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Climate Change Impacts on the Hydrology and Biogeochemistry of Arctic Rivers

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1.1 Introduction

Rivers integrate. Moreover, they integrate over a fixed and definable area (the watershed), so their discharge and chemistry at any given point is a function of upstream processes in both terrestrial and aquatic environments. As a consequence, changes in river discharge and chemistry can be powerful indicators of climate change impacts at the scale of whole watersheds.

The Arctic is central to considerations of climate change impacts. Warming is greatest in the Arctic and the Arctic is particularly sensitive to warming, so climate change has already dramatically impacted terrestrial, freshwater, and marine components of the Arctic system (Hinzman *et al.* 2005; Serreze, Holland and Stroeve 2007; White *et al.* 2007; see also Chapter 2). Arctic soils contain vast quantities of ancient organic matter that may be released as permafrost thaws, fueling a positive feedback loop and exacerbating warming (Zimov, Schuur and Chapin 2006; Schuur *et al.* 2008). The

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Arctic also contains several of Earth's largest rivers. These rivers exert a disproportionate influence on the ocean because they transport more than 10% of global river discharge into the Arctic Ocean, which contains only ~1% of global ocean volume (McClelland *et al.* 2012). Arctic rivers drain vast watersheds, and trends in their discharge and chemistry are already providing strong insights into changes occurring over the Arctic landmass (Peterson *et al.* 2002; Holmes *et al.* 2012).

Here we describe the pan-Arctic watershed and highlight important characteristics of its principal rivers, and then provide an overview of available data related to the discharge and chemistry of Arctic rivers. Recognizing that comprehensive observational data are fundamental to understanding and responding to Arctic change (SEARCH 2005; Jeffries *et al.* 2007), we focus on multiyear time series, as these datasets are essential for detection of trends that may be related to climate change. We then consider projections of future changes in Arctic river discharge and chemistry. Our analysis is pan-Arctic in scale, with an emphasis on the largest Arctic rivers in Russia, Canada, and Alaska.

1.2 The pan-Arctic watershed

There are many different ways to define the spatial extent of the Arctic. Depending on one's definition, the area of the Arctic landmass can range from under 10×10^6 km^2 to over 20×10^6 km^2. For example, a rather restrictive definition was chosen by the Circumpolar Arctic Vegetation Map project, which considered the Arctic to be the region north of the tree line. Based on this definition, the Arctic covers an area of only 7.1×10^6 km^2, including Greenland and the Canadian Archipelago (Walker *et al.* 2005). At the other extreme, some studies have bounded the Arctic based on the drainage area of the Arctic Ocean, Hudson Bay, and part of the Bering Sea, which encompasses an area of about 20.5×10^6 km^2 (Holmes *et al.* 2001). When Greenland and the Canadian Archipelago are included, the Arctic grows to about 24×10^6 km^2 (McGuire *et al.* 2009). Depending on one's interests, any of these definitions may be appropriate.

For this chapter, we follow the definition now used by the Arctic Great Rivers Observatory (www.arcticgreatrivers.org), which defines the Arctic based on hydrology and considers the pan-Arctic watershed as the region draining into the Arctic Ocean plus the watersheds of the Yukon River and rivers entering the Bering Sea north of the Yukon River (Figure 1.1). Based on this definition, the pan-Arctic watershed covers 16.8×10^6 km^2 (Table 1.1). This region is smaller than the most expansive definitions of the Arctic because it does not include Greenland, the Hudson Bay drainage, or the Canadian Archipelago, but it does include the principal rivers entering the Arctic Ocean—which in several cases have watersheds extending well below 60° N (Figure 1.1).

There are 14 rivers in the pan-Arctic watershed that have mean annual discharges exceeding 25 km^3 y^{-1} (Table 1.1). Remarkably, 12 of these rivers are in Russia. The Yenisey, Lena, and Ob' are each among Earth's largest rivers, having mean annual discharges exceeding 400 km^3 (Table 1.1). Six rivers in the pan-Arctic watershed have basin areas exceeding 500 000 km^2 (the Ob', Yenisey, Lena, Mackenzie, Yukon, and Kolyma). Combined, the watersheds of these "*Big 6*" Arctic rivers cover 11.2×10^6 km^2, or 67% of the pan-Arctic watershed (Table 1.1, Figure 1.1). The next

Table 1.1 Characteristics of the Arctic's largest watersheds. The rivers designated as the "Big Six" have been part of the multinational PARTNERS and Arctic Great Rivers Observatory (Arctic-GRO) projects since 2003 (www.arcticgreatrivers.org), and the "Middle 8" are the next eight largest watersheds.

Watershed	Watershed area[a] (10^6 km^2)	Discharge[b] (km^3 y^{-1})	Runoff (mm y^{-1})	Sediment yield[c] (t km^{-2} y^{-1})	Tundra[d] (%)	Permafrost[e] (%)	Continuous permafrost (%)	Discontinuous permafrost (%)	Sporadic permafrost (%)	Isolated permafrost (%)	Population[f] (no. people)	Population density (people/km^{-2})
"Big Six"												
Ob'	2.95	427	145	6	1	26	2	4	9	11	28 063 236	9.51
Yenisey	2.56	673	263	2	1	88	33	11	19	25	8 056 579	3.14
Lena	2.40	588	245	8	1	99	79	11	6	3	1 077 226	0.45
Mackenzie	1.75	316	181	74	1	82	16	29	27	10	465 338	0.27
Yukon	0.83	208	251	72	6	99	23	66	10	0	146 411	0.18
Kolyma	0.65	136	209	19	4	100	100	0	0	0	77 764	0.12
"Middle 8"												
Indigirka	0.34	54	159	36	7	100	100	0	0	0	29 332	0.09
Pechora	0.31	164	529	38	23	39	13	4	11	11	556 183	1.78
Severnaya Dvina	0.29	104	369	12	0	0	0	0	0	0	1 286 552	4.46
Khatanga	0.29	108	372		8	100	100	0	0	0	14 930	0.05
Yana	0.23	39	170	18	3	100	100	0	0	0	23 435	0.10
Olenek	0.22	48	218	6	12	100	100	0	0	0	4 368	0.02
Taz	0.15	43	287	7	0	100	6	64	30	0	14 793	0.10
Pur	0.10	32	320	7	0	100	4	76	20	0	2 59 955	2.73
Pan-Arctic WS	16.8	~3700	~220		15	76	45	13	10	8	42 241 712	2.52
"Big 6"	11.2	2348	210	21	1.4	75	35	16	13	11	37 886 554	3.40
"Middle 8"	1.9	592	312	19	8	76	60	9	5	2	2 189 538	1.13
Remainder	3.7	~760	~205		61	83	73	8	2	0	2 165 620	0.58

[a]Watershed areas are given for the entire watershed, not just the area above the downstream-most gauging stations.
[b]Mean annual discharge is based on observational records for the downstream-most gauging station, extrapolated to the entire watershed assuming that the unmonitored portion of the watershed has the same runoff as the monitored region of the watershed. Discharge values for the "Big Six" rivers are from Holmes *et al.* 2012 and are averages for the 1999–2008 period. Discharge from the Pechora, Severnaya Dvina, Yana, and Olenek are also averages from 1999–2008. Recent observational discharge records are not available for the other rivers, so the values gives represent averages from the following periods: Indigirka 1937–1998, Khatanga 1965–1991, Taz 1962–1996, Pur 1939–2003.
[c]Sediment yield values are from Holmes *et al.* 2002.
[d]The tundra classification comes from the Circumpolar Arctic Vegetation Map (Walker *et al.* 2005) and includes all categories of tundra.
[e]Permafrost extent and classification comes from International Permafrost Association's Circum-Arctic Map of Permafrost and Ground Ice Conditions.
[f]Population statistics come from the LandScan 2009 Global Population database (www.ornl.gov/landscan).

Figure 1.1 Map of the 16.8×10^6 km^2 pan-Arctic watershed, showing its major rivers. Together the basins of the "Big 6" rivers (shown in dark gray) cover 67% of the pan-Arctic watershed, whereas the watersheds of the "Middle 8" rivers (shown in light gray) cover 11% of the pan-Arctic watershed (see Table 1.1). The dark gray line indicates the boundary of the pan-Arctic watershed.

eight largest Arctic watersheds (the "*Middle 8*") together only cover an additional 1.9×10^6 km^2, much less than the basin area of the Ob', Yenisey, or Lena rivers alone. This demonstrates the importance of inclusion of the largest rivers in order to achieve pan-Arctic synthesis, but also highlights the challenge of scaling-up further because each additional river beyond the *Big 6* achieves only incremental gains.

Extrapolation to the remaining third of the pan-Arctic watershed not encompassed by the *Big 6* is tenuous, given that the regions are fundamentally different in many ways. For example, whereas on average the watersheds of the *Big 6* rivers are only 1.4% tundra, the *Middle 8* rivers have 8% tundra and the remainder of the pan-Arctic watershed is 61% tundra (Figure 1.2, Table 1.1). Similarly, continuous permafrost increases from 35% in the *Big 6* to 60% in the *Middle 8* to 73% in the remainder, and human population density decreases moving from the *Big 6* to *Middle 8* and then the remainder of the pan-Arctic watershed (Figure 1.2, Table 1.1). Thus, strategic sampling of smaller rivers combined with modeling will be required to better constrain estimates of contemporary and future biogeochemical fluxes from the pan-Arctic watershed to the Arctic Ocean, or understand processes occurring throughout the pan-Arctic watershed. Regardless of scale, capturing seasonality is critical for estimating

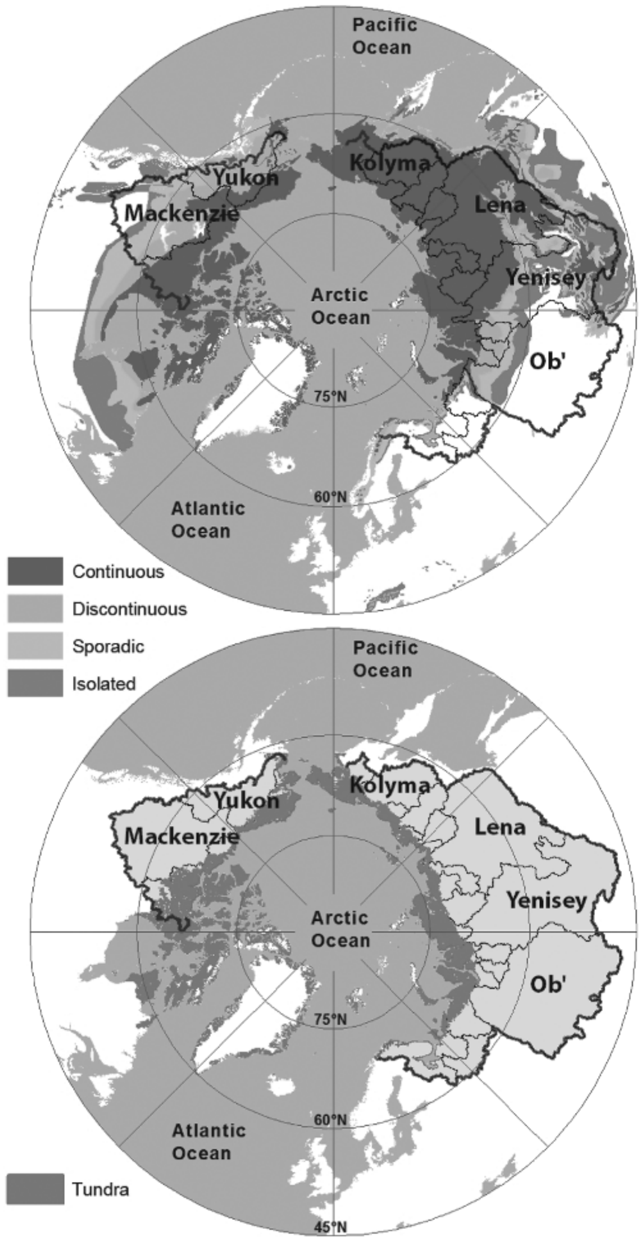

Figure 1.2 Distribution of Arctic permafrost (upper panel) and tundra (lower panel). Continuous permafrost indicates that >90% of the land surface is underlain by permafrost, discontinuous indicates 50–90%, sporadic indicates 10–50%, and isolate indicates <10% of the region contains permafrost. (See insert for color representation.)

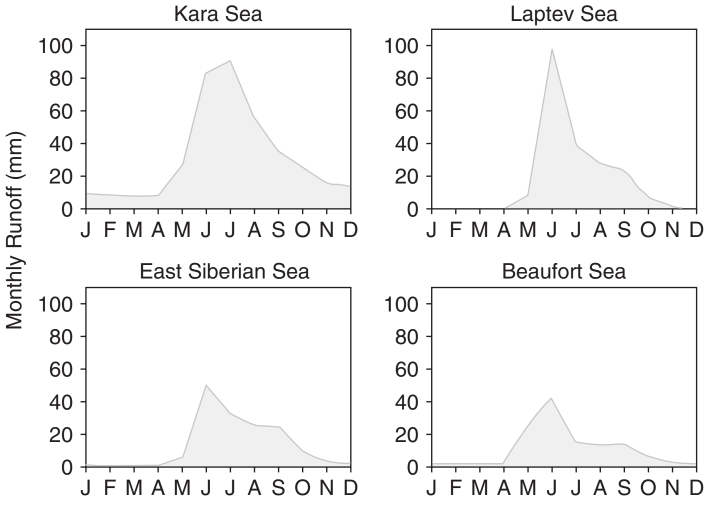

Figure 1.3 River runoff climatologies (mm/month) for four regions around the pan-Arctic domain. Data are average monthly runoff for 1990–1999. Regional runoff climatologies were calculated using the following rivers: Kara Sea (Norilka, Ob, Pur, and Yenisey), Laptev Sea (Anabar, Lena, Olenek, and Yana). East Siberian Sea (Alazeya, Indigirka, Kolyma), Beaufort Sea (Anderson, Kuparuk, Mackenzie). Adapted from McClelland *et al*. (2012).

biogeochemical fluxes from Arctic rivers. Runoff is low around the pan-Arctic domain during the winter and increases to peak values during the May/June timeframe as a consequence of snowmelt (Figure 1.3). The importance of summer runoff (the proportion of annual runoff that occurs during the summer months) varies from region to region, but in general values during the summer months are intermediate relative to those observed in the winter and spring. These seasonal variations in runoff are accompanied by significant variations in water chemistry (discussed in detail below).

1.3 Observational data—historical to contemporary time series

1.3.1 Discharge

Major efforts to monitor river water discharge began in the 1930s on the Eurasian side of the Arctic and the 1960s on the North American side. The records resulting from these monitoring efforts have provided a rich source of data for analyses of variability over a wide range of spatial and temporal scales (e.g., Peterson *et al.* 2002; Yang *et al.* 2002; Yang *et al.* 2003; Déry *et al.* 2005; Déry and Wood 2005; McClelland *et al.* 2006; Yang *et al.* 2007; Déry *et al.* 2009; Shiklomanov and Lammers 2009; Overeem and Syvitski 2010; Rawlins *et al.* 2010). River discharge is currently increasing around much of the pan-Arctic domain, with a strong upward trend in annual values beginning in the 1960s for the Eurasian rivers (Peterson *et al.* 2002) and the late 1980s for the North American rivers (Déry *et al.* 2009). However, quantitative estimates of changes in Arctic river discharge are strongly dependent on the specific rivers and timeframes considered. For example, McClelland *et al.* (2006) analyzed data from 16 Eurasian rivers and 14 North American rivers draining into the Arctic Ocean from 1964 through 2000 and found that annual river discharge increased at a rate of 5.6 km^3 per year. Scaled to include ungauged areas within the Arctic Ocean watershed, the increase in annual river discharge was estimated to be 7.4 km^3 per year. Over this timeframe, the net change in river input to the Arctic Ocean reflected a relatively large increase from Eurasia (~10%) moderated by a smaller decrease from North America (~6%). McClelland *et al.* (2006) also examined discharge from 42 rivers in the Hudson Bay region and identified a decrease in annual river discharge of 2.4 km^3 per year, amounting to a ~12% change over the 1964–2000 time period. In contrast, Overeem and Syvitski (2010) analyzed data from nine Eurasian rivers and ten North American rivers within the pan-Arctic domain from 1977 through 2007 and found that river discharge increased in both regions (net change of ~10%) over this more recent timeframe. Given the substantial variability in discharge that Arctic rivers exhibit from year to year, as well as potential linkages between river discharge and longer-term modes of variability in the Arctic such as the North Atlantic Oscillation (Peterson *et al.* 2006), analyses that cover broader time periods are most conducive to examining potential climate change effects. One effort that may be particularly useful in this regard is the annually updated Arctic Report Card (http://www.arctic.noaa.gov/reportcard/). Discharge data for the six largest Eurasian Arctic rivers (Ob', Yenisey, Lena, Severnaya Dvina, and Pechora) as well as four North American Arctic rivers (Yukon, Mackenzie, Peel, and Back) is being tracked as part of this effort (Shiklomanov, http://www.arctic.noaa.gov/reportcard/rivers.html). The time series for the Eurasian rivers begins in 1936 and the time series for the North American rivers begins in 1970. At present the records extend through 2008 and both show overall positive trends in river discharge.

The observed increases in river discharge are broadly consistent with increased net precipitation over the pan-Arctic watershed that is predicted by climate models as a consequence of anthropogenic greenhouse-gas emissions (Wu, Wood and Stott 2005; Holland, Finnis and Serreze 2006; Nohara *et al.* 2006). However, major uncertainties with respect to historical Arctic climate data have hindered empirical assessments of precipitation-discharge linkages in the region (Rawlins *et al.* 2006). A recent synthesis of observed and modeled climate data across the pan-Arctic pointed toward intensification of the freshwater cycle (Rawlins *et al.* 2010), but the relative importance of changes in precipitation and evaporation with respect to trends in river discharge remained unclear. Thawing permafrost does not have great potential to influence river discharge through direct release of frozen water stocks (McClelland *et al.* 2004), but changes in evaporation associated with permafrost thaw may be an important consideration (Hinzman *et al.* 2005). For example, deeper flow paths through the landscape as permafrost thaws will, to some degree, oppose the effect of warmer temperatures on evaporation. Changes in the seasonality of precipitation (i.e., relative amounts of snow versus rainfall) may also have a strong influence on the annual water balance (Rawlins *et al.* 2006).

1.3.2 Biogeochemistry

In contrast with the discharge records discussed above, time-series data for water chemistry of Arctic rivers are relatively scarce. While the discussion below highlights key examples of observed changes in water chemistry, we are just beginning to develop suitable data sets for tracking changes in river-borne constituents at the pan-Arctic scale. For the largest Arctic rivers, we now have a robust baseline with respect to water chemistry that is essential for evaluating future changes, but (in most cases) we do not yet have long enough data sets to identify ongoing changes that may be linked to climate change.

Eurasia The vast majority of river water entering the Arctic Ocean comes from Eurasia, most of it from Russia. During the Soviet period, Russia maintained an extensive water-quality monitoring network as part of the Unified Federal Service for Observation and Control of Environmental Pollution (OGSNK). The resulting data were not widely available during the Soviet period, largely for political reasons (Zhulidov *et al.* 2000). In the post-Soviet era, however, the data have become more readily available, and sample collection has continued, albeit at a much reduced level. Unfortunately, few of the publications based on these data present time series. Instead, constituent concentrations or fluxes are generally presented as a single value (usually mean annual) with incomplete information about how the value was derived (for example, Telang *et al.* 1991; Gordeev *et al.* 1996; Kimstach, Meybeck and Baroudy 1998; Rachold *et al.* 2004). Although these publications provide clues about spatial differences among rivers, they are of relatively little use for detecting change over time, especially when details of sampling dates or sampling and analytical protocols were not given.

In the hope of establishing a baseline against which to evaluate future changes, Holmes *et al.* (2000) investigated concentrations and fluxes of nitrate, ammonium, and phosphate for 15 Russian Arctic rivers. Using the OGSNK database, they presented monthly averages, generally based on 10–20 years of data. Striking patterns in the data, in particular remarkably high ammonium concentrations, led to uncertainty about the reliability of the OGNSK data (Holmes *et al.* 2000). An expedition to the Ob' and Yenisey rivers in June 2000 was organized to collect new samples in order to evaluate the quality of the long-term data set (Holmes *et al.* 2001). Four different groups, including the laboratories that produced the long-term data set, independently analyzed the Ob' and Yenisey river samples that were collected. Unfortunately, whereas three of the groups obtained similar results, the laboratories that produced the long-term data set found very different results, at least with respect to ammonium (Holmes *et al.* 2001). The unavoidable conclusion was that there were significant data quality issues with the OGSNK dataset. This was one of the motivations for the PARTNERS Project (described in more detail below), which began a standardized program to collect and analyze samples for the six largest Arctic rivers in Russia, Canada, and Alaska in 2003.

Time-series data have been published for suspended sediment flux from the eight largest Arctic rivers, six of which are in Russia (Holmes *et al.* 2002). The database was most complete for the Ob' River, with sampling dating back to the 1930s, whereas other rivers had shorter or less complete datasets. Dramatic differences are apparent when comparing sediment yield for the different rivers. For example, the two largest North American rivers (the Mackenzie and Yukon) together transport ~180 MT of suspended sediment per year, whereas the Arctic's largest river (the Yenisey), with a greater annual discharge than the Mackenzie and Yukon combined, transports only about 5 MT of suspended sediment per year (Holmes *et al.* 2002). Long-term trends were not apparent in the data, except for the Yenisey River where there was a pronounced decrease in sediment flux resulting from the construction of a dam at Krasnoyarsk in 1967 (Holmes *et al.* 2002).

Several studies have obtained information about the biogeochemical composition of Russian Arctic rivers by sampling their plumes or entering their mouths during oceanographic cruises. For example, Lobbes, Fitznar, and Kattner (2000) obtained organic matter and nutrient data from 12 rivers that were sampled during a series of oceanographic cruises during the mid-1990s. Similarly, the plumes of the Ob' and Yenisey rivers were sampled during oceanographic cruises carried out by the SIRRO project (Kohler *et al.* 2003). Semiletov and colleagues (Semiletov *et al.* 2011) sampled the Lena River during oceanographic cruises, and they also conducted sampling trips along the length of the Lena River. Although these and other studies on Russian Arctic rivers have provided important snapshots in time, few have collected the seasonal and multiannual data that are needed to investigate the impacts of climate change on river biogeochemistry.

Alaska One of the few long-term Arctic datasets with respect to geochemical measurements exists for the upper Kuparuk River on the North Slope (Alaska), which has been studied since 1978 (McClelland *et al.* 2007). Research on the upper Kuparuk River in the late 1970s and early 1980s examined concentrations of nutrients and organic matter and the export of these constituents (Peterson, Hobbie and Corliss 1986; Peterson *et al.* 1992). A recent study using the long-term dataset from the upper Kuparuk River found that annual nitrate export increased by approximately fivefold and annual dissolved organic carbon (DOC) export decreased by about 50% from 1991 to 2001 (McClelland *et al.* 2007). The reported decrease in DOC export was centered on the freshet in May and was principally credited to a decline in river discharge. Conversely, increased nitrate export occurred throughout the spring-summer from May to September and was mainly as a result of increasing concentrations (McClelland *et al.* 2007). The underlying mechanism responsible for the increase in nitrate concentrations in the upper Kuparuk remains unclear, but it is hypothesized to relate to changes in soils and vegetation associated with warming in the region.

The Yukon River has been the focus of a number of biogeochemistry orientated studies in recent years and was also studied by the U.S. Geological Survey from 1978–1980. Striegl *et al.* (2005) found a decrease in discharge-normalized DOC export by the Yukon during the growing season when comparing data from 1978–1980 versus 2001–2003. Within parts of the Yukon River basin the proportion of annual discharge derived from groundwater was increasing. For example, at Eagle Village groundwater increased from ~15% of annual flow in the early 1950s to >20% today (Walvoord and Striegl 2007). In the Striegl *et al.* (2005) study, groundwater near the mouth of the Yukon had an average DOC concentration of $\sim 2.5\,mg\,L^{-1}$ and DIC concentration of $50\,mg\,L^{-1}$ versus mean annual river water DOC concentrations of $\sim 8.0\,mg\,L^{-1}$ and DIC concentrations of $24\,mg\,L^{-1}$. Therefore, increased groundwater contribution to river discharge resulted in decreased DOC export and increased HCO_3^- export when normalized to discharge as described by Striegl *et al.* (2005).

In recent years, carbon has been a particular focus of research on the Yukon River. Loads and yields of dissolved and particulate organic and inorganic carbon have been derived for the mouth of the river and several tributaries (Striegl *et al.* 2007; Spencer *et al.* 2009; Guo *et al.* 2012). Carbon dynamics within the Yukon River watershed have also been examined via stable and radiocarbon isotopes (Guo and Macdonald 2006; Guo, Ping and Macdonald 2007; Raymond *et al.* 2007; Striegl *et al.* 2007), and through studies examining organic matter composition (Gueguen *et al.* 2006; Cai, Guo, and Douglas 2008; Elmquist *et al.* 2008; Spencer *et al.* 2008). Nutrient loads and yields have also been derived for the mouth of the Yukon as well as for a number of upstream mainstem sites and tributaries (Guo *et al.* 2004; Dornblaser and Striegl 2007; Cai *et al.* 2008; Guo *et al.* 2012). Toxic substances such as mercury (Hg) have also recently been investigated in the Yukon River, providing a benchmark for the future as thawing of permafrost may accelerate the mobilization of Hg increasing export and potential Hg methylation in Arctic regions (Schuster *et al.* 2011). Therefore, recent years have seen a number of biogeochemical studies within the Yukon River, providing a boon of information for studies in the future to examine how this system responds to climate change.

Canada The Mackenzie River is by far the most studied of any of the Canadian Arctic rivers. Despite this, there are few long-term time-series records of its biogeochemistry. The PARTNERS and Arctic-GRO projects, which are discussed in more detail below, have collected biogeochemical measurements on the Mackenzie since 2003, sampling where the Mackenzie River empties into the Mackenzie River Delta before its ultimate delivery to the Arctic Ocean (McClelland *et al.* 2006). Similarly, the Water Survey of Canada maintains a long-term database for total suspended solids (TSS) at this same location (www.wsc.eg.gc.ca). In contrast to the rarity of long-term time series, however, several authors have compiled detailed within-year datasets for a variety of biogeochemical constituents within the Mackenzie basin. Although their use is limited for discerning long-term trends, these within-year records do provide a clear understanding of the overall biogeochemistry of this system, and how the concentrations of various constituents change across the hydrograph. Weekly measurements during the open water season from the East Channel of the Mackenzie River Delta exist for a suite of constituents, including TSS, DOC, major ions, pH, and dissolved and particulate nutrients (Anema *et al.* 1990; Lesack *et al.* 1998; Tank, Lesack and McQueen 2009; Gareis, Lesack and Bothwell 2010; Tank *et al.* 2011). Emmerton (2006) and Emmerton, Lesack and Vincent (2008) have also collected weekly within-year measurements for a broad suite of constituents on the Mackenzie River, in addition to the Arctic Red and Peel Rivers (the two other major tributaries to the Mackenzie River Delta).

In addition to detailed measurements over time, several authors have undertaken extensive synoptic surveys of biogeochemistry across the Mackenzie catchment, by collecting single time-point measurements on multiple tributaries within the larger river basin. For example, Yi *et al.* (2010) undertook extensive synoptic and time-series surveys of $\delta^{18}O$ and $\delta^{2}H$ within the Mackenzie catchment to explore basin-wide hydrology and quantify the importance of evaporation and snowmelt in the broader catchment. Similarly, Reeder, Hitchon, and Levinson (1972) and Millot *et al.* (2002, 2003) used major ion data to examine weathering processes within the larger Mackenzie basin. These latter authors both found a wide variation in major ionic composition, with variations in overall composition and elemental ratios that reflected the underlying lithological variation throughout the Mackenzie River basin (Millot *et al.* 2003).

Outside of the Mackenzie system, the majority of time-series biogeochemical measurements for Canadian Arctic rivers have been collected by government agencies, and published in government documents. Apart from the government literature, biogeochemical surveys do exist for selected locations, although the measurement record typically ranges from intensive within-year surveys to records extending a few years in length. For example, a series of studies have been conducted in two adjacent streams on Melville Island, where measurements of DOC, dissolved organic nitrogen, dissolved inorganic nitrogen, and suspended sediments were used to explore between-catchment processes and elucidate the relative importance of stormflow, baseflow, and snowmelt to overall constituent fluxes (Lafreniere and Lamoureux 2008; Lewis *et al.* 2011). Similarly, on Nunavut's Boothia Peninsula, time series measurements of suspended sediments were used to quantify controls on sediment yields and its relationship with discharge in three proximate streams (Forbes and Lamoureux 2005). In the southern Yukon Territory, within-year time series measurements were used to explore controls on DOC export in a catchment underlain by discontinuous permafrost (Carey 2003). Finally, a multiyear time series was used to explore controls on mercury flux from the Nelson and Churchill Rivers, and included a characterization of DOC flux (Kirk and Louis 2009).

Data for Canadian Arctic riverine biogeochemistry presented in government publications ranges from series of individual measurements to averages of constituent concentrations measured over a given period of record, with a wide range in the number of observations and years of measurement available depending on the river and constituent of interest (e.g., Environment Canada 1976, 1978, 1982). Some of this constituent concentration data has also been summarized in the GEMS/GLORI database as mean constituent concentrations per river (www.gemswater.org; Meybeck and Ragu 1995), along with data for other world rivers. These data compilations established the underlying biogeochemistry of a suite of Canadian Arctic rivers, and revealed a large degree of variation in Canadian Arctic riverine biogeochemistry. For the purposes of analyzing trends over time, however, data for Canadian Arctic rivers is often difficult to access and assess. For example, much of the collected data has not been published to date, and measurement frequency and length of data series often differs between rivers and constituents. Where government data has been compiled in government documents, long-term means rather than individual data points are often presented, and analytical methods may not be reported or differ between studies. Increasingly, however, the raw data are available at GEMStat (www.gemstat.org), which also includes information on methods.

1.3.3 Pan-Arctic assessments

The only cohesive, multinational assessment of Arctic riverine biogeochemistry to date was initiated in 2003 as the PARTNERS Project (Pan-Arctic River Transport of Nutrients, Organic Matter, and Suspended Sediments), which in 2009 evolved into the Arctic Great Rivers Observatory (Arctic-GRO; www.arcticgreatrivers.org). These projects collect biogeochemical data for the six largest rivers draining to the Arctic Ocean: the Ob', Yenisey, Lena and Kolyma rivers in Russia, and the Yukon and Mackenzie rivers in North America (Figure 1.1, Table 1.1). Despite a number of previous and ongoing studies that have examined Arctic riverine biogeochemistry, an understanding of processes at the pan-Arctic scale has been hampered by differences

Table 1.2 Flow weighted concentrations and minimum and maximum measured concentrations (in parentheses) for selected constituents measured as part of the PARTNERS Project (2003–2007). Flow weighted concentrations are calculated from modeled yearly constituent flux, and are derived from the data presented in Holmes *et al.* (2012) and Tank *et al.* (in press). Minimum and maximum measured concentrations are taken directly from the PARTNERS dataset (www.arcticgreatrivers.org).

	Ob′	Yenisey	Lena	Kolyma	Yukon	Mackenzie
DIN ($\mu g\,L^{-1}$)	200.7 (0.2–858.0)	79.8 (3.2–224.6)	57.4 (5.4–242.0)	60.2 (0.8–141.4)	123.7 (59.0–387.8)	89.3 (37.1–174.0)
DON ($\mu g\,L^{-1}$)	256.6 (99.1–421.0)	173.8 (62.0–306.6)	232.5 (121.3–379.5)	155.6 (43.7–259.3)	226.7 (75.0–460.2)	103.3 (49.6–144.6)
TDP ($\mu g\,L^{-1}$)	40.4 (15.2–62.6)	15.2 (7.5–22.7)	10.4 (4.1–18.0)	10.1 (4.5–14.7)	9.8 (2.0–18.0)	10.0 (7.8–11.2)
Si ($mg\,L^{-1}$)	3.4 (1.8–8.9)	2.7 (1.9–3.8)	2.3 (1.6–3.8)	2.5 (1.8–3.8)	3.3 (2.2–6.5)	1.9 (1.5–2.2)
DOC ($mg\,C\,L^{-1}$)	9.6 (5.5–12.0)	7.3 (2.9–13.0)	9.8 (5.2–14.8)	7.4 (2.9–10.3)	7.1 (2.2–15.1)	4.6 (3.1–5.7)
Ca ($mg\,L^{-1}$)	15.8 (10.9–37.1)	17.9 (7.6–30.3)	15.5 (11.8–28.4)	11.2 (8.7–14.8)	31.0 (22.4–48.7)	35.2 (28.4–38.5)
Na ($mg\,L^{-1}$)	6.3 (4.1–13.3)	6.4 (2.6–9.6)	9.0 (3.2–41.5)	1.5 (1.1–2.2)	2.6 (1.7–4.0)	7.7 (4.8–12.7)
Mg ($mg\,L^{-1}$)	4.2 (2.9–9.1)	3.8 (1.9–5.6)	4.5 (3.3–9.0)	2.4 (1.8–3.4)	7.4 (4.2–11.7)	9.6 (7.9–10.5)
Cl ($mg\,L^{-1}$)	5.5 (3.1–12.3)	9.7 (2.6–16.1)	17.5 (4.6–81.4)	0.3 (0.1–0.6)	0.9 (0.5–1.3)	10.1 (5.2–22.1)
Sr ($\mu g\,L^{-1}$)	100.5 (63.9–218.8)	132.0 (55.6–224.2)	112.8 (83.3–286.5)	56.5 (41.1–70.6)	125.2 (80.2–208.0)	190.1 (113.3–271.6)
SO_4 ($mg\,S\,L^{-1}$)	2.5 (1.3–5.0)	3.1 (1.1–5.7)	4.0 (1.7–11.8)	3.4 (2.0–6.3)	10.3 (4.3–18.7)	15.7 (11.1–18.7)

in methodology between studies and a tendency to collect samples only during the summer months (Holmes *et al.* 2000; McClelland *et al.* 2008). Similarly, the short timespan of many previous studies necessarily limits their usefulness for assessing trends over time. Because the PARTNERS and Arctic-GRO projects have a consistent sampling and analytical scheme across all rivers, and collect samples regularly across the spring freshet, summertime period of higher biological activity, and wintertime (under-ice) period, their datasets have been useful for establishing a rigorous baseline for biogeochemistry on large Arctic rivers.

Sampling for PARTNERS occurred between 2003 and 2007. The Arctic-GRO project has been in operation since 2009 and is currently funded through 2016. Although the time series of these projects is still relatively short, it is detailed enough to quantify seasonal and spatial trends in biogeochemical flux from these large Arctic rivers and to assess interannual variability. These datasets have now been used to determine the between-river variation in numerous constituents (see Table 1.2). For example, constituents such as alkalinity, barium, and calcium show elevated mean concentrations in North American rivers compared to their Russian counterparts, while many constituents show clear between-river variation at the continental scale (Andersen *et al.* 2007; Raymond *et al.* 2007; Cooper *et al.* 2008; McClelland *et al.* 2008; Zimmerman *et al.* 2009; Holmes *et al.* 2012; Tank *et al.* in press). Conversely, seasonal within-constituent variation in concentration are strikingly coherent across these six large rivers, with organic constituents increasing at elevated discharge, and inorganic constituents diluting at high flow (Figure 1.3; Raymond *et al.* 2007; Holmes *et al.* 2012; Mann *et al.* 2012).

By focusing measurements across the full seasonal cycle, these databases have significantly refined our estimates of constituent flux from large Arctic rivers. For instance, because organic constituents increase with increasing flow (Figure 1.4), quantifying the concentration of organic constituents during the high-flow spring freshet is critical for determining their yearly flux. Recent estimates using the PARTNERS dataset have calculated that 46% of DON flux, and 49% of DOC flux from these six rivers occurs during the two months surrounding peak flow (Holmes *et al.* 2012), and PARTNERS-based estimates of pan-Arctic riverine DOC flux are substantially higher than previous estimates based largely on summertime measurements alone (Raymond *et al.* 2007; Holmes *et al.* 2012). Even for constituents that do not become more

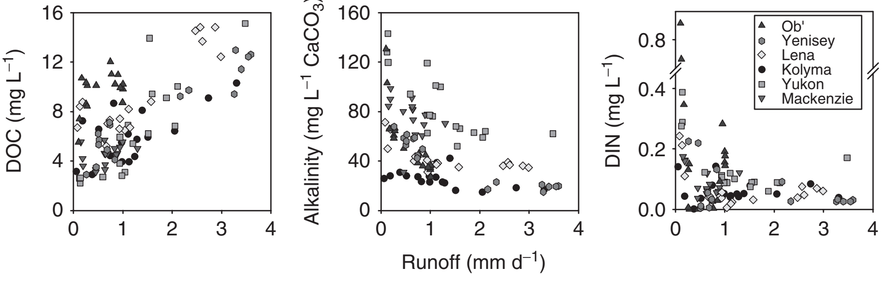

Figure 1.4 Measured concentrations of DOC, alkalinity, and DIN for each of the six PARTNERS rivers, plotted against runoff for the day of the measurement. In these large Arctic rivers, inorganic carbon is always greater than 90% of total alkalinity (Tank *et al.* in press).

concentrated with increasing flow, a lack of spring and wintertime measurements created considerable uncertainty in estimates of their flux, and calculations of flux using seasonally-representative data have clarified many flux estimates (McGuire *et al.* 2009; Tank *et al.* in press). PARTNERS-derived estimates of seasonal and annual constituent flux have also been used to examine the importance of riverine biogeochemistry to processes at the pan-Arctic scale, such as DOC degradation in the Arctic Ocean (Manizza *et al.* 2009), the relative importance of inorganic and organic riverine nitrogen for Arctic Ocean productivity (Tank *et al.* 2012), and the importance of factors such as permafrost and runoff for regulating dissolved inorganic C fluxes from the Arctic basin (Tank *et al.* in press).

1.4 Projections of future fluxes

1.4.1 Discharge

Continental runoff, driven by changes in net precipitation, is expected to increase at high latitudes with global warming. Different studies focusing on the Arctic have predicted a wide range of responses depending on the specific models and greenhouse gas emissions scenarios under consideration, but there is broad agreement among the studies that river discharge will increase (Miller and Russell 2000; Holland *et al.* 2006; Holland *et al.* 2007; Rawlins *et al.* 2010). Although precipitation and evaporation both increase with warming, the projected increases in precipitation outpace the increases in evaporation. Based on results from ten models that participated in the Intergovernmental Panel on Climate Change Fourth Assessment Report, Holland *et al.* (2007) estimated a net precipitation increase of 16% over the pan-Arctic watershed from 1950 through 2050. This included a 4% change from 1950 to 2000 that agreed well with the overall change in pan-Arctic river discharge that was observed during the latter half of the twentieth century (McClelland *et al.* 2006). While the suite of model results all indicated an increase in net precipitation, broad differences in the magnitudes of change among models pointed to a large degree of uncertainty in the precise trajectory of future increases (Holland *et al.* 2007).

1.4.2 Carbon

Of particular relevance with respect to the Arctic and climatic change is organic carbon (OC) cycling and storage as current estimates state that northern permafrost soils contain approximately one-half of global soil carbon (Gorham 1991; Tarnocai *et al.* 2009). A recent study estimated that northern soils contain almost 1700 Pg of OC, 88% of which is in permafrost (Tarnocai *et al.* 2009). Permafrost covers most of the pan-Arctic watershed (Table 1.1, Figure 1.2) and although it can be quite variable in depth (from tens to hundreds of meters), there is always a seasonally thawed active layer at the surface that varies in thickness from centimeters to meters (Brown *et al.* 1998; Frey and McClelland 2009). Increasing air temperatures result in permafrost thaw and degradation, which includes a deepening of the active layer, talik formation, thermokarst development, expansion and creation of thaw lakes, lateral permafrost thawing and a northward migration of the southern permafrost boundary (Zhang *et al.* 2005; Frey and McClelland 2009). Such degradation of permafrost has a number of impacts on hydrology, ecosystem dynamics and biogeochemical cycling in the Arctic and is leading to a significant impact on carbon biogeochemistry across the pan-Arctic including the mobilization of previously stored OC. As the OC that has been locked away in permafrost thaws into the contemporary carbon cycle, much of it may be metabolized by microorganisms in soils, exported into rivers and the ocean where it is also metabolized by microorganisms, ultimately resulting in the transfer of a significant portion of this large carbon reservoir to the atmosphere leading to a positive feedback on climate change (Striegl *et al.* 2005; Holmes *et al.* 2008; Osburn *et al.* 2009).

The response to climate change of OC export from Arctic rivers remains unclear with both an increase in export (Frey and Smith 2005; Guo *et al.* 2007) and a decrease in export predicted (Striegl *et al.* 2005; McClelland *et al.* 2007; Walvoord and Striegl 2007). In any case, because permafrost soils store a large amount of ancient carbon (Gorham 1991; Zimov *et al.* 2006; Zimov, Schuur, and Chapin 2006; Tarnocai *et al.* 2009), as they thaw the age of OC in rivers and streams may be useful as an integrator of the degree of permafrost degradation within the watershed. Currently, Arctic rivers have been shown to export predominantly modern DOC from recently fixed plant material and organic-rich surface soils (Amon and Meon 2004; Benner *et al.* 2004; Neff *et al.* 2006; Raymond *et al.* 2007). Seasonal trends in the radiocarbon age of DOC have been observed in the six largest Arctic rivers as well as tributaries, with an enrichment in Δ^{14}C-DOC (more modern DOC) during the spring flush period in comparison to late-summer DOC (Guo and Macdonald 2006; Neff *et al.* 2006; Raymond *et al.* 2007). Such a trend supports the idea of an increase in age of DOC exported through the summer months as the active layer thaw depth increases and a greater proportion of ancient carbon is mobilized from permafrost soils. Guo *et al.* (2007) reported data from three Arctic watersheds in North America (Yukon, Sagavanirktok and Mackenzie Rivers) and showed that particulate organic carbon (POC) may increase in age with permafrost degradation and resulting river-bank erosion, and hypothesized that future variability in DOC age could be due to changes in plant ecology (a shift from tundra to leaf-bearing plants). Although there is no general consensus it seems that the majority of evidence is pointing toward the fact that as the Arctic warms and permafrost degrades, concurrent increases in active layer depth will result in a greater mobilization of ancient OC into Arctic rivers. To date there is little evidence for an increase in aged DOC in Arctic rivers and streams, yet numerous studies have highlighted long-term permafrost degradation and a deepening in active layer (Frauenfeld *et al.* 2004; Oelke *et al.* 2004; Payette *et al.* 2004; Zhang *et al.* 2005; Osterkamp 2007).

While the release of DOC from soils to aquatic flow paths largely represents a net source of CO_2 to the atmosphere, much of the DIC (the sum of $CO_{2(aq)}/H_2CO_3$, HCO_3^- and CO_3^{2-}) found in freshwater represents a net CO_2 sink. Of the DIC species, bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}; which is minimal at pH < 9) are predominantly derived from chemical weathering, which is one of the primary sinks for CO_2 on land. Chemical weathering causes CO_2 dissolved in water to be transformed to bicarbonate, with all the bicarbonate produced during silicate rock weathering being derived from CO_2 fixation, and half of the bicarbonate produced during carbonate rock weathering being derived from CO_2 and the remainder from the dissolution of carbonate rock. Thus, the production of bicarbonate along the aquatic continuum can serve as a counterbalance to the CO_2 loss that occurs when DOC is mobilized from soils in the organic component of the aquatic C cycle.

Both increases in runoff and decreases in permafrost extent are expected to increase bicarbonate flux from northern catchments. Although bicarbonate concentrations within catchments dilute with increasing runoff (Figure 1.4), the dilution in large Arctic rivers and elsewhere is not great enough to offset overall increases in water yield; within rivers, yearly bicarbonate fluxes increase with increasing yearly runoff (Raymond and Oh 2007; Tank *et al.* in press). Because of these seasonal concentration differences (dilution during the spring freshet, and high concentrations during wintertime low flows) any seasonal variation in the expected increase in Arctic river discharge will have an important effect on the magnitude by which bicarbonate flux increases. Increased discharge that occurs across the hydrograph as a result of an overall intensification of the hydrologic cycle (Rawlins *et al.* 2010), for example, should have relatively less of an impact per unit volume than increases that are concentrated during the winter months, which capture the highest bicarbonate concentrations (Figure 1.3; Walvoord and Striegl 2007; St. Jacques and Sauchyn 2009). Such recent increases in wintertime base flow have been documented for multiple catchments in North America, and appear to result from decreased permafrost, which acts as an effective barrier to recharge (Walvoord and Striegl 2007; St. Jacques and Sauchyn 2009; Ge *et al.* 2011). Because permafrost also restricts surface water to rock interaction (e.g., Frey and McClelland 2009), its degradation may increase bicarbonate flux via two related mechanisms: first, by increasing overall runoff through an increased contribution of (bicarbonate-rich) groundwater to surface flux; and second, by allowing increased weathering as a result of increased water percolation to deeper mineral soils.

Relatively few studies have directly assessed the effect of climate-related change on bicarbonate flux. In Alaska's Yukon River basin, an increase in summertime bicarbonate flux between the 1970s and 2000s (Striegl *et al.* 2005, 2007) occurred alongside increasing base flows (presumably resulting from decreases in permafrost) during this same period (Walvoord and Striegl 2007). In Alaska's North Slope region, a steady increase in alkalinity (largely composed of bicarbonate) has been documented in Toolik Lake, and attributed to a deepening active layer, and thus greater weathering of mineral soils (Hinzman *et al.* 2005). Using the PARTNERS dataset, Tank *et al.* (in press) showed that bicarbonate flux from these large catchments increased with increasing runoff and decreasing permafrost. Studies that have focused on other weathering constituents (Ca, Na, Mg), or total inorganic solids, have shown these fluxes to be higher in low permafrost catchments, indicating that bicarbonate should follow these same trends (MacLean *et al.* 1999; Petrone *et al.* 2006; Frey, Siegel and Smith 2007). Further work to quantify the magnitude of the bicarbonate response to changing climate, and in particular the potential effect of changes in weathering rate on C sequestration, will greatly improve our ability to predict future changes in the C cycle at the landscape scale.

1.4.3 Major ions

Generally, predictions for the flux of major ions from Arctic rivers with changing climate are similar to the predictions for bicarbonate, above, with increased fluxes likely to result from both increases in runoff and decreases in permafrost extent. For runoff, for example, modeled yearly fluxes of both Ca and Na increased within the PARTNERS rivers with increasing yearly discharge. The effect of permafrost on the flux of major ions has been previously reviewed by Frey and McClelland (2009). As mentioned above, several authors have examined trends in major ion concentration and flux across gradients of permafrost extent, and found total inorganic solid concentrations (the sum of eight anion and cation species; Frey, Siegel and Smith 2007), and major cation fluxes (Na, K, Ca, Mg; MacLean *et al.* 1999; Petrone *et al.* 2006) increased with decreasing permafrost extent, which likely reflected a decreased contribution of groundwater to surface flow and decreased water-rock interactions with increasing permafrost extent (MacLean *et al.* 1999; Frey and McClelland 2009). Increases in active layer depth have also been linked to increased fluxes of major ions, and changes in the relative contribution of various ions to overall flux. For example, Keller, Blum, and Kling (2010) found increasing fluxes of Ca relative to Na and Ba in river water in northern Alaska between 1994 and 2004, which indicated increasing thaw depths and the exposure of more readily weatherable carbonate rocks, which are elevated in Ca relative to Na and Ba. Other authors have found that permafrost was enriched in total soluble cations (Kokelj and Burn 2005) and selected cations (Ca and K; Keller, Blum and Kling 2007) compared to the active layer, which indicated that weathering of these constituents will increase with increasing active layer depths.

1.5 Conclusions

Rivers integrate processes occurring throughout their watersheds, so trends in river chemistry and discharge have great capacity for tracking widespread terrestrial change. In addition to diagnosing impacts of climate change and other disturbances on land, altered land-to-ocean hydrologic and biogeochemical fluxes also have profound impacts on the chemistry, biology, and physics of the ocean, particularly the Arctic Ocean, which receives a disproportionate supply of river water in comparison to other ocean basins.

Despite the recent strides in our understanding of the biogeochemistry of Arctic rivers, there are still numerous gaps in our knowledge. Most obviously, there are few datasets that are yet long enough to detect trends over time, which on Arctic rivers have typically required decadal or longer time series (Peterson *et al.* 2002; Striegl *et al.* 2005; McClelland *et al.* 2006; Déry *et al.* 2009). Second, although the PARTNERS and Arctic-GRO projects' focus on large rivers has allowed for a dataset that captures greater than 50% of the runoff from the Arctic basin (Table 1.1), it misses much of the Arctic's most northerly regions (Table 1.1, Figure 1.2). Thus, using this dataset to understand riverine biogeochemistry across the pan-Arctic, and its potential for future change, results in estimates that are relatively uncertain. In particular, processes occurring in catchments largely underlain by tundra, continuous permafrost (Table 1.1), or where rapid transit time through relatively small catchments limits within-catchment biogeochemical cycling, are not well captured by these data. To date, there have been no systematic efforts to compare the few time series measurements that do exist for these watershed types and regions (McClelland *et al.* 2007; Keller, Blum and Kling 2010; Lewis, Lafreniere, and Lamoureux 2011) to patterns in concentration and flux at the mouths of large rivers.

To fully understand how Arctic riverine biogeochemistry will change with changing climate, a continued focus on the collection of time-series data, coupled with increased efforts to establish time series of biogeochemistry for rivers across the continuum of

Arctic landscapes, is clearly needed. Each river water sample can tell an important story, but the stories can only be read if the samples are collected. There should also be a concerted effort to archive time-series samples from numerous Arctic rivers, large and small. The archived samples would then be available for analysis in the future as new questions are asked or new analytical methods are developed.

Finally, improved understanding of the current rates of change and projections of future change will require the application of a new generation of integrated earth system models. Given the multitude of changes already underway in the Arctic and the tight coupling of atmospheric, terrestrial, and aquatic components of the Arctic, application of models that explicitly link above and below ground cycles of water, energy, carbon, and nutrients with global and regional atmospheric circulation models is urgently needed. Only coupled land-surface atmosphere models will be able to provide mechanistic understanding of the complex ways in which the Arctic will respond and contribute to global change in the coming decades.

Ironically, although the Arctic is a large producer of fossil fuels, there is little that can be done in the Arctic to mitigate the impacts of anthropogenic climate change. Instead, societal actions outside of the Arctic, mainly reducing fossil fuel combustion and halting tropical deforestation, will be required to dampen the impacts of climate change on Arctic ecosystems.

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