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Increasing Alkalinity Export from Large Russian Arctic Rivers

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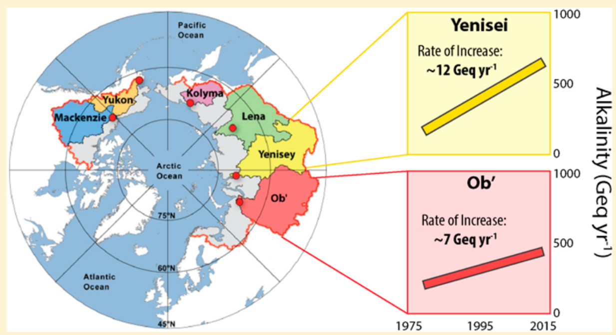
Supporting Information

ABSTRACT: Riverine carbonate alkalinity (HCO_3^- and CO_3^{2-}) sourced from chemical weathering represents a significant sink for atmospheric CO_2. Alkalinity flux from Arctic rivers is partly determined by precipitation, permafrost extent, groundwater flow paths, and surface vegetation, all of which are changing under a warming climate. Here we show that over the past three and half decades, the export of alkalinity from the Yenisei and Ob' Rivers increased from 225 to 642 Geq yr^{-1} (+185%) and from 201 to 470 Geq yr^{-1} (+134%); an average rate of 11.90 and 7.28 Geq yr^{-1}, respectively. These increases may have resulted from a suite of changes related to climate change and anthropogenic activity, including higher temperatures, increased precipitation, permafrost thaw, changes to hydrologic flow paths, shifts in vegetation, and decreased acid deposition. Regardless of the direct causes, these trends have broad implications for the rate of carbon sequestration on land and delivery of buffering capacity to freshwater ecosystems and the Arctic Ocean.



INTRODUCTION

Riverine carbonate alkalinity, in the form of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions, represents an important biogeochemical flux of carbon from land to ocean. Delivery of carbonate alkalinity by rivers controls the calcium carbonate ($CaCO_3$) saturation state in the ocean and can function as a sink for atmospheric carbon dioxide (CO_2) over millennial to geologic time scales.[1,2]

The rate of weathering and production of carbonate alkalinity is ultimately controlled by the availability of weatherable minerals and the supply of weathering agents.[3−6] Temperature also controls weathering directly via reaction kinetics and mineral solubility[7] and indirectly via impacts on the hydrologic cycle, soil respiration, and plant productivity, making it an important overall determinant of alkalinity production.[3] Water from precipitation acts as the vehicle for both the acidic reactant and the transport of weathered products from land to ocean.[8] For this reason, any process that affects hydrology, specifically the area or time of contact between water and mineral surfaces, will play an important role in the production of alkalinity.[9] Anthropogenic drivers, such as climate change, acid precipitation, agriculture, mining, and the use of concrete in the built environment may also influence the production and delivery of alkalinity to rivers.[6,10,11]

In the Arctic, a number of the above processes that drive the production of alkalinity are changing in the wake of rising ambient surface temperatures and the concomitant effects on permafrost, hydrology, and surface vegetation.[12−14] Permafrost thaw and thermal degradation from higher air temperatures allow for enhanced connection between surface waters and deeper groundwater pathways.[15] In thawed soils, infiltrating surface waters experience longer residence times, more contact with unweathered mineral surfaces, and additional mixing with mineral-rich groundwater; all of which result in higher rates of alkalinity production and export.[12,16] Furthermore, both permafrost thaw and regional shifts in climate have contributed to a significant increase in river discharge from the six largest Eurasian rivers to the Arctic Ocean.[17,18] These increases in soil permeability and water delivery are impacting biogeochemical fluxes of inorganic constituents across the Pan-Arctic watershed.[12] Warming in the Arctic also has the potential to increase microbial and plant respiration in soils, which would result in more CO_2 available for weathering.[13,19,20] In addition to climate-related changes, the Arctic has experienced a decline in acid deposition due to the reduction of nitrogen and sulfur oxides generated by industrial activity,[21−23] which can either enhance or diminish weathering depending on the buffering capacity of the system.[6,24]

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In this study, we combine previously unpublished Union of Soviet Socialist Republics (USSR) era long-term (17 years) alkalinity data sets from the Yenisei and Ob' Rivers with more contemporary long-term (13 year) data sets. The recent data is derived from the Pan-Arctic river transport of nutrients, organic matter and suspended sediments (PARTNERS) and subsequent Arctic Great Rivers Observatory (Arctic-GRO) projects. The Yenisei and the Ob' represent the largest and third largest Arctic rivers, respectively, in terms of annual discharge to the Arctic Ocean, and the fifth and 13th largest rivers, respectively, ranked by discharge globally.[25] Both basins encompass boreal, subarctic, and Arctic ecoregions, ultimately draining north into the Arctic Ocean. The USSR data set features concentration data for the years 1974−1990, with monthly data on each river for every year. The PARTNERS (2003−2006) and Arctic-GRO (2009−2015) data sets contain alkalinity data from samples collected at base flow (under ice), the spring freshet, and late summer each year. These data, in concert with available daily discharge data starting in 1978, allowed for robust modeling of total annual fluxes of alkalinity from the Yenisei and Ob' Rivers. This flux data is then used to assess long-term multidecadal trends in alkalinity export from these major Arctic rivers to the Arctic Ocean through recent history.

■ MATERIALS AND METHODS

Data Acquisition. River discharge was measured by hydrologic gauging stations at Igarka in the Yenisei Basin and Salekhard in the Ob' Basin (Supporting Information (SI) Figure S1). For the Ob', the sampling site is the same as the gauging station (SI Figure S1). For the Yenisei, water samples were collected at Dudinka, approximately 215 km north (downstream) of the gauging station (SI Figure S1). The offset between sampling and gauging station for the Yenisei was determined to be negligible, following lag-time estimates from Holmes et al.[26] Daily discharge measurements for years 1978−2015 were obtained for both rivers from the ArcticRIMS Project (http://rims.unh.edu) and from the Arctic-GRO project Web site (http://arcticgreatrivers.org). Discharge data for the Yenisei from 2012 to 2013 were omitted from this study due to the diversion of upward of 100 km^3 of water to fill the newly completed Boguchany Dam, resulting in artificially low flows for those years.

The Yenisei (n = 211) and Ob' (n = 219) Rivers were sampled for alkalinity as part of a special USSR National Biomonitoring Program. Each sample represents a composite of left, right, and midstream samples taken from 0.5 m depths, except for winter months (December, February, and March) when only one midstream sample was taken through a hole in the ice. Alkalinity was determined via fixed-end point titrations to a pH of 4.5. Sample collection for the Biomonitoring Program ended concurrent with the beginning of the dissolution of the USSR in 1990.

Alkalinity data for years 2003−2015 were obtained from the PARTNERS (2003−2006) and Arctic-GRO (2009−2015) data sets. Sample sites for these projects were the same as for the USSR Biomonitoring Program, at Dudinka (Ob') and Salekhard (Yenisei). The sampling protocol for the PARTNERS and Arctic-GRO projects are described in previous studies.[26,27] Briefly, from 2009 to 2011, each sample represents a composite of five depth-integrated samples taken across the channel during the open water season. After 2011, each sample represents a composite of a left, right, and midstream surface water samples taken from ∼0.5 m depths, similar to the USSR protocol. During winter, a single midchannel surface water sample was taken from a hole in the ice. Samples were then filtered via a 0.45 μm capsule filter into high density polyethylene (HDPE) bottles for transport. From 2003 to 2009, total alkalinity was measured via the Gran method using a Hach digital titrator and WTW pH 315i meter. Starting in 2010, alkalinity was measured via the fixed-end point method on a Mettler Toledo T50. Alkalinity was calculated using the online USGS calculator (https://or.water.usgs.gov/alk/). All concentrations were converted to μeq L^{-1} for this study.

Load Analyses. Daily alkalinity fluxes (Geq d^{-1}) were calculated using the FORTRAN Load Estimator (LOADEST) program[28] and then summed to calculate annual loads (Geq yr^{-1}). The calibration equation was derived using the Adjusted Maximum Likelihood Estimator (AMLE) and the regression model number was set to default (MODNO = 0), allowing for selection of the best model based on Akaike Information Criteria. Annual fluxes for years 1978 to 2015 were modeled as single batch for each river. For years missing concentration data, the LOADEST calibration equation was used to model the daily fluxes from the available daily discharge data. Missing daily discharge data from the Ob' (1995−1997) and artificially low discharge in the Yenisei (2012−2013) precluded export modeling for those years.

■ RESULTS

Water Discharge. Annual discharge for the Ob' River did not change significantly over the past 40 years (Figure 1A). Discharge in the Yenisei River increased steadily by an average of 2.42 km^3 yr^{-1} (r^2 = 0.36, p-value = 0.0002), representing a +14.7% change over 40 years (Figure 1B). The rate of change for the Yenisei River corresponds well with the reported 2.0 km^3 yr^{-1} increase found for the six largest Eurasian rivers.[17] The discrepancy between discharge changes in the Ob' and Yenisei is likely explained by differing increases in net precipitation, water use, and water balances over time within the basins. The Ob' Basin contains 22.9% croplands and has experienced greater human impact than the Yenisei, which contains only 6.2% agricultural lands.[29] It is conceivable that growing human water usage in the Ob' has offset any potential precipitation increases over time. Furthermore, the Yenisei (88% permafrost) has experienced relatively more thawing over the past 40 years than the Ob' (26% permafrost).[29] Although permafrost thaw does not contribute much to riverine discharge via the release of frozen water,[30] it can alter the balance between infiltration and evaporation and lead to higher water retention and discharge.[31]

Increasing Alkalinity and Export. From 1974 to 2015, alkalinity concentrations increased significantly for both the Ob' (Figure 1C) and the Yenisei (Figure 1D) Rivers. Linear regressions of point measure concentrations resulted in significant positive slopes. For the Ob', concentrations increased by 21.8 μeq L^{-1} yr^{-1} (r^2 = 0.39, p-value <0.0001), with the highest rate of change observed in the winter months (Figure 1C). Despite the increasing discharge in the Yenisei, alkalinity has also risen at a similar rate to the Ob' at 18.9 μeq L^{-1} yr^{-1} (r^2 = 0.57, p-value < 0.0001) while also exhibiting the highest rate of change during winter (Figure 1D). In the Arctic, riverine discharge is lowest in the winter months when most precipitation and surface water is frozen, resulting in high concentrations of dissolved inorganic constituents under ice.[26]

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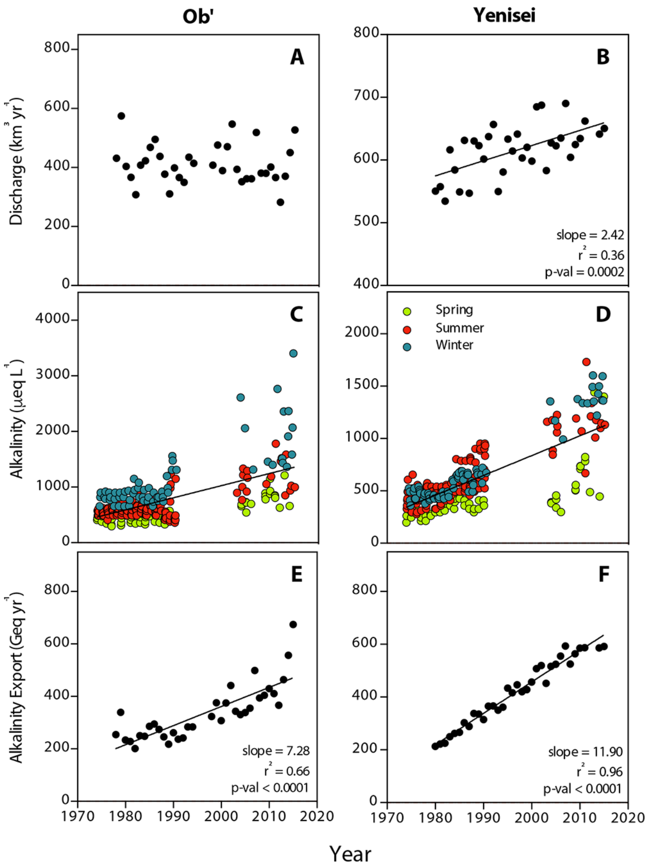

Figure 1. Water and alkalinity export for the Ob' and Yenisei Rivers. Panels show time series for annual discharge (A and B), alkalinity (C and D), and annual alkalinity export (E and F) for years 1974 to 2015. Alkalinities are separated by season into Spring (May−June, green), Summer (July−October, red), and Winter (November−April, blue). Gap in alkalinity data after 1990 resulted from the beginning of the dissolution of the USSR.

As a result of increasing alkalinity concentrations and, in the case of the Yenisei River, simultaneously increasing discharge, the annual export of alkalinity from both rivers has risen dramatically over the past four decades (Figure 1E and F). From 1978 to 2015, export from the Ob' increased by 134% from 201 to 470 Geq yr^{-1}, at an average rate of 7.28 Geq yr^{-1}. Similarly, over the same time frame, alkalinity export from the Yenisei increased from 225 to 642 Geq yr^{-1}, at a rate of 11.90 Geq yr^{-1} (a + 185% increase). Annual flow-weighted mean concentrations (FWMC) increased at a very similar rate in both rivers (0.185 versus 0.169 μeq L^{-1} yr^{-1} for the Ob' and Yenisei, respectively), highlighting the additive role of discharge in the relatively greater rate of increase in Yenisei. Proportionately, these increases are more than an order of magnitude larger than those observed over the same period in the Mackenzie River (+12.5%).[32] The observed increases in export in this study are larger still than those reported for the heavily impacted Mississippi River Basin (seventh largest river ranked by discharge globally), where increasing water delivery and widespread agriculture resulted in a 59% increase in alkalinity delivery over a 47-year period.[5] Given that low sulfate (SO_4^{2-}) fluxes in both of these systems indicate sulfide oxidation is at most a minor contributor to alkalinity generation,[33] these increases in alkalinity production and delivery from both rivers correspond to a substantial increase in CO_2 sequestration over time (See section 'The Role of Basin Specific Characteristics' below for estimates).

Potential Drivers for Increased Weathering. A preeminent control on this increasing alkalinity production and export in both basins may be the increase in surface air temperature (SAT) over time. Average SATs in northern latitudes have increased by approximately 1.5 °C over the past 40 years, at a rate nearly double the global average.[34] Alkalinity export in both the Ob' and Yenisei Rivers showed strong linear correlations with mean annual northern hemisphere temperature (Figure 2). Higher SATs may have direct and indirect effects on weathering via permafrost thaw,[12] microbial respiration,[19,20] and the enhanced productivity of surface vegetation.[13] Higher temperatures directly increase the rate of silicate dissolution.[35] Rising temperatures in the Arctic also lead to permafrost thaw, which exposes unweathered mineral surfaces, increases residence times of infiltrating water, and increases mixing with mineral rich groundwater, all of which promote alkalinity production and export.[12,15] Similar temperature-induced changes to glacial cover, discharge, and chemical and mechanical weathering rates in Iceland were found to increase alkalinity fluxes by a factor of 2−3 for each degree Celsius.[36] Moreover, it has been suggested that rising temperatures and higher levels of atmospheric CO_2 promote and fertilize plant growth in the Arctic (known as "Arctic Greening"), which in turn enhances production of soil CO_2 and causes changes in soil hydrologic conditions.[13,37] It is important to note that this enhanced productivity may be countered by increases in water stress and disturbance with warming, which limit plant growth and respiration.[38] Similarly, microbial respiration of soil organic matter and production of CO_2 is generally thought to increase under warmer temperatures,[19,20] although there is considerable debate as to whether microbial communities acclimate to warmer conditions.[39−41] Resolving the magnitude and direction of these biologic effects are critical, since the related below-ground changes are key drivers of chemical weathering.[3,13,42]

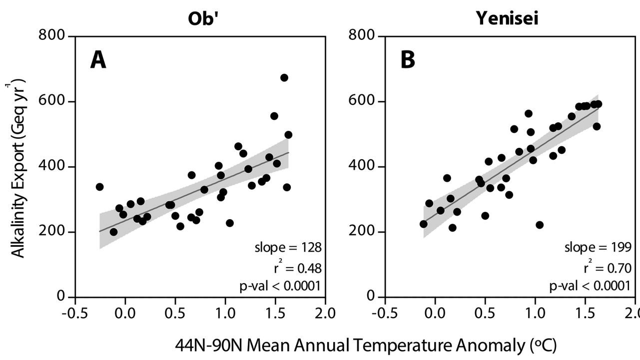

Figure 2. Alkalinity export versus mean annual temperature anomalies for the Ob' (A) and the Yenisei (B) Rivers. Temperature anomaly data are for latitudes 44N-90N from NASA GISTEMP zonal estimates.[34,56] Gray bands indicate the 95% confidence intervals.

In addition to climate related changes, declines in the production and deposition of nitric and sulfuric (N + S) acids may have allowed for the recovery of preindustrial pH levels and therefore explain the observed increase in alkalinity. In order for the deposition of strong acids to have caused the historic depression of alkalinity, the availability of weatherable carbonates in the basins would have had to have been limited

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such that the pH dropped below ~6.5 (the bicarbonate-carbonic acid equilibrium), resulting in a net consumption of HCO_3^-.[6,43] Throughout Russia, acid precipitation has substantially decreased over the last four decades.[21,22] This decrease may be evident in the ion chemistry of the Ob' and Yenisei Rivers; we observed significant declines in the [Ca^{2+} + Mg^{2+}]:[Alkalinity] ratios over the last 10-year range of our data for both the Ob' and Yenisei (SI Figure S2), which indicates an increasing role for carbonic acid mediated weathering over time and is consistent with a recovery from acid deposition.[24,44] Because the production of alkalinity is dependent on both the supply of acids and the availability of weatherable minerals (especially carbonate minerals that control the buffering capacity), N + S acid deposition may also increase alkalinity. For instance, in well buffered regions where the availability of carbonate minerals is not limited, N + S acid deposition has been shown to increase alkalinity fluxes by increasing the supply of weathering agents and the dissolution of carbonate minerals.[10] It is important to note that recovery from N + S acid deposition and warming-induced shifts in permafrost and hydrology are not mutually exclusive drivers of alkalinity increase. In some circumstances they may be complementary. For instance, both warming-induced permafrost thaw (via the exposure of weatherable carbonate minerals) and the decrease in N + S acid deposition could have acted synergistically to increase the buffering capacity of the system and retain a greater proportion of weathered HCO_3^- as alkalinity. Regardless, as with many of the observed alkalinity trends globally, the array of overlapping changes that have taken place in the Arctic over the last few decades make it difficult to assess the importance of any single driver.[6,11]

The Role of Basin-Specific Characteristics. Despite their similar trends in increasing alkalinity export, there are important differences between the Yenisei and Ob' River Basins. It has been suggested that increases in discharge and decreases in permafrost extent should drive larger alkalinity fluxes from Arctic watersheds.[45] Increases in discharge result in larger overall annual water yields, which have been shown to enhance annual alkalinity fluxes in major rivers.[46] The Yenisei fits this predicted pattern; increasing discharge has led to growing annual water yields and a corresponding rise in alkalinity fluxes. Moreover, with a Basin dominated by permafrost that has undergone active layer thawing at a rate of 0.81 cm yr^{-1} from 1980 to 2002,[47] it is also likely that the Yenisei has experienced some level of thaw-induced increase in alkalinity production and export. The increasing flux of alkalinity from the Ob', however, cannot be explained by rising discharge, since discharge did not vary significantly over the past 40 years (Figure 1A). The permafrost contained in the Ob' watershed is predominantly discontinuous, sporadic, or isolated (92.3% of all permafrost in the Basin), meaning that it is found in mostly small, thaw-deteriorated patches.[45] These patches of noncontinuous permafrost may be subject to more thaw given the higher hydrologic permeability and lower thermal insulation in the surrounding soil, thereby exposing fresh mineral surfaces for weathering.[48,49] Alternatively, the patchier permafrost distribution in the Ob' could have facilitated more hydrologic connectivity with mineral-rich groundwater,[12] thereby increasing alkalinity. Catchments with discontinuous permafrost in boreal Alaska were similarly associated with higher nitrate fluxes[50] and the signature of carbonate weathering in seasonally deeper flow paths.[51]

The Ob' Basin has considerable agricultural coverage (22.9%), and also a relatively high population density for an Arctic river basin (9.51 people km^{-2}).[29,45] This high proportion of croplands and anthropogenic footprint may have also played a role in the observed increasing alkalinity fluxes. Previous studies in the Mississippi Basin have shown that alkalinity fluxes were strongly controlled by land-cover, with cropland sub-basins exporting 5−6 times as much as forested sub-basins.[5] Large-scale application of lime ($CaCO_3$) to agricultural soils of the Ob' Basin may also have contributed to an increase in alkalinity available for export, as it did in the Ohio River Basin,[52] although detailed record of rates and application dates are unavailable.[53] Ammonium fertilizers applied to croplands, which are often nitrified to produce nitric acids, can also promote chemical weathering, provided there are enough carbonate minerals to retain a pH of 6.5 or higher.[6] The declining [Ca^{2+} + Mg^{2+}]:[alkalinity] observed in the Ob' and Yenisei basin (SI Figure S2), however, suggests a diminishing role for nitrogen acids (and thus the application of fertilizers) as a proximate cause of the rise in alkalinity.

Another important difference pertains to the geologic source of alkalinity to both rivers. A previous study on the geochemical weathering signatures of Arctic rivers determined that present-day alkalinity in the Ob' was derived predominantly from carbonate weathering (77.9%) compared to silicate (22.1%).[33] In comparison, the relative contributions in the Yenisei Basin between carbonate and silicate weathering were similar (~53.3% carbonate and ~46.7% silicate).[33] The higher contribution of silicate-derived alkalinity to the Yenisei suggests that its role as a CO_2 sink has increased more substantially than for the Ob', provided the proportional contributions of silicate versus carbonate weathering were similar in the past. Indeed, based on these static carbonate and silicate contributions to weathering, we estimate that the Ob' and Yenisei Basins have sequestered an additional ~33 and ~62 Tg of C as CO_2 over the last 35 years (~0.9 and ~1.8 Tg yr^{-1}), respectively. Assuming a 1980 alkalinity export baseline for each river, this additional sequestered C represents a 63 and 93% increase for the Ob' and Yenisei, respectively.

Alkalinity versus discharge (C-Q) relationships (Figure 3) highlight the effects of dilution and seasonality in both rivers.

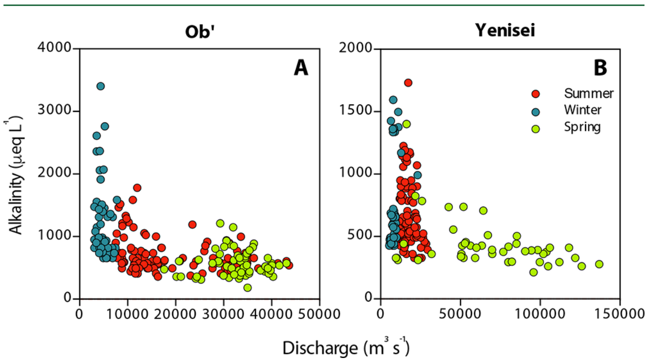

Figure 3. Alkalinity versus instantaneous discharge for the Ob' (A) and Yenisei (B) Rivers. Seasonal color codes correspond to Figure 1.

Both the Ob' and Yenisei Rivers display clear dilution of alkalinity, with the highest discharge and lowest concentrations in the spring during the freshet (Figure 3). The Ob' River C-Q relationship is modulated, with concentrations transitioning gradually between seasons (Figure 3A). The Yenisei River displays a much sharper transition in the C-Q relationship,

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with low concentrations during the spring freshet and a more discharge independent range of concentrations during summer and winter (Figure 3B). The Ob' Basin contains more low-lying wetlands (8.5%) and croplands (22.9%) than the Yenisei (2.6 and 6.2%, respectively), which likely play a role in modulating the C-Q relationship.[29] The relatively greater permafrost extent in the Yenisei Basin in comparison to the Ob' Basin (88% versus 26%, respectively) and particularly the much greater continuous permafrost extent (33% versus 2%, respectively), results in relatively less recharge and percolation to deeper soils, contributing to a more responsive hydrograph with higher peak discharge with steep rising and falling limbs.[45]

Implications for Regional Carbon Budgets. The finding that both the Yenisei and Ob' Rivers exhibited such dramatic increases in alkalinity export of similar magnitude over the past 35 years raises questions about how the C balance of the region will be affected by ongoing climate change. Encompassing a Eurasian Arctic watershed perspective, it seems likely that similar increases in alkalinity export will have occurred in other major Eurasian river basins such as the Lena and Kolyma, as they have greater permafrost extents and have exhibited similar historical increases in discharge as the Yenisei.[17] By our estimates, using the static proportions of carbonate and silicate weathering from Tank et al. 2012 and assuming similar discharge-proportional increases in alkalinity export as the Ob' and Yenisei for the Lena and Kolyma, the four largest Eurasian rivers (Ob', Yenisei, Lena, and Kolyma) have together sequestered more than 120 Tg of additional C as CO_2 over the past three and half decades (~3.4 Tg yr^{-1}).

The Arctic is projected to continue warming at a rate of 0.6 °C per decade, more than twice as fast as the global average.[54] This added warming is estimated to thaw and release ~92 Pg of C from permafrost soils by 2100.[54] With this additional thaw, longer hydrologic residence times, higher soil permeability, and enhanced contact with newly exposed mineral surfaces will likely contribute to further rises in alkalinity export by arctic rivers. The potential for climate-driven changes in alkalinity production emphasizes the need to include inorganic C processes when we are considering the how the carbon cycle will respond to global change. More specifically, it reinforces the importance of ongoing long-term observational efforts though projects like the Arctic-GRO to better ascertain the extent to which increased alkalinity production and export has and continues to offset CO_2 released from permafrost thaw. Fundamentally, understanding the drivers of this increasing alkalinity export, as well as improving future projections of its magnitude are of key importance for examination of carbon sequestration in the terrestrial environment as well as the susceptibility of the Arctic Ocean to acidification.[32,54,55]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b01051.

> Description of the alkalinity methods, map of study sites (Figure S1), cation to alkalinity ratios over time (Figure S2) (PDF)
>
> Excel file containing all raw and modeled discharge, alkalinity, cation, LOADEST export, flow-weighted concentrations, and CO_2 sequestration estimates (Drake_ES&T_Data.xls) (XLS)

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Notes

The authors declare no competing financial interest.

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