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Long-term Trends in Arctic Riverine Chemistry Signal Multi-faceted Northern Change

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1 **Long-term Trends in Arctic Riverine Chemistry Signal Multi-faceted Northern Change**

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40

41 **Abstract**

42 **Large rivers integrate processes occurring throughout their watersheds, and are therefore sentinels of**
43 **change across broad spatial scales. Riverine chemistry also regulates ecosystem function across**
44 **Earth’s land-ocean continuum, exerting control from the micro- (e.g., food web) to the macro- (e.g.,**
45 **carbon cycle) scale. In the rapidly warming Arctic, a wide range of processes have been hypothesized**
46 **to alter river water chemistry. However, it is unknown how the land-ocean flux of waterborne**
47 **constituents is changing at the pan-Arctic scale. Here, we show profound shifts in the concentration**
48 **and transport of biogeochemical constituents in the six largest Arctic rivers (the Ob’, Yenisey, Lena,**
49 **Kolyma, Yukon, and Mackenzie) since 2003, near river mouths capturing two-thirds of the pan-Arctic**
50 **watershed. While some constituent fluxes increase substantially at the pan-Arctic scale (alkalinity and**
51 **associated ions), others decline (nitrate and associated inorganic nutrients) or are overall unchanged**
52 **(dissolved organics). These clear but divergent trends diagnose a multi-systems perturbation that**
53 **indicates alteration of processes ranging from chemical weathering on land, to primary production in**
54 **the coastal ocean. We anticipate these findings will refine models of current and future functioning of**
55 **the coupled land-ocean Arctic system, and spur research on scale-dependent change across the river-**
56 **integrated Arctic domain.**

57

58 **Main**

59 Large rivers are planetary linchpins, connecting vast swaths of terrestrial landmass to the
60 world’s coastal oceans. On land, rivers integrate patchy landscapes and the variable biogeochemical
61 processes that these landscapes host, as water moving through watersheds incorporates the chemical
62 signature of its flow path. In the coastal ocean, the chemical signature of water transported by rivers
63 regulates nearshore biogeochemical^{1,2} and ecological^{3,4} function; over broader scales, river water and its
64 composition modify ocean physics¹. Nowhere is this more consequential than in the Arctic, where ~11%
65 of Earth’s riverine discharge drains into an enclosed basin containing ~1% of global ocean volume⁵. This
66 drainage occurs predominantly via six large rivers (Figure 1, Extended Data Table 1). As a result,
67 quantifying trends in river water chemistry at a constrained series of downstream sites allows us to
68 diagnose change across much of the pan-Arctic watershed, better understand the current functioning of
69 the connected land-ocean Arctic system, and predict what the future may hold for this rapidly changing
70 region⁶.

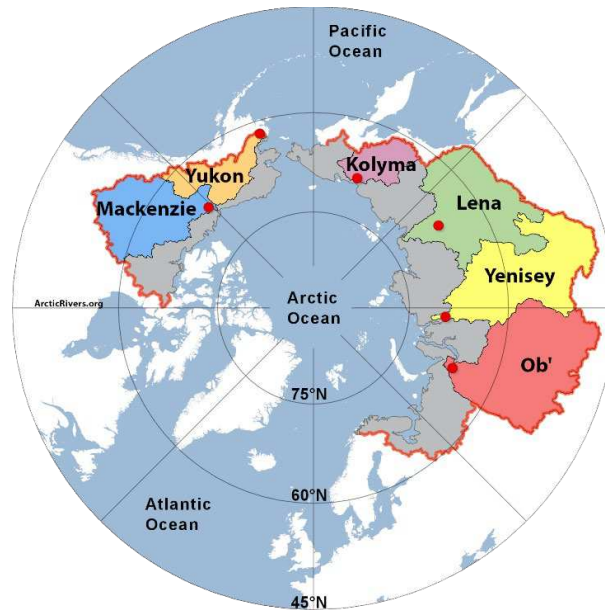


Figure 1: The six great Arctic rivers that are the focus of this assessment. Sampling locations are indicated by red dots. The $16.8 \times 10^6 \text{ km}^2$ pan-Arctic watershed is delineated by the red line.

71 Past work on north-flowing rivers has established significant increases in discharge across the
 72 pan-Arctic since the early-mid 20th century^{7,8} (Figure 2), attributed to intensification of the hydrologic
 73 cycle⁹. Such increases in water transport suggest that we should expect long-term change in the riverine
 74 flux (i.e., total riverine transport, as mass time⁻¹) of biogeochemical constituents, particularly for
 75 constituents such as organic carbon that are transport, rather than supply, limited in the north^{10,11}.
 76 Similarly, there is a broadly articulated expectation that permafrost thaw will increase the transport of
 77 organic matter, nutrients, and ions to aquatic networks, and thus their delivery to the coastal ocean¹²⁻¹⁴.
 78 However, these assessments miss that change in the north is multi-faceted, with factors such as
 79 shrubification¹⁵, temperature-induced increases in biogeochemical processing rates by heterotrophic
 80 and autotrophic microbes¹⁶⁻¹⁸, disturbances such as wildfire¹⁹, and human modifications such as river
 81 impoundment²⁰⁻²², changing land use²³, and changing industrial emissions²⁴ often occurring
 82 simultaneously, with the potential for antagonistic effects^{e.g., 25}. Even for permafrost thaw, deepening
 83 flowpaths²⁶ or processes such as sorption^{27,28} can lead to patterns in mobilization that vary between
 84 sites or regions²⁹.

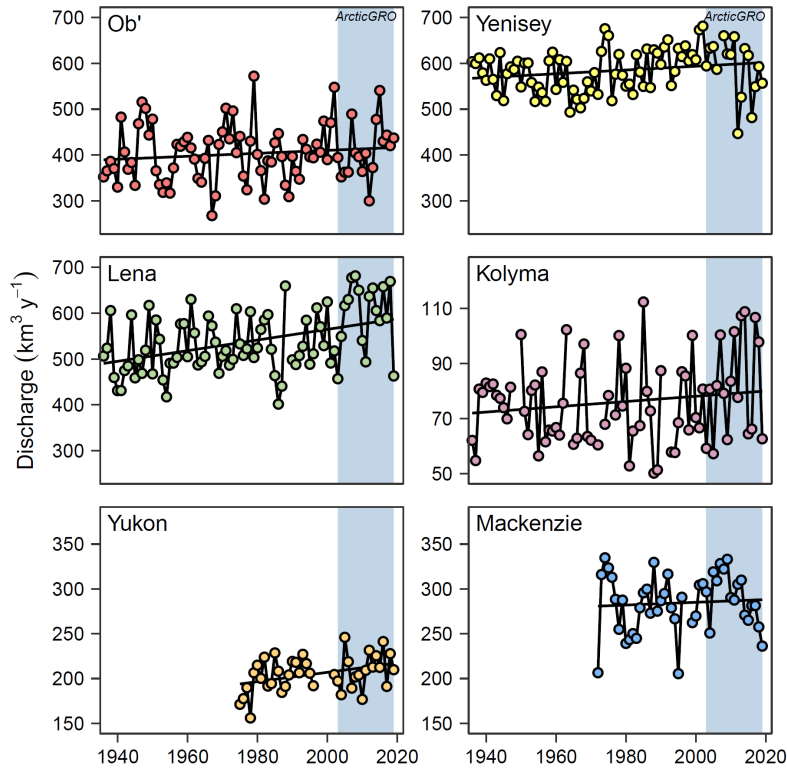


Figure 2: Long-term discharge record for each of the six great Arctic rivers. The timespan of the ArcticGRO data record is indicated with blue shading.

85 Here, we examine a nearly twenty-year record of coupled river discharge and chemistry
 86 (Extended Data Figure 1) collected from the six largest rivers that drain to the Arctic Ocean. These rivers:
 87 the Ob', Yenisey, Lena, and Kolyma in Russia, and the Mackenzie and Yukon in North America, capture
 88 two-thirds of the Arctic Ocean watershed area (Figure 1, Extended Data Table 1). This data record is the
 89 result of our group's ongoing efforts via the Arctic Great Rivers Observatory (ArcticGRO;
 90 www.arcticgreatrivers.org), which — given the challenge of collecting methodologically-consistent and
 91 seasonally-representative samples across these diverse jurisdictions and sites — represents an
 92 unparalleled resource for exploring Arctic riverine change. Our analyses reveal trends at magnitudes
 93 that signal broad-scale perturbation throughout the pan-Arctic, but with divergent trajectories that shed
 94 light on variable mechanisms of change. We use these insights to consider potential drivers of effect and

95 the consequences of observed change, and to explore where knowledge gaps are hampering our ability
96 to understand current and future functioning of the land-ocean Arctic system.

97

98 **Pronounced, but divergent trends in Arctic riverine flux**

99 We focus our assessment on three chemical constituents that are important drivers of
100 biogeochemical function across the land-ocean Arctic domain, and that are also representative of
101 broader constituent classes. These are: dissolved organic carbon (DOC; representative of the broader
102 organic matter pool including organic-associated nutrients); alkalinity (representative of many dissolved
103 ions); and nitrate (NO_3^- ; representative of dissolved inorganic nutrients, including ammonium (NH_4^+) and
104 silica (SiO_2)) (Extended Data Figure 2). To assess constituent flux, we applied a modelling approach that
105 couples daily discharge data with more sporadic concentration measurements, and makes use of the
106 known relationship between concentration and discharge to determine flux (*see Methods*)³⁰. Of our
107 focal suite, only alkalinity experienced a pan-Arctic (i.e., six rivers combined) increase in annual flux over
108 our period of record (Figure 3a). Nitrate declined significantly, while DOC, which has often been a focus
109 of study given its role as a rapid-cycling component of the contemporary carbon cycle, showed no
110 discernable change at the pan-Arctic scale (Figure 3b-c). Change that did occur, however, was
111 substantial, with a 32% decline in NO_3^- and an 18% increase in alkalinity over a period of 17 years. An
112 assessment of trends in flux across the broad suite of constituents measured by the ArcticGRO program
113 (Extended Data Figure 3) reveals patterns within constituent classes (i.e., Extended Data Figure 2) that
114 generally track those for the focal constituents. For example, trends in flux for ions closely affiliated with
115 alkalinity (Ca^{2+} , Mg^{2+} , Li^+ , Sr^{2+}) largely tracked that constituent; nutrients (SiO_2 and NH_4^+) showed a pan-
116 Arctic decline similar to that for NO_3^- ; and patterns for total dissolved phosphorus were similar to those
117 for DOC. Given that these constituents are regulated by processes ranging from chemical weathering² to
118 biological uptake¹⁶⁻¹⁸ on land; and modify processes ranging from ocean acidification³¹ to primary

119 production⁴ in the coastal ocean, the ecological and biogeochemical ramifications of the changes we
120 observe are likely profound.

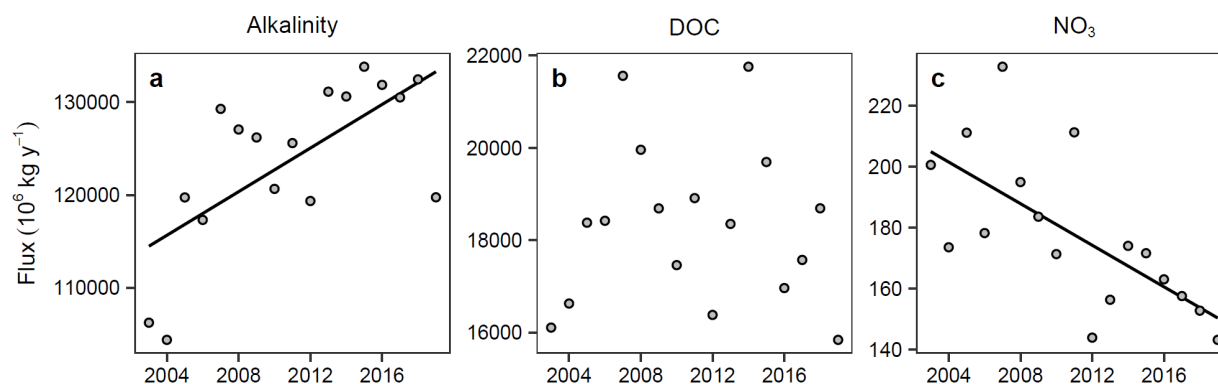


Figure 3: Trends in annual constituent fluxes of alkalinity (as CaCO₃), dissolved organic carbon (DOC), and nitrate (as NO₃-N), summed across the six great Arctic rivers. Fluxes are provided as 10⁶ kg y⁻¹. Thiel-Sen slopes with p<0.05 are indicated as lines within each panel. Statistical outputs are provided in Table S1.

121

122 **Concentration and discharge direct changing flux**

123 In some cases, river-specific trends in constituent flux deviated from the pan-Arctic sum. For example,

124 NO₃⁻ increased modestly in the Yukon (p=0.12), and showed little change in the Ob' (p=0.70) despite the

125 pan-Arctic decline described above; alkalinity patterns for the Mackenzie (negative trend slope; p=0.54)

126 contrasted with clear increases elsewhere; and DOC increased in the Ob' and decreased in the Yenisey

127 (p<0.02) in the face of limited change in other rivers (p=0.23–0.84); (Figure 4a). In part, these patterns

128 appeared to be driven by river-specific trends in discharge, which decreased in the Mackenzie (p=0.02)

129 and Yenisey (p=0.09) over the 17-year length of our data record (Figure 4b) despite the longer-term

130 increase in discharge documented for the pan-Arctic domain^{7,8} (Figure 2). Examining the mechanisms

131 underlying these changes in constituent flux requires that we disentangle inter-annual and long-term

132 change in water discharge from co-occurring trends in concentration. This task is complicated by the fact

133 that constituent concentrations vary seasonally and with discharge itself. We use two distinct

134 approaches to resolve these two known concerns.

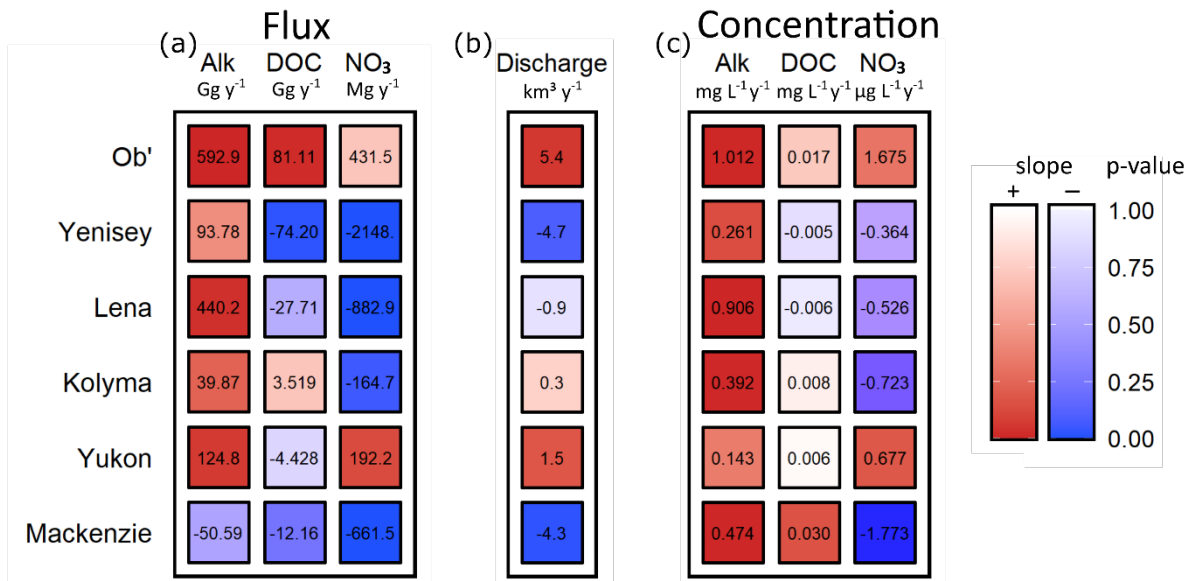


Figure 4: Annual trends for: (a) constituent flux; (b) discharge; and (c) concentration for each of the six great Arctic rivers. In each panel, the Sen's slope (numerical value) and p-value of the trend (shading) are shown. Flux and concentration trends for the full ArcticGRO constituent list are shown in Extended Data Figures 3 and 5, respectively; detailed statistical outputs are provided in Tables S1 and S2.

135 First, we use an approach to directly examine trends in measured concentrations, via trend
 136 analyses that are binned by season to account for seasonal variation in concentration unrelated to
 137 directional change over time (see *Methods*). We target this approach specifically to account for changes
 138 to the within-year seasonality of sampling across the two-decade timespan of the ArcticGRO program.
 139 Results from this direct trend analysis for concentration (Figure 4c) are generally similar to those for flux,
 140 described above (Figure 4a). Increases in alkalinity are widespread ($p=0.00$ – 0.14 in all rivers except the
 141 Yukon), nitrate concentrations decline (albeit modestly) across most rivers, and trends for DOC
 142 concentration are largely absent ($p=0.73$ – 0.96) in all rivers except for the Mackenzie, where DOC
 143 concentration increases modestly over time ($p=0.16$).

144 Second, we assess changes in flux controlled for inter-annual variation in discharge via a flow-
 145 normalization modelling approach that removes variation in discharge across years, but retains within-
 146 year (i.e., day-to-day) seasonality. Although this method does not generate an estimate of “true” flux, it
 147 is preferred when the analytical emphasis is mechanistic in nature (see also *Methods*)³², because it

148 overcomes year-to-year fluctuations in discharge that can obscure underlying change. These flow-
149 normalized fluxes show trends that largely reflect those for concentration presented above (Figure 4c),
150 with some notable refinements: increases in alkalinity and decreases in NO_3^- become more robust, and a
151 decrease in DOC emerges for the Kolyma while the DOC increase in the Mackenzie is maintained
152 (Extended Data Figure 4). Overall, patterns for flow-normalized fluxes are remarkably similar to our best
153 estimates of true flux and concentration presented above, with broad-scale increases in alkalinity and
154 declines in NO_3^- , and variable and modest trends for DOC. Taken as a whole, these broad but divergent
155 trends diagnose a multi-systems perturbation to the pan-Arctic system, with effects profound enough to
156 reach the mouths of large northern rivers.

157

158 **Divergent trends diagnose multi-systems change**

159 The array of factors that might reasonably enable long-term change in riverine chemistry is diverse,
160 varying regionally in magnitude and across chemical constituents in effect (Figure 5, Supplemental Text).
161 As just one example, abrupt permafrost thaw (i.e., thermokarst) is a regionally-specific phenomena
162 dependent on the presence of ground ice³³ that is generally understood to increase the transport of
163 some constituents to riverine networks (e.g., inorganic nutrients)²⁹, but potentially decrease others (e.g.,
164 DOC, in cases where landscape collapse increases mineral sorption, or diverts hydrologic flow paths
165 through mineral soils)^{34,35}. As a result, the variation in response that we describe above can be used to
166 diagnose drivers of change, and develop approaches to assess future functioning of the land-ocean
167 Arctic system.

168 For some chemical constituents, known factors of change are both relatively widespread and
169 consistent in their directionality (Figure 5; Supplemental Text). In the case of alkalinity and related ions,
170 for example, exposure to deeper soils via either active layer deepening or thermokarst-associated
171 permafrost thaw will typically increase mineral weathering by increasing water contact with deeper

172 mineral soils^{36,37}. Acting synergistically, shrubification³⁸ and increased temperature-driven organic
 173 matter processing³⁹ will increase weathering rates via processes such as increasing soil pore water
 174 acidity. Because these processes are coherent in their directionality and geographically widespread, the
 175 net result appears as a cohesive increase in concentration and flux throughout the pan-Arctic domain.

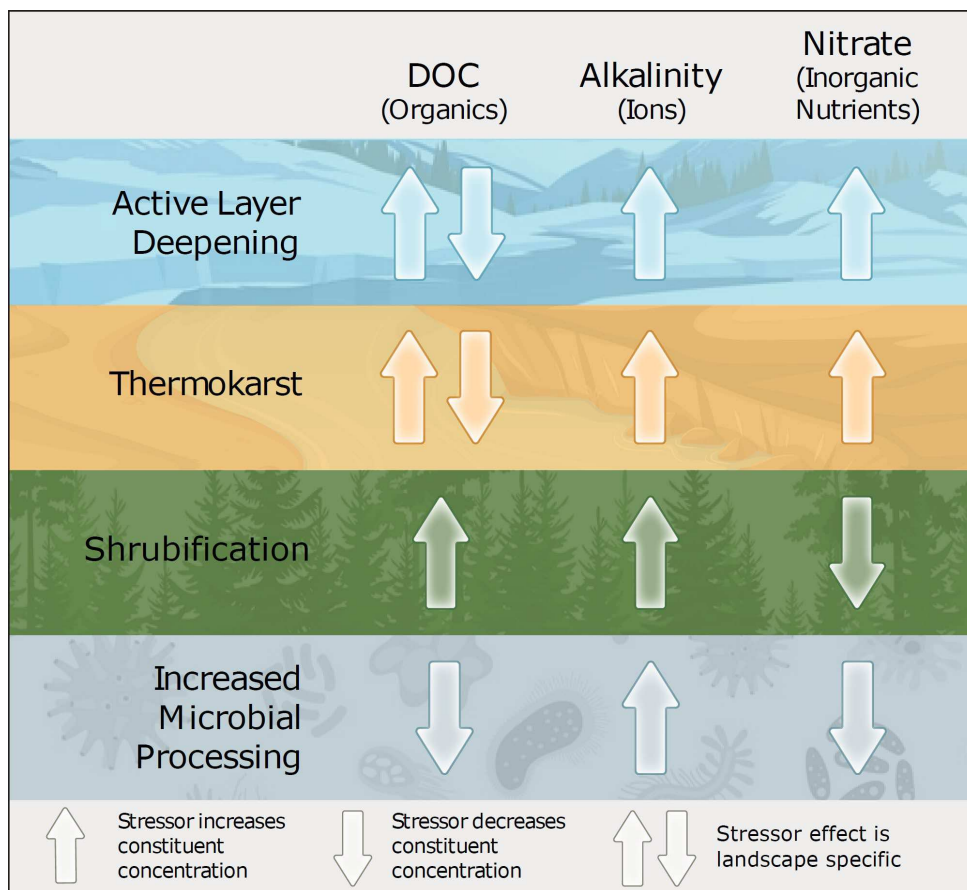


Figure 5: A conceptual diagram to illustrate key drivers of change of Arctic riverine chemistry, and their anticipated direction of effect for each of the three focal constituents. The Supplemental Text provides an overview of the literature evidence for this conceptual exercise, in addition to a description of drivers that are regional in their effect, or exert control largely outside of the timespan of the ArcticGRO data record.

176 For other constituents, variation in the directionality of factors of change appears to cause a
 177 muted overall response. In the case of DOC, for example, permafrost thaw can either increase⁴⁰ or
 178 decrease³⁴ loading to aquatic systems, depending on the composition of soils subject to thaw³⁵. While
 179 greening will increase vegetation and litter substrates for leaching and therefore the transport of
 180 organic matter to aquatic networks⁴¹, temperature-driven increases in mineralization^{18,42} and potential

181 rapid processing of novel organic matter substrates⁴³ act in opposition to this effect. Across these large
182 Arctic rivers, the net result appears to be a dissipation of effect with transport through aquatic
183 networks, and little net change in DOC delivery to the coastal ocean over the timespan of this
184 assessment.

185 Finally, in some cases, geographically widespread processes appear to overwhelm counteracting
186 drivers. For example, although we broadly expect permafrost thaw to increase inorganic nitrogen
187 delivery to aquatic networks²⁹, our analyses reveal declines in the transport of NO_3^- (and other inorganic
188 nutrients) to the Arctic Ocean from large Arctic rivers. This suggests that factors such as temperature-
189 driven increases in nitrogen cycling¹⁷ or nitrogen uptake and/or immobilization^{16,44} may currently be
190 overwhelming local increases in mobilization²⁹, when assessed at the large-river watershed scale. These
191 findings underline the importance of taking a systems approach to understanding Arctic change, with an
192 acknowledgement that biogeochemical cycles are inherently linked across elements and space.

193

194 **Broad perturbation in linked biogeochemical cycles across the land-ocean Arctic domain**

195 Our analyses diagnose changes to the land-ocean Arctic system that are pervasive enough to leave few
196 biogeochemically-active elements unscathed. As a result, these findings likely signal domain-scale
197 change to ecosystem function. On land, ecosystem models have predicted increases in organic matter
198 loading to fluvial networks in the changing north⁴⁵. The lack of this signal at river outflows, therefore,
199 suggests possible increases in carbon mineralization and associated outgassing during transit through
200 watersheds, and thus an acceleration in carbon cycling within Arctic fluvial networks. Increasing
201 alkalinity is suggestive of increases in chemical weathering, but in a region where a predominance of
202 carbonate over silicate weathering, coupled with substantial sulfide oxidation in some watersheds,
203 causes the ratio of CO_2 consumption: alkalinity generation to be overall low relative to the global mean².
204 Increasing SO_4 fluxes in rivers where SO_4 appears to be largely derived from sulfides (Extended Data

205 Figure 3; Yukon, Kolyma⁴⁶) may in fact indicate increasing bicarbonate liberation in the absence of CO₂
206 fixation².

207 In the coastal ocean, riverine inputs of DIC result in CO₂ outgassing to the atmosphere⁴⁷. The
208 magnitude of this effect relative to weathering-induced CO₂ fixation on land, and its change, will play a
209 key role in determining the carbon balance of the Arctic system. Acting concurrently, the declining NO₃⁻
210 that we document is consistent with negative feedbacks for Arctic Ocean biological productivity and CO₂
211 uptake from the atmosphere, which is generally thought to be increasing as seasonal sea ice declines
212 and nutrients become more available⁴⁸. However, the Arctic Ocean also has globally low N:P ratios
213 because its shelf sediments are a significant nitrogen sink through denitrification⁴⁹. As a result,
214 decreases in riverine NO₃⁻ transport coupled with increasing discharge will increase stratification and
215 decrease availability of nutrients for biological production. The changes will play out alongside other co-
216 occurring processes, such as changes to the dilution effect of river water on ocean pH² with increasing
217 alkalinity, and consequent effects of this change on primary production⁵⁰.

218

219 **Conclusions**

220 In addition to implications for the current and future functioning of the land-ocean Arctic
221 system, our findings point to several important considerations for understanding change. Particularly for
222 bio-reactive constituents (DOC, nutrients), this work illustrates the importance of scale. Widespread
223 declines in constituents such as NO₃⁻ in the face of local processes known to increase land-water
224 mobilization suggests a fulcrum-like redistribution in biogeochemical cycling at the landscape-scale,
225 where fine-scale uptake and processing is increasing at the expense of communities downstream. How
226 the balance between local mobilization and broader-scale processing may shift for the smaller
227 catchments encircling the Arctic Ocean that have much shorter in-river transit times (see, for example,
228 NO₃⁻ trends in refs. ^{51,52}), or for other bio-reactive constituents (dissolved organic matter and other

229 inorganic nutrients) remains an open question. However, this potential scale-dependent variation in
230 river mouth trends will be an important determinant of the geographic distribution of change in the
231 Arctic nearshore. Teasing apart the relative importance of various drivers of change, and how they will
232 vary with time and across constituents, will require process-based models, as already developed for
233 alkalinity³⁹ and DOC⁴⁵, in addition to models that are linked across elements and space⁴⁷. These models
234 must inherently co-consider multiple drivers of change, including those not directly discussed above
235 (e.g., impoundment, declining acid deposition, land use and land cover change; see also Supplemental
236 Text). The datasets we draw on for our analyses are remarkable for their geographic cohesion and their
237 relative length. However, they also diagnose profound change occurring in real time. This work clearly
238 calls for continued, coordinated observation of the land-ocean Arctic system. More importantly,
239 however, it reinforces the need for rapid attention to Earth's warming climate, and its multiplicative
240 effects in the north.

241

242 **Online Methods**

243

244 **Sample collection and dataset coverage**

245

246 *Water chemistry:* We began sampling the six largest Arctic rivers for water chemistry in the summer of
247 2003. The project was initially called PARTNERS (Pan-Arctic River Transport of Nutrients, Organic Matter,
248 and Ssuspended Sediments), and was expanded and renamed the Arctic Great Rivers Observatory
249 (ArcticGRO) in 2008. Sample collection for the data presented in this paper occurred 5-7 times per year,
250 with the exception of a short break during 2007-08 (Extended Data Figure 1). Water chemistry samples
251 are collected as far downstream on each of the six Great Arctic rivers as logistically feasible, at Salekhard
252 (Ob'), Dudinka (Yenisey), Zhigansk (Lena), Cherskiy (Kolyma), Pilot Station (Yukon), and Tsiigehtchic
253 (Mackenzie) (Figure 1; Extended Data Table 1). Between 2003 and 2011, open water sampling was
254 conducted using a D-96 sampler⁵³ equipped with a Teflon nozzle and Teflon sample collection bag,
255 which enabled depth-integrated and flow-weighted samples. Samples were collected at five roughly
256 equal increments across the river channel and combined in a 14-L Teflon churn, resulting in a single
257 composite sample. Beginning in 2012, open-water sampling was conducted by collecting three near-
258 surface samples on each of the left-bank, right-bank, and mid-points of each river, and combining these
259 to form a composite sample. Across the full period of record, wintertime (under ice) samples were
260 collected by drilling a hole at the river's mid-point, and collecting a sample from below the ice surface.

261

262 Within years, the timing of sample collection has changed slightly over the ArcticGRO period of record.
263 Early collection schemes (2003-06 and 2009-11) focused on the spring freshet (three or more samples

264 per year), with further sample coverage through the more broadly-spread late summer (period of
265 deepest thaw of the seasonally-frozen active layer; one to four samples) and winter (typically one
266 sample) periods. Given the paucity of cross-site comparable data for these rivers at the outset of the
267 ArcticGRO program, this sampling scheme was designed to maximize coverage during the high flows of
268 the spring, when constituent concentrations are changing rapidly and the majority of constituent flux
269 occurs⁵⁴. In 2012, sampling shifted to become evenly spread across the annual cycle, with samples
270 collected bi-monthly (i.e., six samples per year), and months of collection alternating between years.
271 Sample processing (i.e., filtering and preservation) occurs within 24 hours of sample collection. As
272 described above for sample collection, processing protocols were identical across all sites. Processed
273 and preserved samples were shipped to Woods Hole, MA, where they were distributed to specialized
274 laboratories for individual analyses. A complete description of processing and analytical methodologies
275 is available on the ArcticGRO website (www.arcticgreativers.org), and archived at the Arctic Data
276 Center⁵⁵. The focal constituents highlighted in this paper were analyzed as follows: For DOC, on a
277 Shimadzu TOC analyzer, following acidification with HCl, sparging, and using the 3 of 5 injections that
278 resulted in the lowest coefficient of variation; for alkalinity, following acid titration using a Hach digital
279 titrator (2003-2009) and Mettler Toledo model T50M titrator (2010 onwards); for NO₃⁻ (as NO₃⁻ + NO₂⁻)
280 colorimetrically using a Lachat Quickchem FIA+ 8000 (2003-2011) and Astoria (2012 onwards)
281 autoanalyzer.

282
283 *Discharge:* All Arctic-GRO discharge measurements are from long-term gauging stations operated by
284 Roshydromet, the US Geological Survey, and the Water Survey of Canada. On the Ob', Yukon, and
285 Mackenzie Rivers, gauging stations are identical to the ArcticGRO sample collection location. On the
286 Yenisey, Lena, and Kolyma Rivers, proximate gauging stations were used, at Kyusyur, Igarka, and
287 Kolymskoye, respectively. The effect of this modest offset, and methods for correction, have been
288 described elsewhere⁵⁴. Continually-updated concentration and discharge datasets are available on the
289 ArcticGRO website. Concentration and discharge data used for this analysis (i.e., 2003 – 2019, inclusive)
290 have been archived at the Arctic Data Center (<https://doi.org/10.18739/A2VH5CK43>).

291 292 **Determination of constituent flux using the WRTDS Kalman approach**

293
294 Determining constituent flux requires a modelling approach, because discharge data are typically
295 available at daily (or even more refined) time steps, while concentration measurements are almost
296 always collected much more patchily over time. We used the Weighted Regressions on Time, Discharge,
297 and Season (WRTDS) approach to estimate constituent flux over the ArcticGRO period of record,
298 actualized in the *EGRET* (Exploration and Graphics for RivEr Trends)⁵⁶ package in the R statistical
299 platform⁵⁷. This approach has been shown to provide more accurate estimates of constituent flux than
300 other common statistical techniques used for flux estimation⁵⁸, as a result of the use of weighted
301 regression (see below), and the removal of the requirement for homoscedastic residuals for bias
302 correction⁵⁹. Similar to other flux estimation techniques, the predictive equation takes the form of:

$$303 \ln(c) = \beta_0 + \beta_1 t + \beta_2 \ln(Q) + \beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t) + \varepsilon \quad (1)$$

304
305
306 where c is concentration, Q is discharge, t is time in decimal years, and ε is the unexplained variation,
307 with the sine and cosine functions enabling seasonality within the model³⁰. However, unlike most other
308 flux modelling approaches, the coefficients $\beta_0 - \beta_4$ are not static, but are allowed to vary gradually in Q, t
309 space. This is accomplished via an approach that develops a separate model for each day of the
310 observational record by re-evaluating the relationship between concentration and time, season, and
311 discharge, with a weighting that prioritizes samples closest in Q, t space to the day of estimation⁵⁹. For

312 this work, we use the WRTDS-Kalman modification, which further improves upon the above-described
313 technique by using a first order autoregressive (AR1) model to capture residual autocorrelation⁶⁰. An
314 assessment of measured vs. modelled daily outputs via WRTDS-Kalman is provided in Extended Data
315 Figure 6. Daily WRTDS-Kalman flux outputs have been archived at the Arctic Data Center
316 (<https://doi.org/10.18739/A2VH5CK43>).

317

318 **Calculation of flow-normalized flux, and assessment of flow-normalized trends**

319

320 A complication of evaluating trends in flux is that a substantial amount of variation in concentration is
321 caused by year-to-year variation in discharge, which adds considerable noise to the time series. To
322 assess changes in flux with year-to-year variation in discharge removed, we use the WRTDS *flow*
323 *normalization* technique, which filters out the influence of inter-annual variation in streamflow. This is
324 accomplished by creating a probability density function (pdf) of Q for each day of the calendar year, and
325 producing flow-normalized concentrations and fluxes that integrates over this pdf³². In this way,
326 discharge is normalized across calendar years, but intra-annual variation (i.e., seasonal variation, at a
327 daily time step) is retained. Given the statistical complexity of this smoothing approach, we estimate
328 uncertainty in change over the flow normalized time series using a block bootstrap technique
329 implemented in the R package *EGRETCi*, which creates a posterior mean estimate ($\hat{\pi}$) of the probability
330 of a trend, and assesses trend likelihood as: highly likely ($\hat{\pi} < 0.05$ or > 0.95) very likely ($\hat{\pi}$ 0.05-0.10 or
331 0.90-0.95), likely ($\hat{\pi}$ 0.10-0.33 or 0.66-0.90), or about as likely as not ($\hat{\pi}$ 0.33-0.66)³². Our results are
332 provided as mean and 90% confidence interval outputs from the block bootstrap approach described in
333 ref. ³².

334

335 **Assessment of trends in annual discharge and WRTDS-Kalman constituent flux**

336

337 Daily discharge and flux estimates were summed within years to generate an annual time series, and a
338 Mann-Kendall test was used to analyze the significance of annual trends over time. Within this analysis,
339 trend slopes were calculated using the Theil-Sen method. Trend analyses, and the calculation of slopes
340 were conducted using the *trend* package⁶¹ in R⁵⁷. We report Kendall's p-value and Sen's slope in the
341 main text, and report additional statistical outputs in Table S1.

342

343 **Assessment of trends in concentration**

344 To allow us to examine trends in concentration directly, but account for seasonal variation in
345 concentration measurements that may skew trend detection, we used a Seasonal Kendall test⁶². This
346 approach accounts for seasonality by calculating the Mann-Kendall statistic for each of p seasons
347 directly, and then combines the test statistic for each season (S_p) to create an overall seasonal Kendall
348 statistic (S'):

349

$$S' = \sum_{i=1}^p S_p$$

350

351 We used a modification of the original seasonal Kendall test which accounts for serial dependence by
352 using an autoregressive moving average (ARMA) (1:1) approach⁶³. We defined seasons as spring (May-
353 June), summer (July-October) and winter (November-April), as has been previously established for the
354 ArcticGRO dataset^{54,64}. We further used a seasonal Kendall slope estimator to determine the magnitude
355 of trends, following the Theil-Sen approach as modified for the seasonal Kendall test⁶².

356

357 **Data visualization**

358 Figures 2-4 and Extended Data figures 1 and 3-5 were actualized in R⁵⁷ using *ggplot2*⁶⁵. The correlation
359 cluster analysis shown in Extended Data figure 2 was carried out using the function “heatmap.2” in the
360 *gplots* package⁶⁶ in R.

361

362 **Data availability**

363 Data used for our analyses and daily Kalman outputs are provided as a fixed package at the Arctic Data
364 Center (<https://doi.org/10.18739/A2VH5CK43>). More recent updates of the ArcticGRO water quality
365 and discharge datasets can be found at the project website (www.arcticgreativers.org) and through the
366 Arctic Data Center⁵⁵.

367

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381

382 **Author contributions**

383 *Conceived of the paper and performed data analysis:* SET, RMH, JWM, RGMS, AS, FM, AIS; *Led*
384 *manuscript preparation:* SET; *Initial design of the ArcticGRO (PARTNERS) program:* BJP, RMH, JWM, PAR,
385 RGS, RMWA, LWC, VVG, SZ, AVZ; *Sample and data acquisition:* AVZ, TYG, SZ, NZ, GE, PFS, EAM, RS, MT,
386 LSK; *Performed laboratory analyses:* AS, LS, BP-E, PR, CG, PFS; *Read and commented on the manuscript:*
387 All authors

388

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390

391 **Competing interests:** The authors declare no competing interests.

392

393

394 **Extended Data Table 1:** Characteristics of the six largest Arctic watersheds.

	Watershed Area	Area at gauge	Distance to Arctic Ocean ^a	Mean discharge ^b	Runoff	Permafrost ^c	Continuous Permafrost ^c	Discontinuous Permafrost ^c	Tundra ^d	Forest ^d	Regulated ^e	Mean annual temperature (2003-2019) ^f	Mean annual precipitation (2003-2019) ^f	Population Density ^g
	10 ⁶ km ²	10 ⁶ km ²	km	km ³ y ⁻¹	mm y ⁻¹	(% area)	(% area)	(% area)	(% area)	(% area)	(% area)	°C	mm y ⁻¹	people km ⁻²
Ob'	2.99	2.95	287	409	139	26	2	4	0.1	48.2	14.6	-0.7	604	9.07
Yenisey	2.54	2.44	433 (697)	595	244	88	33	11	0.5	67.9	50.5	-4.4	619	2.85
Lena	2.46	2.43	754 (211)	599	247	99	79	11	1.2	62.5	7.2	-8.9	548	0.45
Kolyma	0.65	0.53	120 (283)	108	205	100	100	0	3.2	16.7	18.9	-10.7	546	0.2
Yukon	0.83	0.83	200	211	254	99	23	66	0.1	68.4	0.0	-4.8	571	0.17
Mackenzie	1.78	1.68	260	295	176	82	16	29	0.0	74.2	4.3	-3.6	547	0.25
Sum	11.25	--	--	2,217	--	--	--	--	--	--	--	--	--	--
Pan-Arctic	16.8 ^h	--	--	~3710 ⁱ	~220	--	--	--	--	--	--	--	--	--

395

396

397

^a Distance from the water chemistry station (discharge gauge) to the Arctic Ocean, including transit distance through river mouth Deltas. Where only one value is presented, water chemistry and discharge data collection are co-located. Data for Russian rivers are from the Hydrometeorological Service of the USSR⁶⁷. Data for North American rivers are estimated from Google Earth.

398

^b Mean annual discharge over the study period

399

^c From Holmes et al. (2013)⁶⁸. Permafrost extent and classification from the International Permafrost Association's Circum-Arctic Map of Permafrost and Ground Ice Conditions.

400

^d Vegetation classes from the 20-class GLDAS/NOAH product⁶⁹, based on a 30 arc second MODIS vegetation data that uses a modified IGBP classification scheme. Tundra is the sum of mixed and bare ground tundra. Forest is the sum of evergreen, deciduous, and mixed forest, and wooded tundra.

401

402

^e Regulated area at the end of the study period, from Lehner et al. (2011)⁷⁰. Includes impoundments that were completed on the Kolyma (2013) and Yenisey (2012) rivers during the ArcticGRO period of analysis.

403

404

^f Mean annual temperature and precipitation from the MERRA2 reanalysis product⁷¹.

405

^g Population density from the Center for International Earth Science Information Network (2018)⁷² gridded population of the world.

406

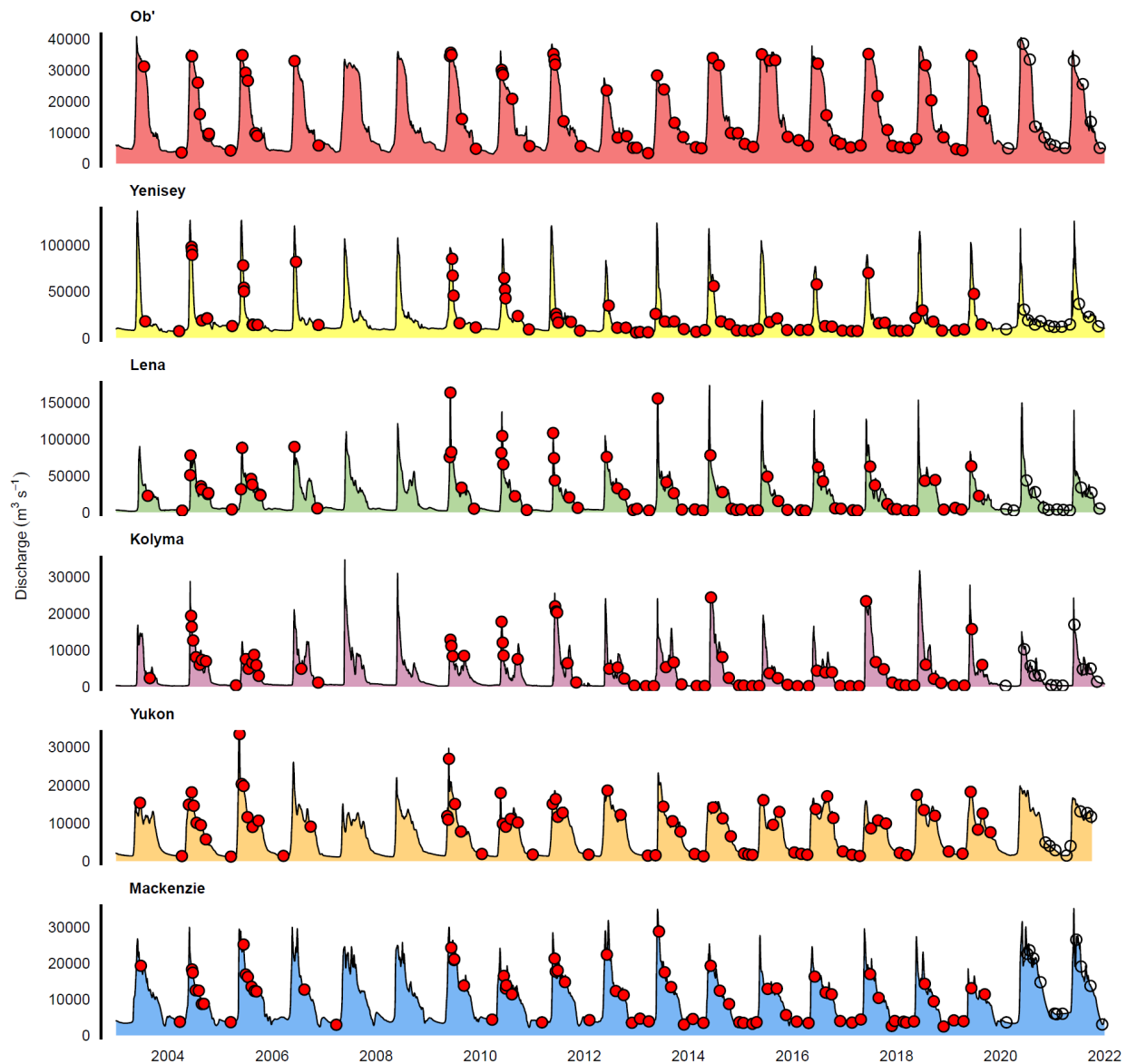
^h Watershed area of 16.8 x 10⁶ km² corresponds to the area demarcated in Figure 1, which does not include drainage to Hudson Bay. The pan-Arctic watershed including Hudson Bay, but

407

excluding the Greenland Ice Cap, covers an area of 22.4 x 10⁶ km² (from Lammers et al. 2001⁷³)

408

ⁱ Estimate derived from Shiklomanov et al. 2021²², for the period covering 1980-2018



409

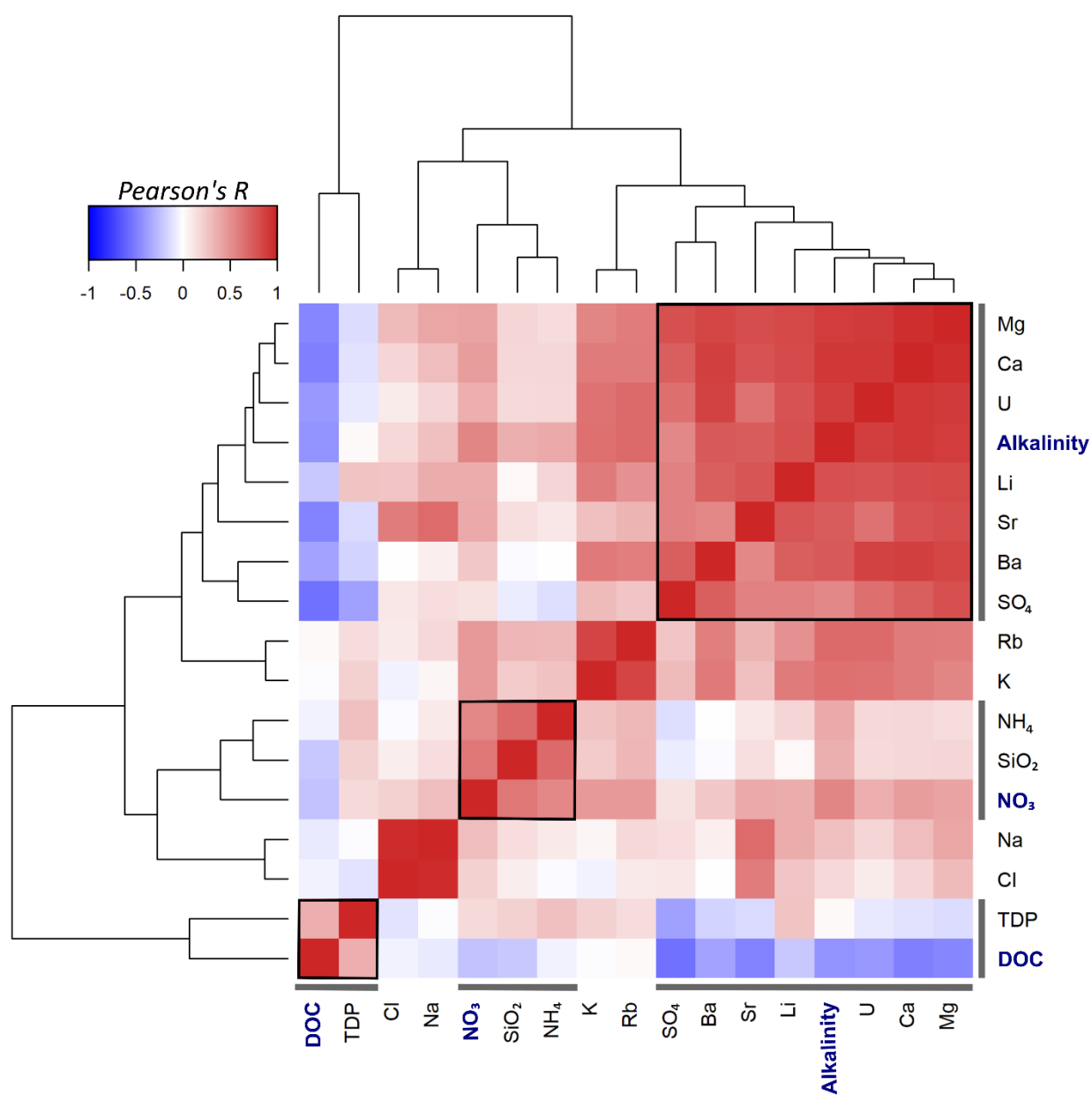
410

411 **Extended Data Figure 1:** Time-series of discharge and concentration measurements across the six Arctic
 412 Great Rivers. Discharge is shown as a continuous time-series for all rivers. Dates of sample collection for
 413 concentration measurements used in this analysis are shown with red circles; clear circles indicate
 414 ongoing data collection.

415

416

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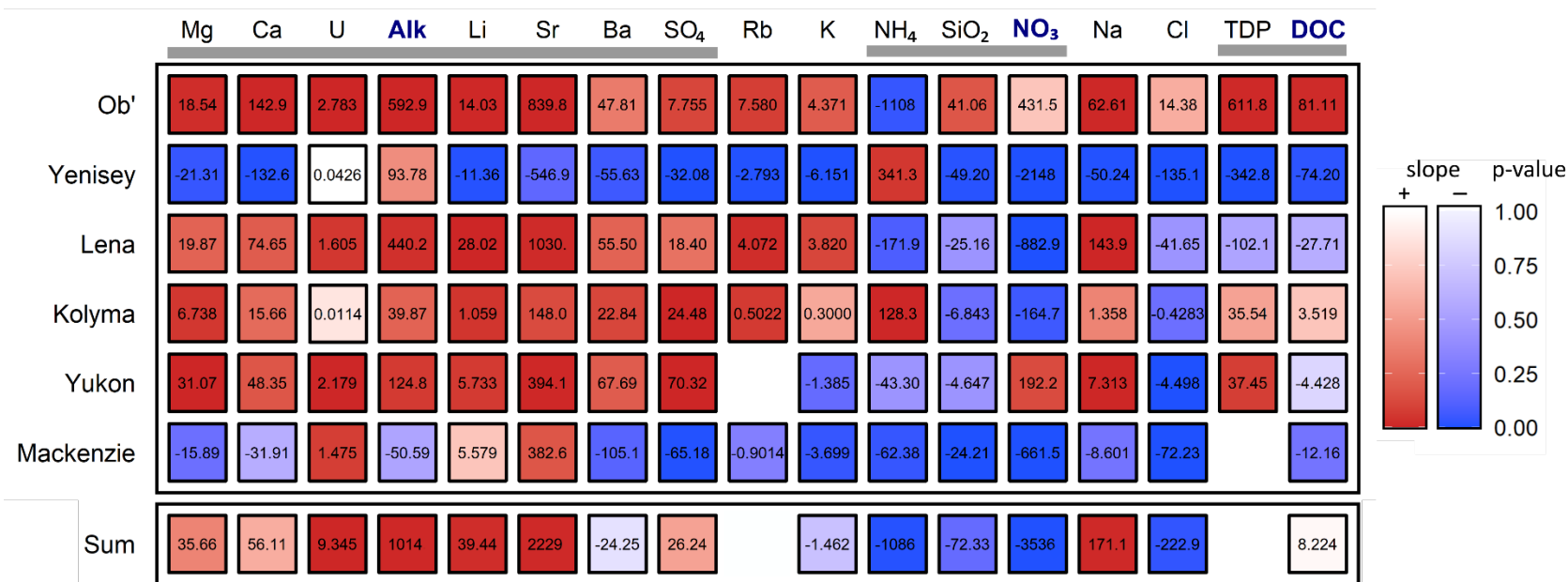


418

419 **Extended Data Figure 2:** A cluster heatmap illustrating correlation between constituents for the full
420 ArcticGRO dataset. Shading indicates the Pearson correlation coefficient, which was used as the distance
421 metric for hierarchical clustering. Focal constituents (alkalinity, nitrate [NO₃-N], and dissolved organic
422 carbon [DOC]) are bolded in blue. Black boxes within the correlation plot and grey shading along axes
423 indicate clusters associated with each focal constituent.

424

425



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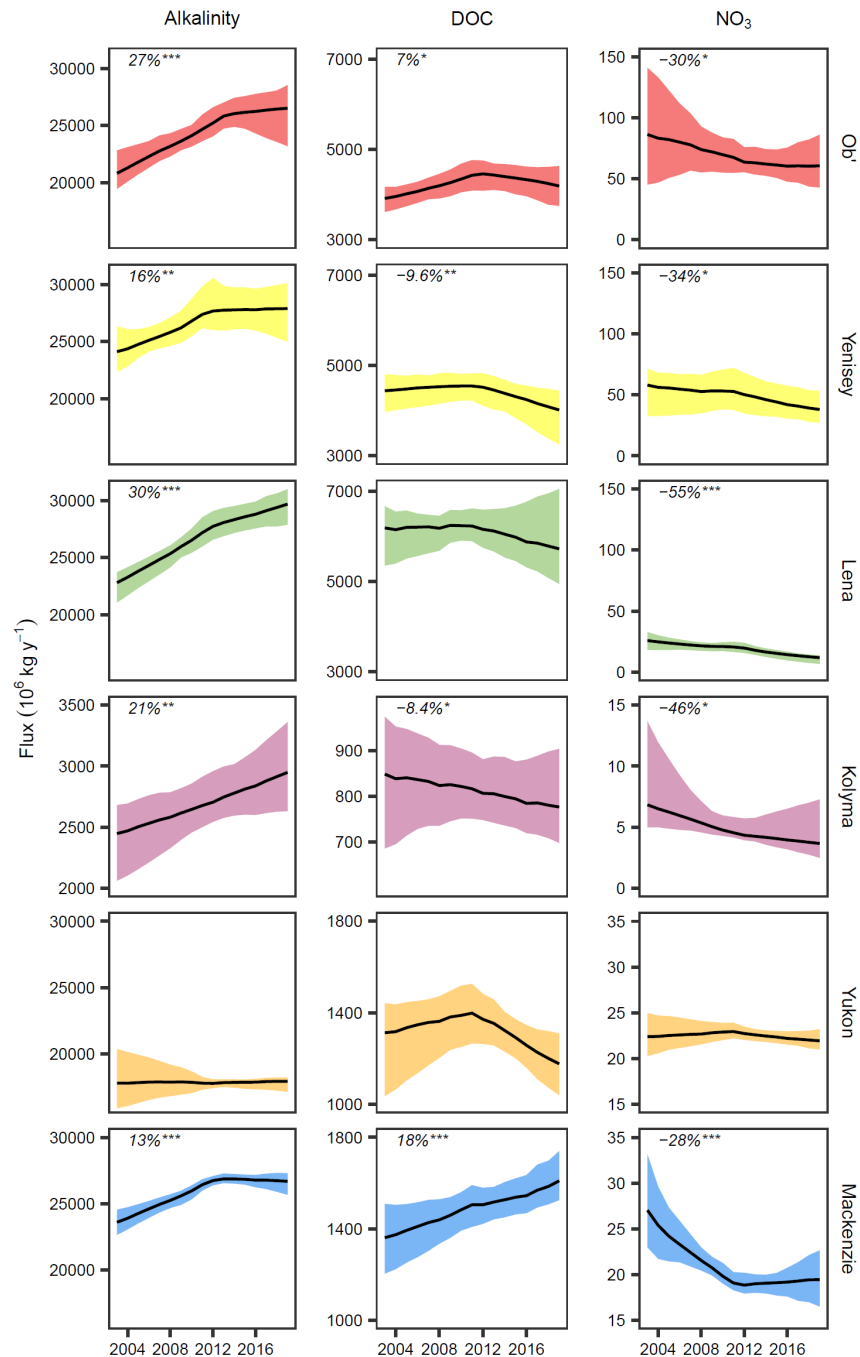
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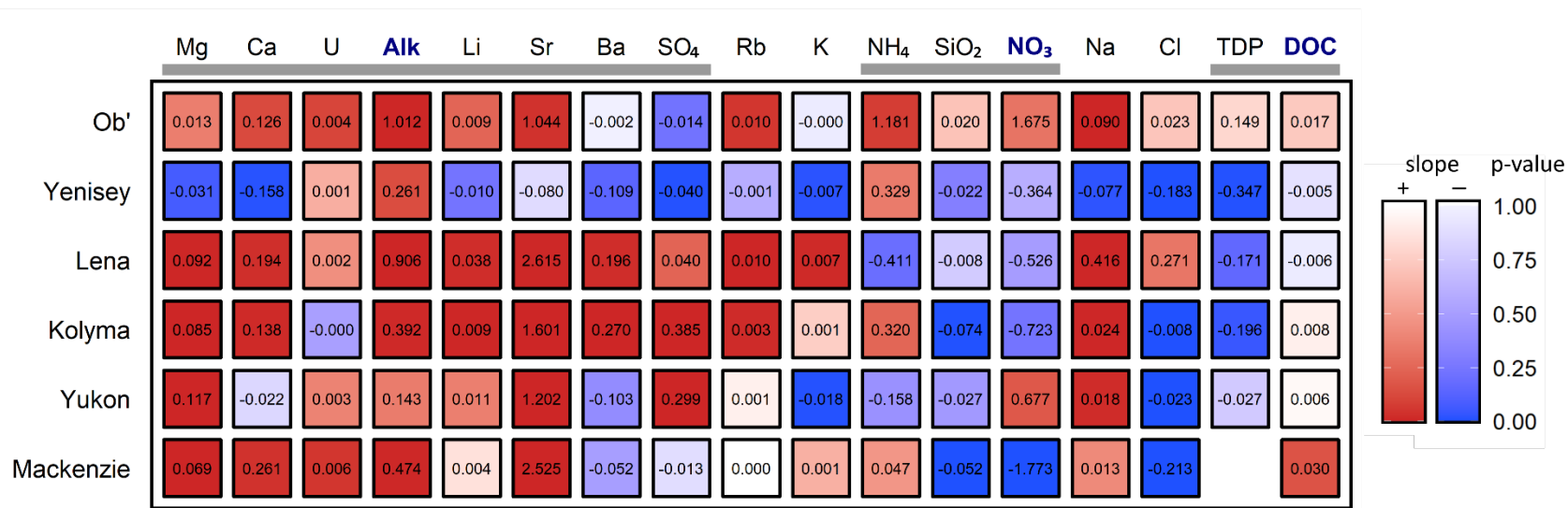
Extended Data Figure 3: Annual trends in constituent flux across the full ArcticGRO dataset, for each of the six great Arctic rivers. Trend analysis is via a Mann-Kendall analysis; the Thiel-Sen slope (numerical value) and p-value of the trend analysis (shading) are shown. Corresponding trends in concentration are provided in Extended Data Figure 5. Grey bars illustrate groupings from Extended Data Figure 2. Units (Gg y^{-1} or Mg y^{-1}) are provided in Table S1.



432

433 **Extended Data Figure 4:** Flow-weighted trends in annual constituent flux for the three focal constituents
 434 (alkalinity, dissolved organic carbon [DOC], and nitrate [$\text{NO}_3\text{-N}$], for each of the six Great Arctic rivers.
 435 The solid line indicates the mean, and shading indicates 90% confidence interval from the block
 436 bootstrap analysis. Asterisks indicate trends that are: ***highly likely (posterior mean estimate $\hat{\pi} < 0.05$ or
 437 > 0.95); **very likely ($\hat{\pi}$ 0.05-0.10 or 0.90-0.95); or *likely ($\hat{\pi}$ 0.10-0.33 or 0.66-0.90), with percentage
 438 change in constituent flux indicated for the period of record. Where no percentage change is shown,
 439 trends were assessed to be about as likely as not ($\hat{\pi}$ 0.33-0.66).

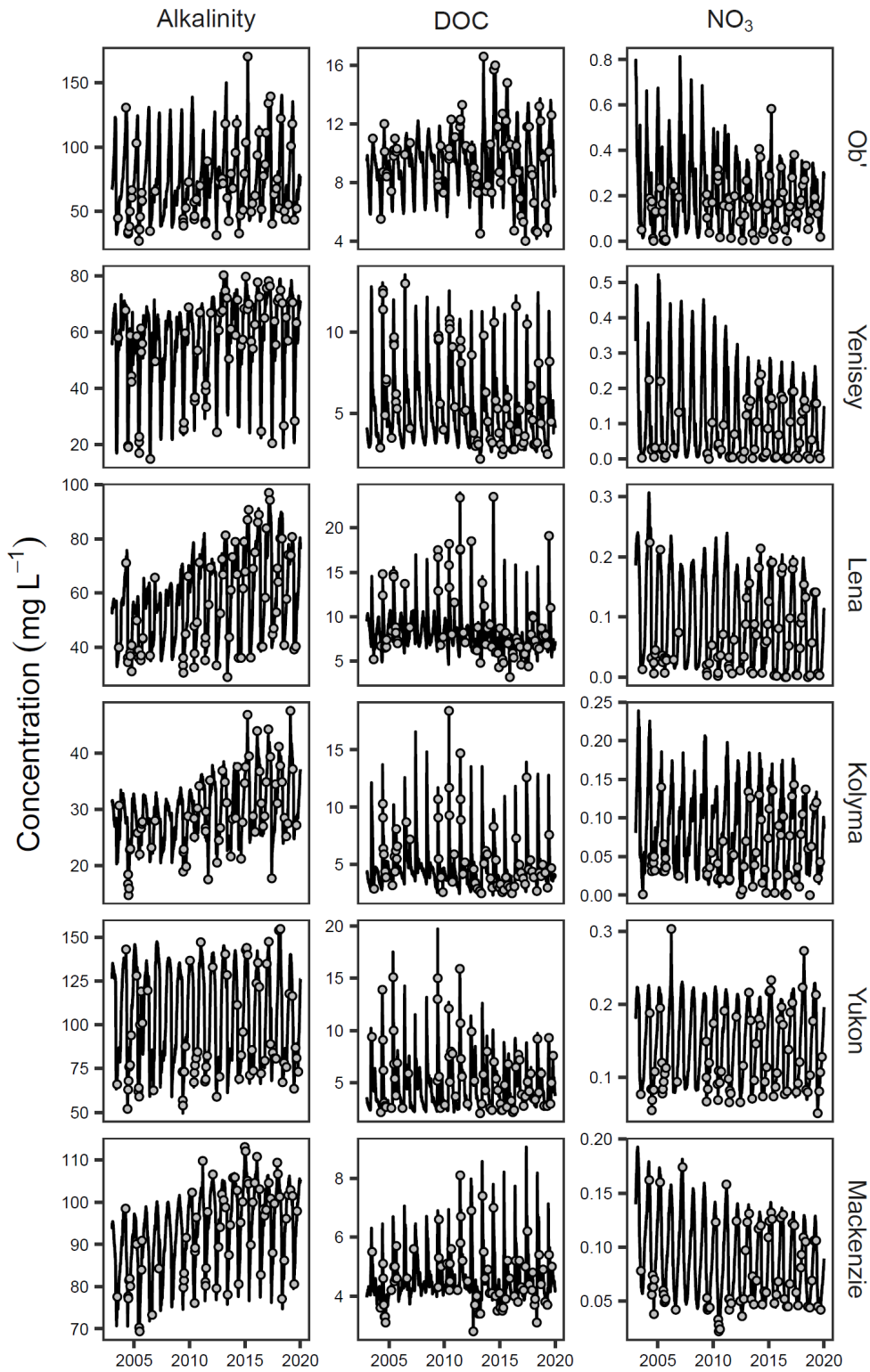
440



441

442

443 **Extended Data Figure 5:** Trends for constituent concentration across the full ArcticGRO dataset, for each of the six great Arctic rivers. Trend
 444 analysis is via a seasonal Mann-Kendall analysis; the Thiel-Sen slope (numerical value) and p-value of the trend analysis (shading) are shown.
 445 Corresponding trends in constituent flux are provided in Extended Data Figure 3. Grey bars illustrate groupings from Extended Data Figure 2.
 446 Units (mg L⁻¹ y⁻¹ or µg L⁻¹ y⁻¹) are provided in Table S2.



447

448 **Extended Data Figure 6:** Measured vs. modelled concentrations of the focal constituent suite, for each
 449 of the six great Arctic rivers. Circles indicate true concentration measurements; lines indicate outputs
 450 from the WRTDS-Kalman model.

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