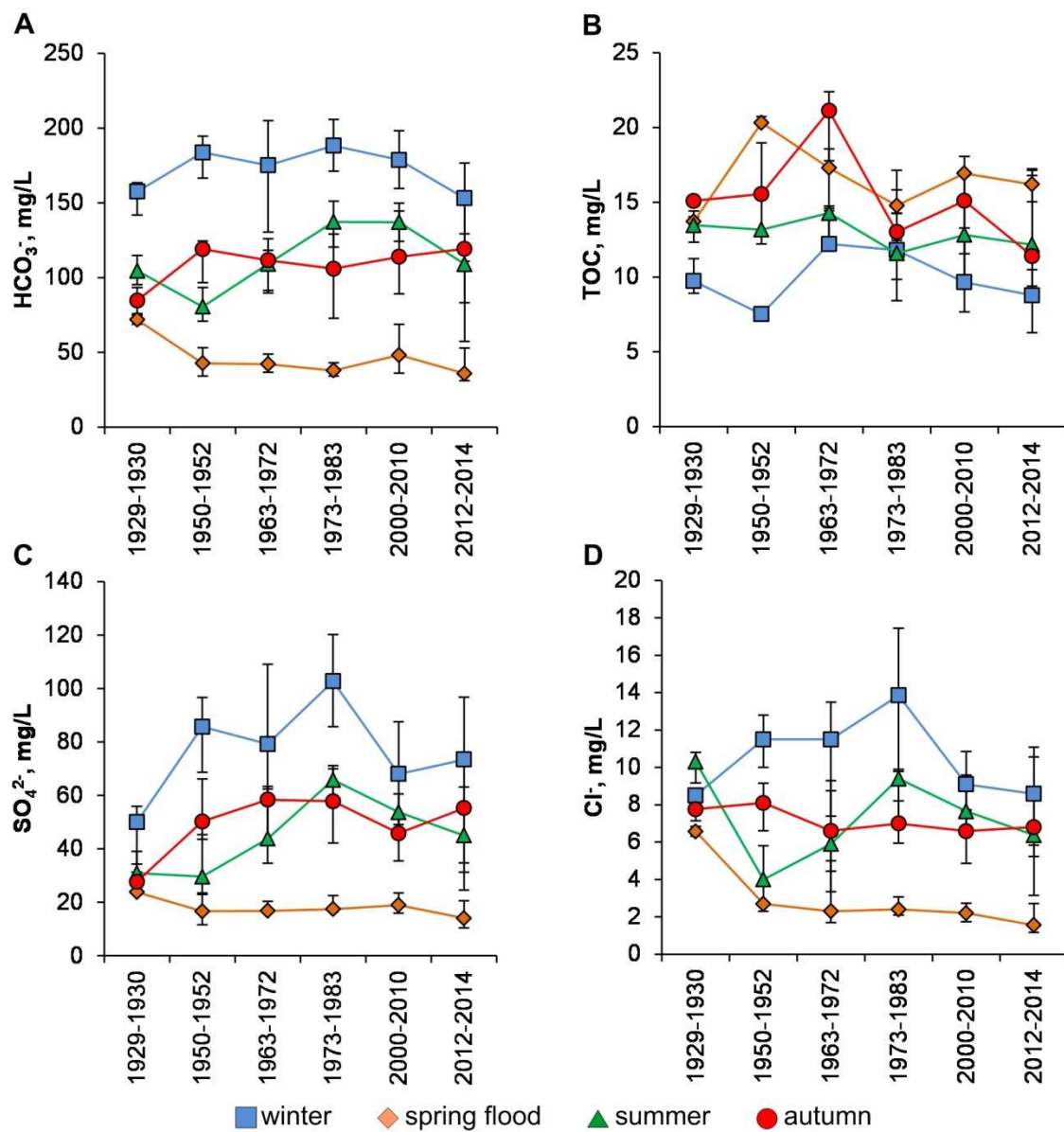
1111 **Fig. 7.** The annual variations and concentration – discharge relationships of N-NO<sub>3</sub> (A), Si (B),  
 1112 Mn (C) and Fe (D). The symbols are the same as in Figs. 5 and 6.

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**Fig. 8.** Annual discharge of the Severnaya Dvina (km<sup>3</sup> y<sup>-1</sup>) since the beginning of observations in 1882 (A) and the rate of change of river discharge between 1882 and 2014, separate for each month (B). The positive numbers indicate increase in discharge while negative numbers signify decrease of discharge, see section 3.2. There is a weak but not significant decrease in Severnaya Dvina annual discharge over past 132 years. Note that discharges of other Arctic rivers are analyzed from 1960<sup>th</sup> (Bring et al., 2017) or from 1936 (McClelland et al., 2004).



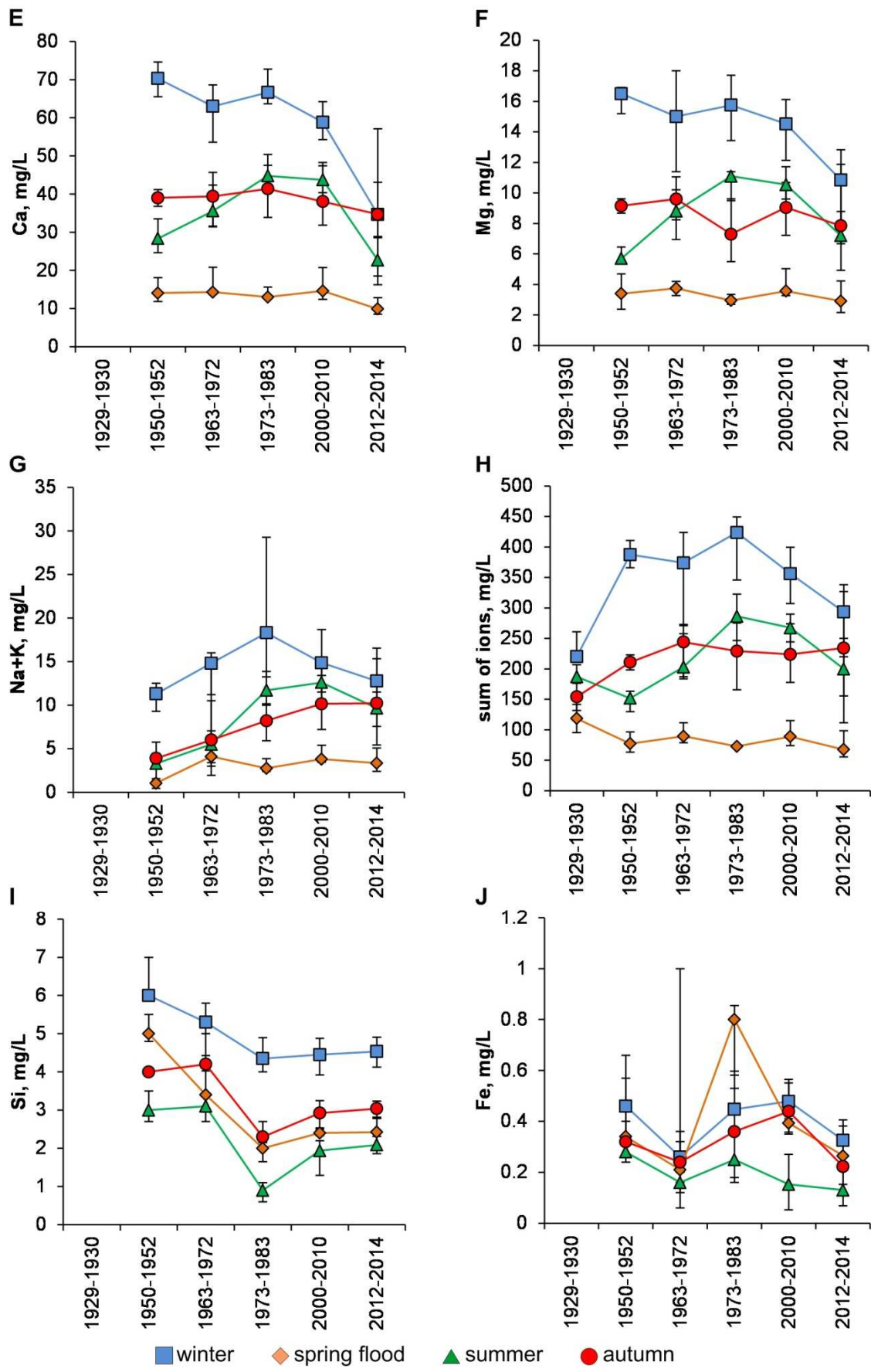
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1133 **Fig. 9.** Mean decadal or multi-annual seasonal concentrations of  $\text{HCO}_3^-$  (A), TOC (B),  $\text{SO}_4^{2-}$   
 1134 (C), Cl (D), Ca (E); Mg (F), Na+K (G), sum of ions (H), Si (I) and Fe (J) of the Severnaya  
 1135 Dvina since the onset of observations (1929 and 1950) until 2014. Note that due to scarcity of  
 1136 historical data, the time spans are different.

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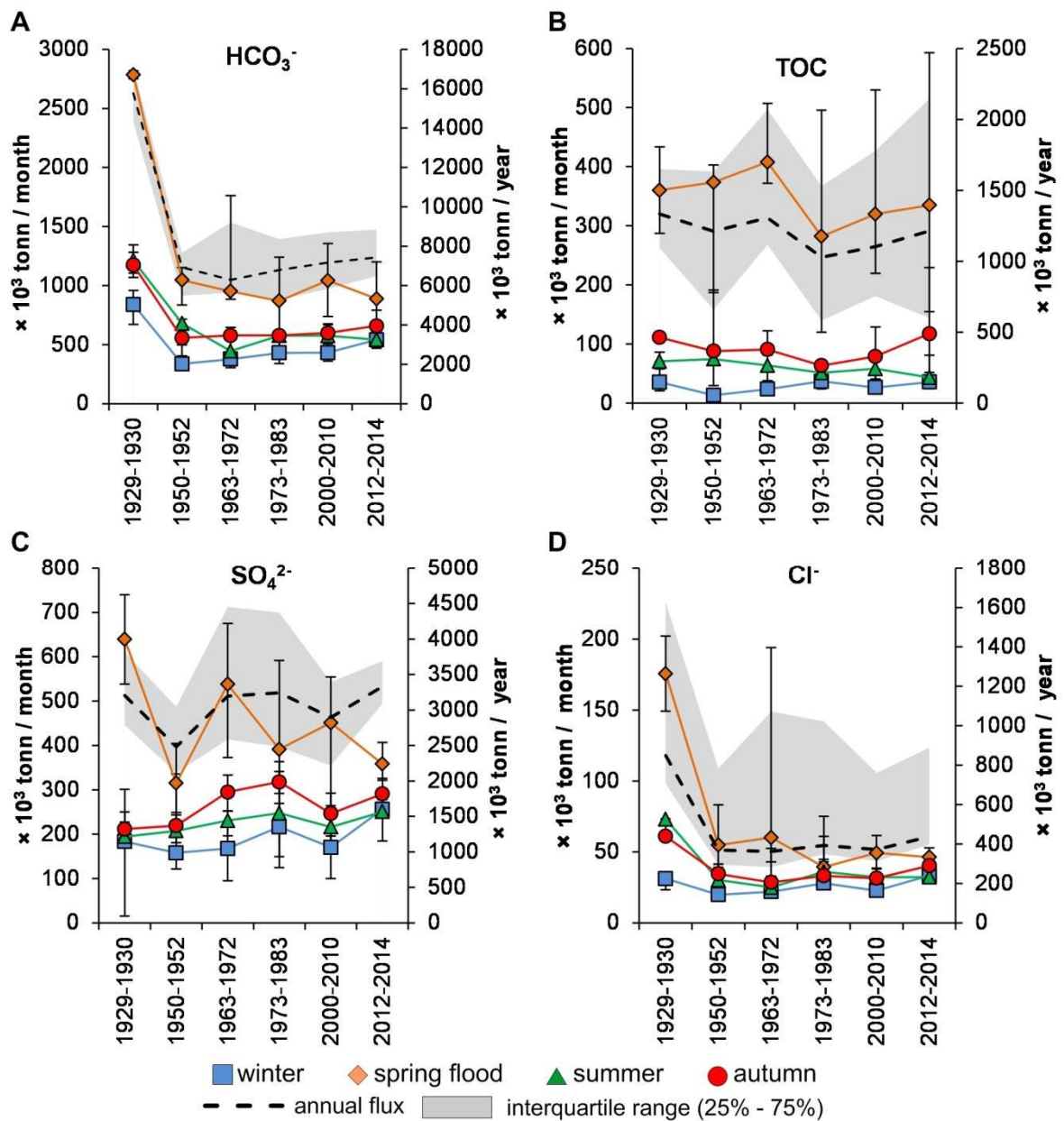
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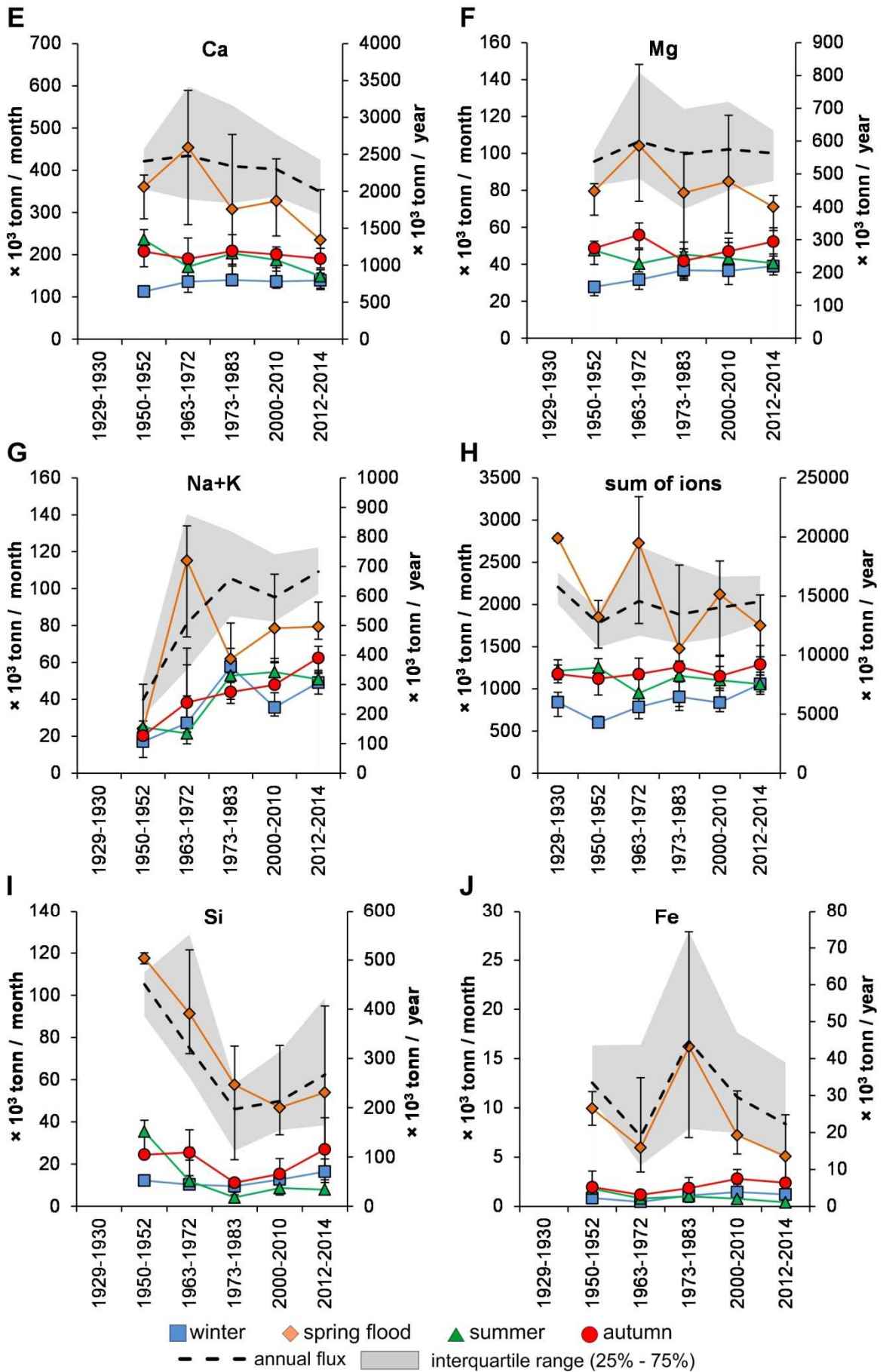
1141 Fig. 9, continued.



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1143 **Fig. 10.** Mean decadal or multi-annual seasonal export fluxes of  $\text{HCO}_3^-$  (A), TOC (B),  $\text{SO}_4$  (C),  
 1144  $\text{Cl}^-$  (D), Ca (E); Mg (F), Na+K (G), sum of ions (H), Si (I) and Fe (J) of the Severnaya Dvina  
 1145 since the onset of observations (1929 and 1950) until 2014. For historical periods (1929-2010),  
 1146 the mean multi-annual fluxes of cations, anions, TOC, Fe and Si were calculated from  
 1147 measured monthly average discharges and calculated monthly average concentrations. Due to  
 1148 scarcity of historical data, fluxes of individual years could not be assessed, and the time spans  
 1149 used for analysis are different. For most recent period (2012-2014), the fluxes are actually  
 1150 measured in this work.





1151

1152 Fig. 10, continued.