11 Changing Biogeochemical Cycles of Organic Carbon, Nitrogen, Phosphorus, and Trace Elements in Arctic Rivers

Jonathan O'Donnell, Thomas Douglas, Amanda Barker, and Laodong Guo

Abstract

Streams and rivers are critical components of Arctic watersheds, functioning as corridors for the movement of water, carbon, and other solutes from headwater streams to larger rivers, estuaries, and the Arctic Ocean. Recent climate change in the Arctic has altered stream and river discharge, temperature, and biogeochemical processes. In this chapter, we summarize the state of research linking watershed hydrology and biogeochemical cycling in Arctic rivers, and how these processes are changing in response to changing climate and disturbance regimes (e.g., permafrost thaw, wildfire). The chapter is divided into three main sections. First, we examine hydrologic controls on stream and river chemistry, including the roles of spring snowmelt and subsurface hydrology as mediated by permafrost characteristics. Second, we summarize recent findings from the literature that describe biogeochemical processes in Arctic rivers, with particular focus on the cycling of organic carbon, nitrogen and phosphorus species, and a suite of trace elements. Third, we identify

J. O'Donnell (✉)
National Park Service, Arctic Network, Anchorage, AK, USA
e-mail: jaodonnell@nps.gov

T. Douglas
U.S. Army Cold Regions Research and Engineering Laboratory, Fort Wainwright, AK, USA
e-mail: Tom.Douglas@erdc.dren.mil

A. Barker
U.S. Army Cold Regions Research and Engineering Laboratory, Fort Wainwright, AK, USA
e-mail: amanda.j.barker@usace.army.mil

L. Guo
School of Freshwater Sciences, University of Wisconsin-Milwaukee, Milwaukee, WI, USA
e-mail: guol@uwm.edu

D. Yang and D. L. Kane (eds.), *Arctic Hydrology, Permafrost and Ecosystems*,
https://doi.org/10.1007/978-3-030-50930-9_11

uncertainties and current gaps in our knowledge of biogeochemical processes in Arctic rivers and recommend steps forward to address these uncertainties.

11.1 Introduction

The Arctic region is characterized by extreme climatologic and physiographic conditions not found elsewhere on Earth (Hinzman et al. 2005). Air temperatures can vary as much as 70 °C between winter and summer and sunlight shifts from total darkness to continuous sunlight. Air temperatures in the Arctic are warming at a faster rate than temperate and tropical regions at lower latitudes and much research is focused on the responses of Arctic systems to this rapid warming and associated changing seasonality (Larsen et al. 2014). Of particular concern is the response of Arctic ecosystems to changing disturbance regimes, including changing hydrology and increasing river discharge, wildfire frequency and severity, and permafrost thaw (Turetsky et al. 2011; Schuur et al. 2015; Walvoord and Kurylyk 2016). Warming and disturbance can alter biogeochemical cycles in both terrestrial and aquatic ecosystems. Recent research has focused on biogeochemical feedbacks from terrestrial ecosystems to the atmosphere and climate system (e.g., Schuur et al. 2015), but there is also considerable interest in the response of aquatic ecosystems to changing conditions in the Arctic, including streams and rivers draining high-latitude watersheds (e.g., Vonk et al. 2015a).

Arctic rivers and streams are important corridors for the movement of water, carbon (C), other nutrients, and a variety of other solutes from headwater streams to larger rivers, estuaries, and ultimately, the Arctic Ocean. The chemical composition of streams and rivers in the Arctic varies considerably across space and time, as dictated by a variety of factors including landscape characteristics (vegetation, lithology), watershed hydrology, latitudes, and in-stream processes (Guo et al. 2004a; Neff et al. 2006; Holmes et al. 2012; Douglas et al. 2013; Pokrovsky et al. 2016, 2018). Arctic river chemistry typically exhibits strong seasonal patterns, with significant differences observed between the peak flows of spring snowmelt and base flow conditions during summer and winter (e.g., Finlay et al. 2006; Guo et al. 2012). Recent work has documented long-term changes in Arctic stream and river chemistry over the past 40–50 years, indicating climate and landscape change may be altering the concentration and flux of various solutes, although specific pathways and mechanisms are not well understood and could be seemingly contradictory (Frey and Smith 2005; Striegl et al. 2005; Toohey et al. 2016; Lung et al. 2018). Given the rapid pace of change in the Arctic, many uncertainties remain regarding the dynamics and trajectory of river chemistry and biogeochemical processes (McGuire et al. 2009).

In this chapter, we summarize riverine sources and transport of chemical species and their biogeochemical processes in Arctic watersheds with a focus on the major biogeochemical compounds of greatest impact in watershed processes. These

include dissolved organic carbon (DOC), nutrients (nitrogen (N) and phosphorus (P)), dissolved silica, and selected trace elements (iron, strontium, uranium, and mercury). We review recent findings from the literature that document how the cycling of these constituents are changing in response to climate change and disturbance in the Arctic and identify knowledge gaps that limit our ability to project how river biogeochemical cycles will be affected in a warmer future.

11.2 Hydrologic Controls on Arctic River Biogeochemistry

11.2.1 Spring Melt Runoff Processes as Major Drivers of Arctic Watershed Biogeochemistry

One unique aspect of Arctic watersheds is the spring snowmelt runoff (freshet). In a short time window in May or June (often in less than 2 weeks), much of the yearly surface water discharge runs from the land through river channels to the sea (Kane et al. 1989; McNamara et al. 1997, 2008; Bowling et al. 2003; Holmes et al. 2012). A white, snow-covered landscape is converted rapidly to a brown and eventually green one (Fig. 11.1). During the spring snowmelt period, discharge is often at peak yearly values and there is a significant dilution of river solutes, yet stream water concentrations of dissolved organic C (DOC) and other nutrients like ammonium (NH_4^+), phosphate (PO_4^{3-}), and nitrate (NO_3^-) reach their highest levels of the year due to hydrologic "flushing" (e.g., Hornberger et al. 1994; Finlay et al. 2006; Raymond et al. 2007; Cai et al. 2008a, b; Guo et al. 2004a, 2012; Douglas et al. 2013).

The snowmelt period is dynamic across a range of spatial scales. For instance, at the macro-scale, the timing of peak snowmelt varies longitudinally within a watershed, with the lower reaches of the river snow-free by mid-June and starting to Greenup, while headwater reaches are still snow-covered and just beginning to melt (Fig. 11.2). As a result, the timing of melt-driven changes in stream and river chemistry varies within an individual watershed. At the micro-scale, carbon (C), nutrients, major elements, and trace metals in the snowpack become constituents in meltwater. An "ionic pulse" of solutes moves downward into the pool at the base of the snowpack (Tranter et al. 1986; Rember and Trefry 2004; Douglas et al. 2017). Elevated solute concentrations before snowmelt are partially caused by ion exclusion from the quasi-liquid water layer, a disordered microthin layer on snow grain surfaces (Dominé and Shepson 2002). As snow and ice crystals approach 0 °C the snow grains start to metamorphose into rounded melt grain clusters. Larger molecules or ions (like sulfate (SO_4^{2-}) and some metals) present as impurities on the snow or ice crystal surface undergo preferential elution compared to smaller ions like chloride (Cragin and McGilvary 1995). As a consequence, DOC, SO_4^{2-}, NO_3^-, lead (Pb), and mercury (Hg) concentrations in the early pulse of snowmelt water that moves across the landscape typically exceed bulk snowpack values (Williams and Melack 1991; Douglas et al. 2017). Though vegetation, soils, and atmospheric deposition are the dominant sources of nutrients, major ions, and trace

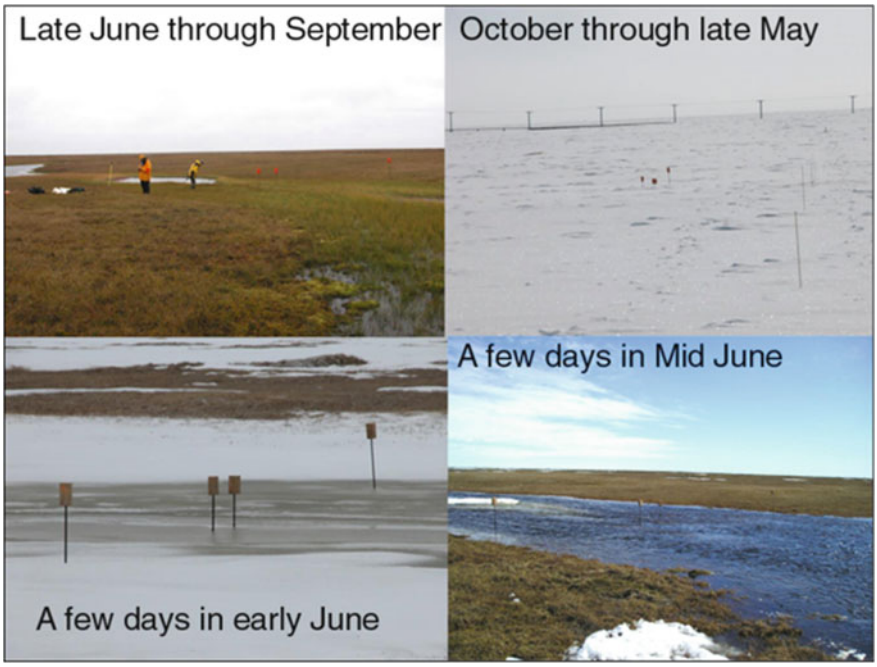

Fig. 11.1 Photographs of a small watershed near Utqiaġvik, Alaska, representing the major seasons and seasonal transitions in Arctic watersheds. Most of the Arctic is snow-covered for up to 8 months of the year. The spring melt period includes a dramatic flux of surface water and biogeochemical compounds that is active for only a few weeks. Photos by T. Douglas

metals in river waters (Rember and Trefry 2004; Cai et al. 2008a; Barker et al. 2014) the snowpack is a source of some chemical species (e.g., Pb, SO_4^{2-}; Douglas and Sturm 2004).

In most Arctic locations, the surface soils of the seasonally thawed active layer are frozen during spring melt, which limits infiltration of snowmelt water into surface soils depending on the previous year's soil moisture and snow water equivalent (Gray et al. 2001), in addition to a variety of other factors including the presence of preferential pathways (Stähl et al. 2004), soil aggregates (Koren et al. 1999), and abundance of air-filled macropores (Niu and Yang 2006). Where permafrost is present, soils and bedrock can be frozen to a depth of up to 300 m. As such, groundwater discharge to surface waters is negligible during snowmelt and the nutrient load in runoff is predominantly controlled by the vegetation cover and soil type (Judd and Kling 2002; Hobbie and Gough 2004). Decaying plant litter and shallow organic-soil horizons at the base of the snowpack are the major sources of DOC and nutrients to river flows during this period (Fig. 11.3). Snowmelt has been found to contain up to 60% of the annual DOC export from major Arctic rivers (Guo et al. 2007; Raymond et al. 2007). This C, leached from vegetation and

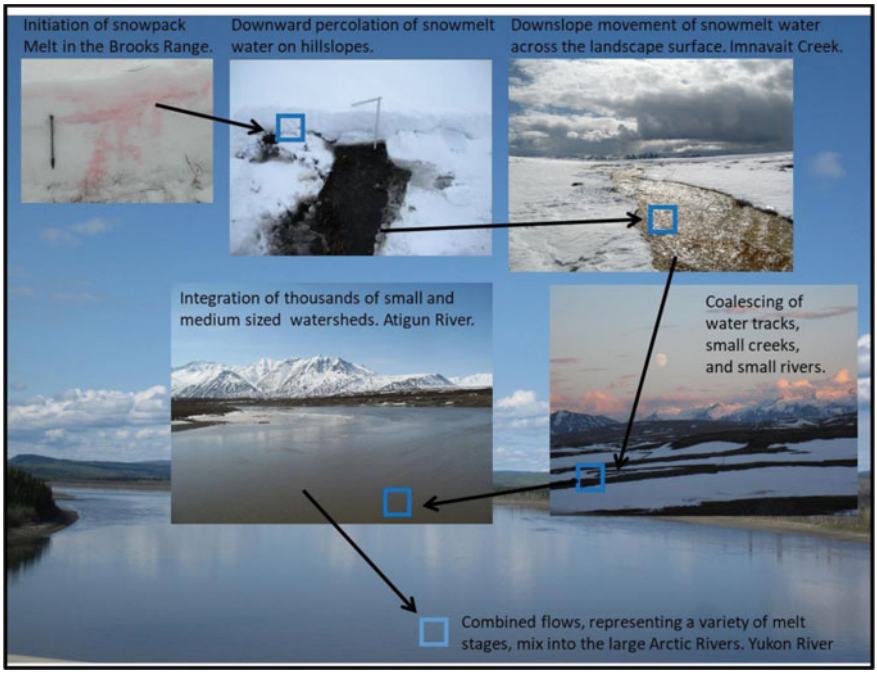

Fig. 11.2 A series of photos, taken within 2 days of one another, exhibiting the different scales and the delayed timing of spring melt across a broad geographical range. Each blue box represents a hydrologic source to the larger system it feeds. Note that in the upstream mountains and on hillslopes snowmelt is just starting while lower elevation small streams are beginning to flow and reach a peak discharge and, at the regional scale, the Yukon River (large background photo) is snow and ice-free and has initiated Greenup. Photos by T. Douglas

surface organic-soil layers, is of the modern age (Neff et al. 2006; Guo and Macdonald 2006) and close to a third of the DOC pool may be biologically labile (Holmes et al. 2008) and over 90% of chromophoric DOM can be photochemically degraded (e.g., Cory et al. 2014) although only a small fraction of soil organic C can be leached out during permafrost thaw (Xu et al. 2009; Gao et al. 2018).

11.2.2 Seasonally Frozen Ground and Permafrost as Controls on Arctic River Biogeochemistry

As noted above, many Arctic watersheds are underlain by permafrost, earth material such as soil, organic matter, or bedrock that has remained below 0 °C for at least two consecutive years. In most cases, permafrost has remained frozen for hundreds to thousands of years. However, recent warming in the Arctic has caused permafrost to warm and thaw (Jorgenson et al. 2006; Romanovsky et al. 2010). This has important consequences for watershed hydrology and the chemical composition

Fig. 11.3 Photos of Imnavait Creek north of the Brooks Range in the Alaskan Arctic during peak spring melt flow (left) and in early fall (right). Note the dark brown color of the water during spring melt which is attributable to the heavy load of particulate organic C, decayed vegetation, and mineral particles. For most of the year, this watershed is a small trickle roughly a few meters wide (fall photo). Photos by T. Douglas

of rivers (Frey and McClelland 2009; Walvoord et al. 2012). Permafrost properties, including thermal and hydraulic characteristics, are important for controlling depth and velocity of subsurface flow paths that contribute to streamflow. The active layer is the shallow surface vegetation and soil above the permafrost that thaws and refreezes on an annual basis (Fig. 11.4). Seasonally thawing of the active layer governs depths of subsurface flow paths during the summer (i.e., the supra-permafrost aquifer; Lamontagne-Halle et al. 2018) and consequently influences leaching and mobilization of solutes from soil horizons.

In the continuous permafrost zone (>90% of the land area underlain by permafrost), groundwater discharge from deep, sub-permafrost aquifers to surface waters is limited (Fig. 11.5). In this area, the permafrost is hundreds of meters thick. By contrast, in the discontinuous permafrost zone to the south (50–90% of the land area underlain by permafrost) the permafrost is warmer and less thick (10–100 m), groundwater discharge is higher and can comprise a larger fraction of river discharge (Walvoord and Striegl 2007). Within the discontinuous zone, slope and aspect can drive the spatial extent of permafrost with north-facing slopes and valley bottoms underlain by permafrost and south-facing slopes and ridge tops are often permafrost-free. Headwater catchments that vary with permafrost extent also exhibit striking variations in discharge patterns and chemical composition (Maclean et al. 1999). The hydrologic mixing of waters from shallow supra-permafrost and deep sub-permafrost aquifers is a key determinant of spatial and temporal variability in stream water chemistry (O'Donnell et al. 2012, 2016). Thermokarst, or the subsidence of the ground surface following the thawing of ice-rich permafrost (Loranty et al. 2018), can also alter stream and river chemistry (Bowden et al. 2008). However, yields and fluxes of C, nutrients, and trace elements via lateral transport from soils to streams, rivers, and the Arctic Ocean during permafrost thaw and coastal erosion are poorly understood although laboratory studies have mimicked

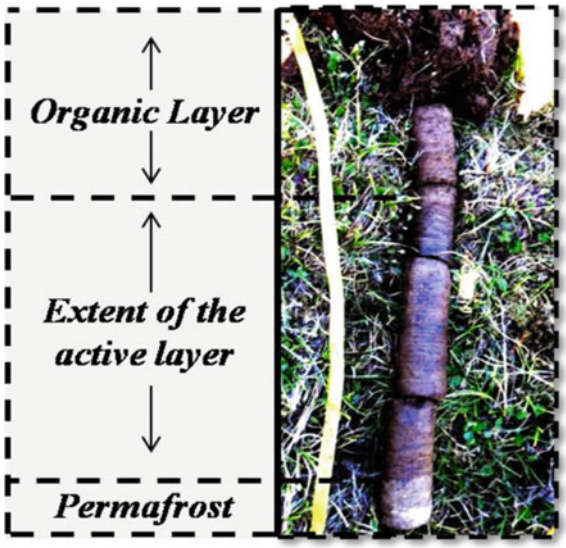

Fig. 11.4 The surface vegetation (dark brown mass) in an 80-cm-long SIPRE core collected in early spring. Note the lighter colored material toward the base of the core. This region, comprised of small (1–2 cm) layers of transition zone ice, is the boundary between the seasonally thawed active layer and the top of the near-surface permafrost. Photos by A.J. Barker

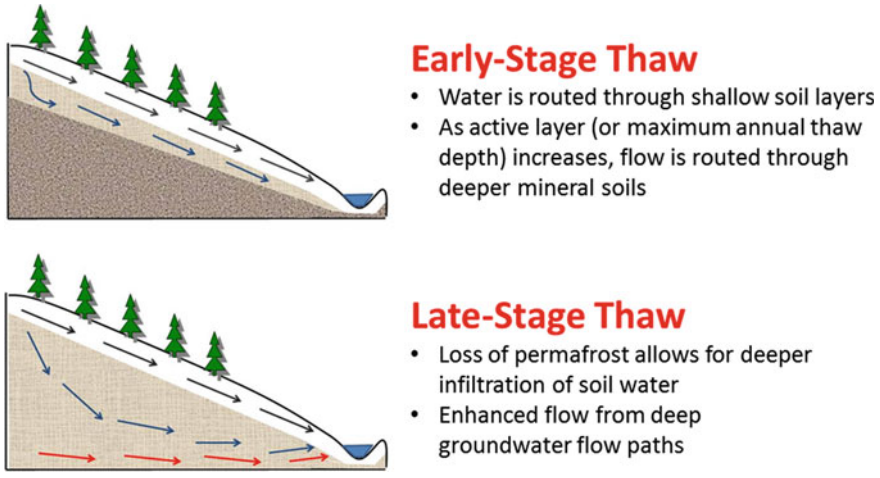

Fig. 11.5 A conceptual model of subsurface hydrologic change associated with thawing permafrost (adapted from Walvoord and Kurylyk 2016)

the permafrost–water interactions and quantified their yields and fluxes of C and nutrients (Dou et al. 2008; Xu et al. 2009; Gao et al. 2018). Much uncertainty exists regarding the effects of permafrost thaw on river chemistry under a warming climate (Liao and Zhuang 2017). Recent findings on this topic are highlighted below.

11.3 Major Chemical Species/Components in the Arctic Stream and River Waters

11.3.1 Dissolved Organic Carbon

DOC is a critical component of aquatic ecosystems and the Arctic C cycle as it functions to regulate water quality and nutrient availability and serves as a substrate for microbially mediated reactions (Cole et al. 2007; Tranvik et al. 2009). DOC can also influence photochemical reactions and interactions with trace metals and organic pollutants, altering their fate, transport, and bioavailability/toxicity (Chin et al. 1997; Aiken et al. 2011; Philippe and Schaumann 2014). Increases in DOC concentration have contributed to the browning of surface waters in some high-latitude regions (Roulet and Moore 2006), affecting the photic zone and rates of primary productivity. In the Arctic, DOC in rivers is sensitive to watershed hydrology (Striegl et al. 2005; O'Donnell et al. 2010, 2012), permafrost presence (Maclean et al. 1999; Frey and McClelland 2009; Olefeldt et al. 2014), active layer thickness (O'Donnell et al. 2016; Harms et al. 2016), wetland extent, and permafrost soil properties (O'Donnell et al. 2016).

Soils of the northern circumpolar permafrost region store approximately 1300 petagrams (Pg) of organic C (Hugelius et al. 2014). As a result, high-latitude rivers tend to have higher DOC concentrations (Finlay et al. 2006) than temperate or tropical rivers (Hope et al. 1994). Regardless of sources, the flux of C in Arctic rivers represents an important component of the high-latitude C budget (McGuire et al. 2009), and the magnitude of this flux is expected to change under projected warming and disturbance scenarios (Frey and Smith 2005; Striegl et al. 2005; Kicklighter et al. 2013). Moreover, inland waters can release C to the atmosphere through microbial and photochemical processes (Kling et al. 1991; Cory et al. 2014), which can function as a positive feedback to the climate system. By incorporating DOC into terrestrial ecosystem and earth system models, it is possible to better constrain C sources and sinks in the Arctic and globally (Kicklighter et al. 2013; Wu et al. 2014).

DOC in rivers is chemically complex, reflecting a broad gradient of compounds ranging in molecular size, structure, and decomposability/reactivity (Xu and Guo 2017). Scientists have developed a variety of analytical techniques to characterize the composition and reactivity of dissolved organic matter (DOM), including bulk measurements of concentration (DOC, dissolved organic N (DON)), optical measurements (ultraviolet (UV)–visible absorbance and fluorescence), chemical fractionation, and high-resolution mass spectroscopy (e.g., FTICR-MS) among others.

In the Arctic rivers, DOM composition varies across space and time, as determined by hydrology and landscape features. Most rivers are dominated by hydrophobic organic acids (e.g., humic and fulvic acids) during the open-water period, which tends to be highly aromatic compounds derived from organic-rich wetland soils (Striegl et al. 2005; Spencer et al. 2008; O'Donnell et al. 2010). During winter or in groundwater-dominated systems, DOM is comprised primarily of low-molecular weight aliphatic compounds and tends to more N-rich (O'Donnell et al. 2012). DOM composition reflects and integrates processing in both the terrestrial (e.g., microbial transformation, sorption to mineral soils) and aquatic ecosystems (e.g., photo-oxidation), and is closely linked to its bio-lability (Holmes et al. 2008). In general, DOM lability is higher in high-latitude rivers than other biomes and tends to decrease with increasing stream size or order (Vonk et al. 2015b). In addition, DOM liability is highly related to chemical composition, molecular size, and specific degradation pathways (e.g., photochemical vs biological degradation; Xu and Guo 2018).

In the Arctic, the majority of riverine DOC is derived from terrestrial sources (Wauthy et al. 2018). The decomposition of plant litter, organic soils, and mineral-associated soil organic matter can drive production of DOC, which is then, transported from terrestrial to aquatic ecosystems through runoff and subsurface flow paths. Recent work has also documented the importance of permafrost thaw on the delivery of ancient DOC to river networks (e.g., Spencer et al. 2015). However, DOC transported in Arctic rivers is mostly contemporary, especially the high-molecular weight (>1 lDa) DOC fraction (Benner et al. 2004; Guo and Macdonald 2006; Raymond et al. 2007) or much younger than both particulate organic C (POC) pool and river sediment (Guo et al. 2007). This indicates riverine DOC derived from old permafrost soil is limited although pre-aged POC derived from permafrost has been measured in Arctic rivers (Guo et al. 2004a, b, 2007). In addition, the ^{14}C ages among DOC, POC, and river sediment changed across different rivers and sampling season, and the relative contributions of DOC from modern primary production and ancient soil organic C also varied with rivers (Fig. 11.6). Young DOC but extremely old POC observed in Arctic rivers are consistent with the experimental results that only a small fraction (<2%) of permafrost TOC is water-soluble and can be released into the DOC pool during permafrost interactions with aquatic environments (Guo et al. 2007; Dou et al. 2008; Xu et al. 2009; Gao et al. 2018).

Given the large stores of permafrost OC in the Arctic terrestrial ecosystem, warming and thawing could potentially release significant amounts of DOC into Arctic waterways should permafrost soils be thawed and flushed into aquatic environments even though only a small fraction of total soil organic C can be released into water-extractable phase (Xu et al. 2009; Gao et al. 2018). Within the soil-derived DOC pool, the aromatic components can be readily decomposed photochemically (Cory et al. 2014) while bio-labile organic acids (e.g., acetate, Ewing et al. 2015) and other carbohydrates and protein-like components can be rapidly degraded microbially regardless of their radiocarbon (^{14}C) ages (Vonk et al. 2013, 2015b; Xu and Guo 2018; Gao et al. 2018). Evidence from ^{14}C

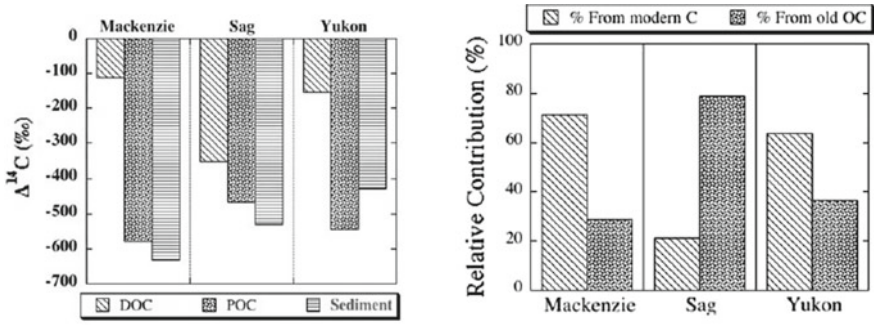

Fig. 11.6 Changes in $\Delta^{14}C$ values (or ^{14}C ages) among DOC, POC and river sedimentary organic carbon pool in the Mackenzie, Sag (Sagavanirktok) and Yukon Rivers (left panel) and relative contributions of DOC from modern primary production and ancient soil organic C in different Arctic rivers, including the Mackenzie, Sagavanirktok (Sag), and Yukon Rivers (right panel, from Guo et al. 2007)

measurements indicates permafrost-derived old DOC is not an important component of the DOC pool in higher order rivers (Guo and Macdonald 2006; Guo et al. 2007; Raymond et al. 2007; O'Donnell et al. 2014; Aiken et al. 2014). This is consistent with the consistently low DOC yields of soil-OC in different aged permafrost (up to 16,000 years BP) from northern Alaska (Guo et al. 2007; Dou et al. 2008; Xu et al. 2009; Gao et al. 2018). Therefore, DOC in Arctic rivers should be mostly derived from surface soil and contemporary terrestrial primary production enhanced by warming, and autochthonous sources of DOC to rivers, include stream periphyton, are generally a minor component of DOC pool in Arctic watersheds (e.g., Mann et al. 2015). However, the contribution of autochthonous DOC to Arctic rivers can be greatly underestimated due to its ^{14}C reservoir effect or old dissolved inorganic C (DIC) ^{14}C ages (Guo et al., *unpublished data*).

DOC concentration and DOM composition vary across watersheds that differ with respect to landscape and subsurface properties. In the Yukon River basin of Alaska and Canada, DOC concentration and flux vary among watersheds according to watershed hydrogeologic characteristics and source water contribution to streamflow (Striegl et al. 2007; O'Donnell et al. 2010). Blackwater streams (i.e., streams dominated by hydrologic and C inputs from wetlands) have high DOC concentrations relative to glacially fed or groundwater-dominated streams. Further, blackwater streams tend to have higher concentrations of aromatic DOM (i.e., high specific ultraviolet absorbance, or $SUVA_{254}$; Weishaar et al. 2003) compared to glacially fed or groundwater-dominated streams which tend to have higher concentrations of low-molecular weight organic acids and aliphatic compounds. Permafrost thermal state (e.g., ground temperatures, rates and timing of seasonal thaw, and active layer thickness) and hydraulic properties (e.g., parent material, ground ice content) also influence spatial patterns of DOC in streams and rivers (Olefeldt et al. 2014; Harms et al. 2016; O'Donnell et al. 2016; Fig. 11.7). More generally,

Fig. 11.7 Arctic rivers drain watersheds that vary with respect to soil and bedrock characteristics and permafrost mineralogy and ground-ice content. In the Alaskan Arctic, watersheds are mostly commonly underlain by ice-poor bedrock (top left), coarse-grained glacial till (top middle), ice-rich, fine-grained glaciolacustrine deposits (top left), ice-rich Pleistocene loess (yedoma; lower left), sand (lower middle), and volcanic deposits (lower right). These watershed properties strongly influence the hydrology and chemical composition of streams and rivers (O'Donnell et al. 2016)

watershed properties that convey water through runoff and shallow subsurface flow paths (supra-permafrost flow; Fig. 11.5) typically yield larger concentrations of DOC in surface waters. Alternately, watersheds that allow for more groundwater discharge from sub-permafrost aquifers typically yield low concentrations of DOC in surface waters.

DOC concentration and flux are highly sensitive to recent warming in high-latitude regions. Numerous measurements and studies have focused on the flux of C in large Arctic rivers and estuaries (Dittmar and Kattner 2003; Raymond et al. 2007; Holmes et al. 2008; Spencer et al. 2008; Guo et al. 2012), given the importance of these riverine fluxes as components of regional-scale terrestrial budgets (McGuire et al. 2010; Kicklighter et al. 2013) and the large C stores in permafrost (Hugelius et al. 2014). In the Yukon River basin discharge-normalized DOC flux has decreased over the past 40 years (Striegl et al. 2005), likely due to permafrost thaw and associated increases in groundwater discharge to streamflow (Walvoord & Striegl 2007). Thawing of permafrost exposes more mineral soils to weathering and provides the potential for extensive physical stabilization (i.e., adsorption) and retention of DOC by soils, reducing the flux to rivers (Kawahigashi et al. 2004, 2006). On the other hand, warming could also increase primary production (e.g., higher plants) in Arctic terrestrial ecosystems, enhancing the release of contemporary DOC to Arctic rivers since river DOC has been found mostly contemporary in all major Arctic rivers (e.g., Benner et al. 2004; Guo and Macdonald 2006; Raymond et al. 2007). Total yearly DOC export has also declined in the much smaller Kuparuk River in northern Alaska, likely due to the decreases in discharge during the spring snowmelt period (McClelland et al. 2007) or possibly

due to the increases in baseflow (e.g., Walvoord and Striegl 2007; O'Donnell et al. 2012). However, DOC flux has increased by nearly 40% in the much larger Mackenzie River in northwest Canada, with much of the change occurring during autumn and winter flow (Tank et al. 2016). This appears to be influenced by permafrost and hydrological conditions and higher rates of plant production, but the exact mechanisms driving this change are still unclear. The different responses to the two terrain types to climate warming and associated disturbances may be driven by geomorphologic characteristics. Model simulations indicate that DOC loading from terrestrial ecosystems to Arctic rivers has increased in recent decades due to the increased water yields (Kicklighter et al. 2013). These seemingly contradictory observations and conclusions between different studies on the increased and decreased DOC fluxes remain to be verified. Future changes in riverine DOC flux will likely depend on the balance of factors that promote DOC production, loss, and hydrologic transport.

Once in a stream or river DOC can undergo in-stream processing which modifies lateral C fluxes from terrestrial ecosystems to the Arctic Ocean. In the northern permafrost region, DOC concentrations vary considerably across the continuum of soils, streams, and larger rivers (O'Donnell et al., unpublished data; Fig. 11.8). DOM composition strongly determines its fate and reactivity along the river reaches. While aromatic and humic-like DOM components are preferentially decomposed through photochemical pathways, carbohydrates and protein-like DOM components are somewhat resistant to photochemical degradation but preferentially utilized by microorganisms (Cory et al. 2014; Xu et al. 2018; Xu and Guo 2018). For example, recent work by Cory et al. (2014) has documented the importance of photo-oxidation of CDOM and DOC by sunlight in the water column of Arctic streams. Complete oxidation of DOC by sunlight and microorganisms results in the release of CO_2 from surface waters to the atmosphere, whereas partial oxidation results in the chemical transformation of the DOC pool prior to transport to downstream ecosystems. In many cases, rates of photo-oxidation outpace rates of DOC mineralization by aquatic microbial communities depending on the DOM composition. Further, the chemical alteration of DOC by sunlight can stimulate microbial mineralization of the residual DOC pool through the production of more bio-labile compounds (Ward et al. 2017). River ecosystems can also function to retain DOC, reducing the flux of C to downstream ecosystems or to the atmosphere. Some evidence suggests that benthic biofilm communities in streams and rivers can function to retain DOC through adsorption processes (Battin et al. 2016).

11.3.2 Major Nutrients: Nitrogen and Phosphorus

N and P are essential nutrients that can govern C-cycle processes, such as rates of primary production and microbial process rates in terrestrial and aquatic ecosystems (Elser et al. 1990; Vitousek and Howarth 1991; Heimann and Reichstein 2008). N occurs in various forms in stream ecosystems, including particulate N, dissolved organic N (DON, e.g., amino acids, proteins, etc.), and dissolved inorganic N (DIN:

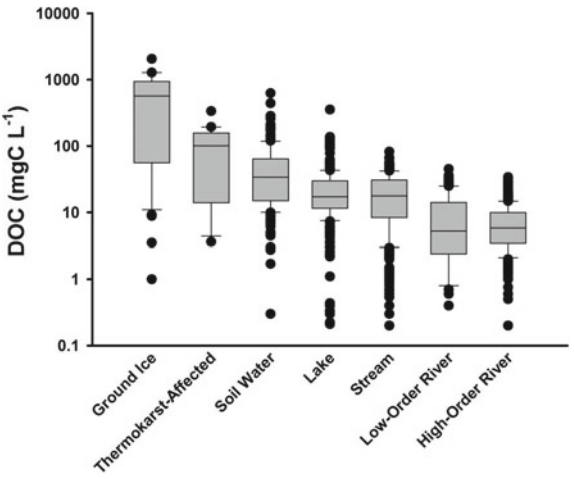

Fig. 11.8 DOC concentrations from different sites (approximately 2500 samples) across the Arctic along the continuum from permafrost soils to large rivers (O'Donnell et al., *unpublished data*)

NO_3^-, nitrite (NO_2^-), and NH_4^+). N-containing compounds can cycle between these various forms through microbially mediated reactions, which are typically controlled by reduction–oxidation (redox) state and availability (Hedin et al. 1998). N can also be assimilated by aquatic vegetation, including benthic algae, moss, phytoplankton, and macrophytes. While P typically limits primary productivity in aquatic systems, increased availability of inorganic N can directly limit or co-limit primary production in some systems (Grimm and Fisher 1986). Some microbial processes, such as nitrification (conversion of NH_4^+ to NO_3^-) and denitrification (conversion of NO_3^- to nitrous oxide (N_2O) and dinitrogen gas (N_2)) can result in the loss of N from the system to the atmosphere. N_2O is a greenhouse gas, and emission of N_2O from aquatic ecosystems can function as positive feedback to the climate system (Beaulieu et al. 2010).

In addition, the abundance, chemical speciation, and export fluxes of nutrients from rivers can be linked to changes in permafrost dynamics, vegetation/land cover, hydrological conditions, and human disturbance in river basins and changes in the ecosystem. Humans have dramatically altered the global N cycle (Vitousek et al. 1997), primarily through N fertilization of agricultural lands and through altering rates of atmospheric deposition. In undisturbed regions of the Arctic, the primary inputs of N to watersheds are through fixation of atmospheric N_2 by N-fixing organisms (e.g., boreal feather mosses) and atmospheric deposition. While terrestrial ecosystems retain a significant fraction of these N inputs, some are released to streams and rivers (Vitousek and Reiners 1975).

Some research indicates that boreal watersheds are losing N, as fluvial N fluxes exceed watershed inputs (Jones et al. 2005). Compared to other forms of N, NO_3^- is highly mobile and can be readily transported via runoff and subsurface flow paths to surface waters, and is often the dominant form of DIN and even TDN in high-latitude streams and rivers (Petrone et al. 2006). Indeed, in the Chena River of interior Alaska, DIN accounted for 60 ± 15% of the total N while DON and

particulate-N comprised 30 ± 8 and 10 ± 9%, respectively (Cai et al. 2008b). However, in the upper Yukon River, DON is the predominant N species, followed by particulate N and then DIN (Guo et al. 2004a, b). The same is true for the lower Yukon River with DON being the major N species (Guo et al. 2012). The predominance of DON in Arctic river waters is consistent with those derived from the leaching of different-aged permafrost soils in northern Alaska (Gao et al. 2018). Under warmer climatic conditions, increased mineralization of soil organic N pools may also increase production and transport of inorganic N to streams and rivers. Still, there are large uncertainties with respect to the fate of N in high-latitude watersheds in response to warming and disturbance (e.g., permafrost thaw; Frey and McClelland 2009). Sources of uncertainty include changing magnitude and seasonality of runoff and river discharge, the release of permafrost nitrogen, and rates of soil and in-stream N processing.

Wildfire, permafrost thaw, and erosional processes are three primary disturbance processes that may alter stream and river chemistry. Wildfires reduce terrestrial N stocks, but also temporarily reduce N retention by vegetation and soil microbial communities. Evidence from the boreal region indicates that wildfire may increase NO_3^- concentrations in headwater streams (Betts and Jones 2009). Wildfire can accelerate rates of permafrost thaw (O'Donnell et al. 2011), and thaw waters are typically enriched with DIN (Ewing et al. 2015). Recently, Ping et al (2011) reported that total N fluxes through coastal erosion along the Alaska Beaufort Sea coastal line could reach 7.76 ± 1.31 10^9 g-N/year during 1950–2000. On the other hand, based on laboratory leaching experiments, different aged permafrost with TN contents ranging from 500 to 12,000 μg-TN can produce soluble DIN, including NO_3^-, NO_2^-, and NH_4^+, varying from 12 to 41 μg-N/g-soil, and DON between 8 and 116 μg-N/g-soil (Gao et al. 2018). Yields of DON from soil TN were only 0.9–3.4% while yields of DIN from TN varied from 0.3 to 2.3% depending on specific soil (Gao et al. 2018). Nevertheless, the overall TDN released from soil can be enormous should permafrost thaw. Within the soil TDN pool, DON is the dominant N species followed by NH_4 and NO_3 and NO_2.

There are three primary sources of P to stream ecosystems, including soil/mineral leaching, anthropogenic input, and atmospheric deposition. Erosion and sedimentation through changes in watershed land use or disturbance can load P into aquatic systems. In soils, most P is found in particulate forms where organic or inorganic P complexes with mineral particles, such as iron (Fe), aluminum (Al), or manganese (Mn) hydroxides (Schlesinger and Bernhardt 2013). Permafrost soil leaching experiments show that yields of PO_4^{3-} from soil ranged from 0.6 to 6 μg-P/g-soil or 0.12 to 1.2% of the total P in soil, while yields of dissolved organic P (DOP) were 1.1–8.1 μg-P/g-soil or 1.2–2.9% of total organic P (Gao et al. 2018). Decomposition of soil organic matter by microbes can also release P, both as DOP and mineralized forms (e.g., PO_4^{3-}). Weathering of parent materials, such as limestone or volcanic deposits, can also contribute P to stream ecosystems. P cycling in streams is controlled by both abiotic processes (e.g., sorption–desorption reactions between surface water and sediments) and biological processes (decomposition of organic matter, assimilation, and immobilization in microbial biomass;

Hendricks and White 2000). In most Arctic streams, P is the primary limiting nutrient governing primary production (Peterson et al. 1985). For example, long-term P fertilization of the Kuparuk River near the Toolik Field Station in northern Alaska has altered stream ecosystem function, leading to enhanced moss and algal productivity, invertebrate production, and fish production (Slavik et al. 2004). In many Arctic streams and rivers, N and P concentrations are very low, and in many cases below detection limits (e.g., O'Donnell et al. 2015). However, given that permafrost soils store large amounts of N and P (Harden et al. 2012; Ewing et al. 2015), warming and disturbance will likely increase both N and P inputs to streams from soils (e.g., Frey et al. 2007; Bowden et al. 2008) although yields of soluble N and P from permafrost are generally low (Gao et al. 2018), driving bottom-up effects on food web dynamics due to the overall large store in the northern high-latitude regions.

Overall, studies of the detailed chemical speciation of nutrients for Arctic rivers are somewhat limited. In contrast to rivers with significant anthropogenic influences such as the Mississippi, where PO_4^{3-} is the predominant P species (Cai and Guo 2009), >80–90% of total P was measured in the >0.4 μm particulate phase in the upper Yukon River, followed by DOP, leaving PO_4^{3-} mostly below the detection limit (Guo et al. 2004a, b). Similarly, particulate organic P is also the predominant P species in the Lower Yukon River (Guo et al. 2012). In the Chena River, particulate P is the dominant P species, especially during the spring freshet, comprising on average 74 ± 10% of the total P while DIP and DOP comprised 19 ± 9% and 7 ± 4% of the total P, respectively (Cai et al. 2008b; Fig. 11.9). A low abundance of dissolved P species in Arctic rivers is likely derived from the high surface reactivity of P or high values of partition coefficient between dissolved and particulate phases (e.g., Lin and Guo 2016). More studies are needed to better understand the transformation of P between dissolved and particulate, and between inorganic and organic P species during soil leaching and transport from land to waterways.

11.3.3 Dissolved Silica

Silicon (Si) is the second most abundant element in the Earth's crust and a critical nutrient for diatoms in aquatic environments (De La Rocha et al. 1998), in addition to being essential to plant productivity and C cycling (Cornelis et al. 2011). Dissolved Si (DSi) exists in river waters as a result of weathering of Si-containing solid phases. In some Arctic rivers, dissolved silica responds differently than other solutes to permafrost dynamics in Arctic river systems. For example, Guo et al. (2004a, b) showed that thawing of the active layer and thus leaching of deeper soil horizon and riverbank erosion gave rise to higher orthosilicic acid ($Si(OH)_4$) and DIC but lower DOC, DOP, and PO_4^{3-} concentrations. Controls on DSi and nutrient exports (when normalized to watershed size) are also different across constituents. For instance, DSi fluxes are primarily governed by latitude (or temperature) and chemical weathering, whereas both N and P fluxes are regulated largely by

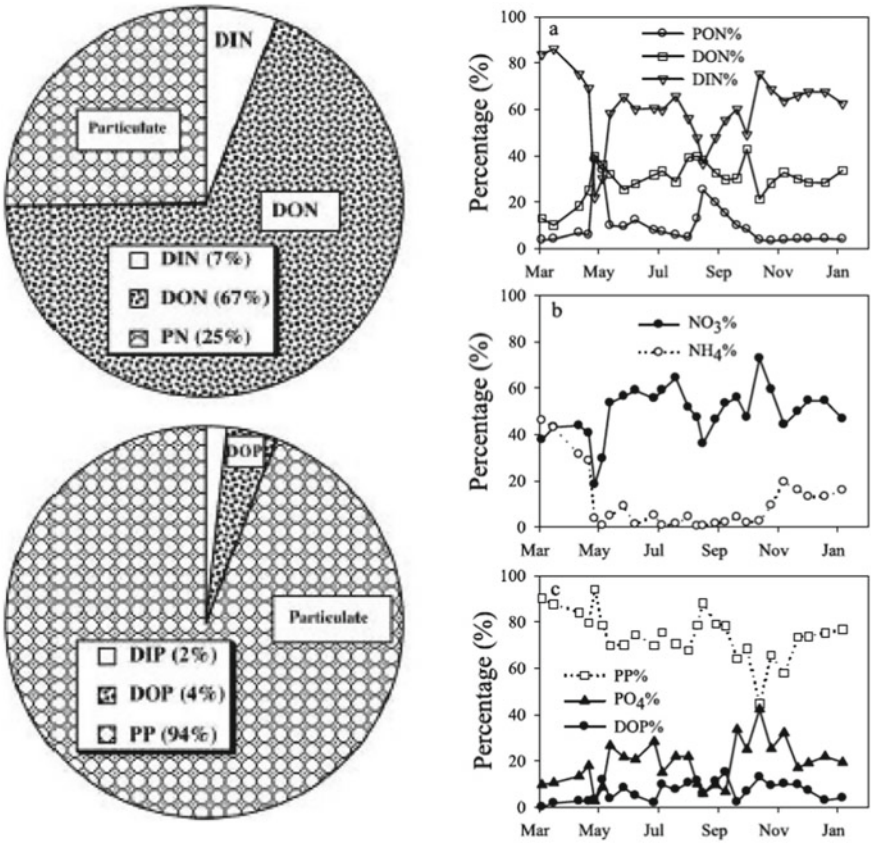

Fig. 11.9 Examples of chemical speciation of N and P in the upper Yukon River (left, from Guo et al. 2004a, b) and Chena River (right panel; from Cai et al. 2008b)

anthropogenic influences or human disturbances (Guo et al. 2004a, b). In comparison with DOC and DIC, the concentration of DSi have been shown to be negatively correlated with DOC concentration, but positively correlated to conductivity and DIC, indicating that $Si(OH)_4$ had a similar source function as DIC but different from DOC and other nutrients, especially during the snowmelt and early ice opening in the Yukon River Basin (Guo et al. 2004a, b).

DSi, as a proxy for silicate mineral weathering, can be used to identify the relative sources of major ions and trace metals in watersheds. As the seasonal thaw expands downward in a given summer thaw season the deeper thawed soils are increasingly comprised of a material that is only exposed to chemical or physical weathering for months or even days per year (Keller et al. 2007, 2010; Douglas et al. 2013; Barker et al. 2014; Fig. 11.10). At the local scale, this is also associated with an oxidation/reduction front that moves downward into the thawed soil

horizon over time. This oxidation/reduction front has major ramifications for the fate and transport of trace elements and nutrients in permafrost watersheds because solubility is often controlled largely by oxidation state and pH (Kimbrough et al. 1999; Barker et al. 2014). Silicate minerals can also be exposed to weathering when the thaw front reaches formerly frozen permafrost soil mineral horizons, leading to the direct release of DSi species into soil solution and local surface waters. Any future expanse of the active layer and degradation of permafrost is expected to impact concentrations of DSi in Arctic river systems (Guo et al. 2004a, b; Holmes et al. 2012; Pokrovsky et al. 2013).

Element cycling in the Arctic is expected to change as a result of increasing air temperatures (Alfredsson et al. 2016) through the expanse of the active layer, degradation of permafrost, and altering of vegetation and snow cover (Tape et al. 2006; Pokrovsky et al. 2013; Vaughan 2013). These changes will likely yield increased concentrations of dissolved Si in Arctic surface waters and the enrichment of the light Si stable isotope (Pokrovsky et al. 2013). Eventually, the formation of new wetlands and expansion of existing wetlands is expected to occur with increasing air temperatures, which have been shown to increase biological fixation and reduce the export of DSi (Sannel and Kuhry 2011). Any decrease in the amount of DSi that is transported to the Arctic Ocean as a result of riverine export will

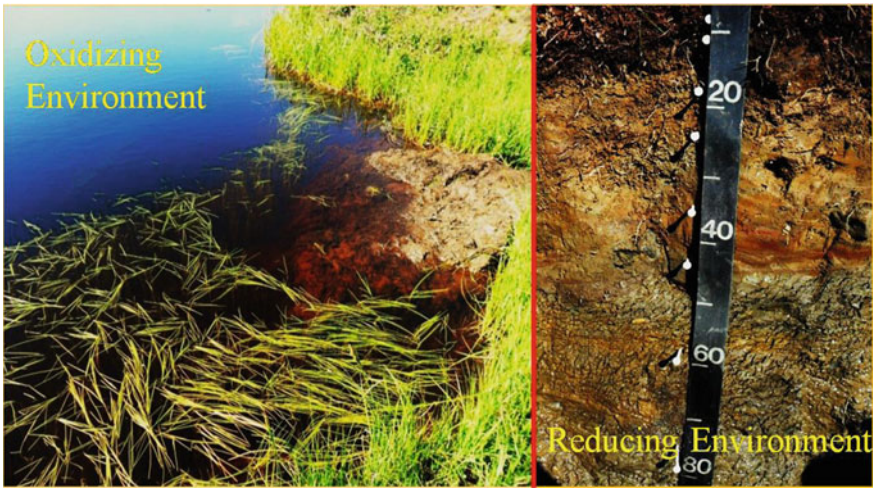

Fig. 11.10 Photographs identifying oxidation and reduction zones in permafrost in the Imnavait Creek watershed north of the Brooks Range in the Alaskan Arctic. Left: the edge of a tundra pond where surface conditions are oxidizing but anaerobic, low pH, and photochemically limited reducing conditions are likely to present at the base of the water column and in the pond sediments. Right: a cross section of a pit excavated in mid-summer with a jackhammer. The seasonal thaw at this time was roughly 45 cm. Note the zone of oxidized Fe just above the seasonal thaw line. Also, note the reduced Fe (grey and gleyed) from 50 to 80 cm depth. This is likely active layer soils that were frozen at the time of the picture that denote a reducing environment. Photos by A. J. Barker

likely result in disturbances to marine biological life and C cycling (Alfredsson et al. 2016). Therefore, the effect of climate change on Arctic terrestrial systems with respect to DSi transport is complex and may yield varying feedback responses.

11.3.4 Trace Metals

Metals comprise a major fraction of soil, surface water, and sediment on Earth and play a significant role in hydro-biogeochemical reactions in the environment. In rivers, metals partition between phases and the fate, transport, mobility, and speciation of metals are controlled by a variety of site-specific environmental parameters, predominantly pH, oxidation state, temperature, soil moisture, hydraulic conductivity, soil type, dissolved oxygen, presence of organic materials/clay minerals, wind, and the presence/concentrations of other competing elements (Loretta and Li 2001; Knechtenhofer et al. 2003; Dinis and Fiúza 2006; Pachana et al. 2010; Liao et al. 2017). A summary of key biogeochemical weathering processes and their associated impact on watersheds is summarized in Table 11.1. In Arctic ecosystems, there are additional landscape-scale controls on the reaction chemistry of metals in rivers (e.g., extreme temperature variations, varying oxidation–reduction conditions seasonally in the subsurface (Fig. 11.10), and the presence of permafrost and seasonally thawed surface soils).

Increasing air temperatures, permafrost thaw, and projected shifting of permafrost boundaries have the potential to affect the fate and transport of metals to surface waters as a result of the unique chemical reactions that occur in the subsurface. Understanding metal reactions directly at the permafrost-active layer boundary can be complicated because there often exist sharp redox transitions,

Table 11.1 Major biogeochemical weathering processes are identified with associated landscape-scale watershed implications. The multiple processes act in concert but are largely seasonally, spatially, and temporally independent of one another

Biogeochemical weathering processes	Implications to watershed
Oxidation/reduction	• Directly affects metal(loid) mobility/toxicity • Redox gradients often present in the subsurface (permafrost-active layer boundary)
Precipitation/dissolution	• Acts as a control on species activity in solution
Adsorption/desorption	• Contributes to fate and transport of species in surface waters • Soil organic matter often coats mineral surfaces in watersheds • Integral to heterogeneous surface reactions
Complexation	• Drives formation of metal ligand complexes • Important for nutrient availability
Microbial activity	• Often consumes or produces CO_2 • Contributes to a variety of element cycles (C, N, O, P, Fe, Mn, etc.) • Primary driver of organic matter decomposition

surface charge gradients, and phase changes (liquid/ice). In the near-surface environment, metals (particularly Fe and Mn) can have multiple oxidation states and thus act as electron donors or acceptors depending on local geochemical conditions. This can impact microbial communities and C speciation/cycling but C cycle processes can, in turn, control metals fate and transport (Pokrovsky and Schott 2002; Page et al. 2013; Stolpe et al. 2013; Salvadó et al. 2015; Emerson et al. 2015; Trusiak et al. 2018). Additionally, seasonal changes and annual freeze–thaw cycles inherent to Arctic freshwater processes influences metal transport to surface waters (Barker et al. 2014; Pokrovsky et al. 2016) and metal cycling in Arctic thaw ponds (Loiko et al. 2017; Pokrovsky et al. 2018; Raudina et al. 2018). As such, the chemical environment of metals in Arctic rivers tends to be highly heterogeneous, dependent on a variety of site-specific factors, and constantly undergoing a transformation. In an attempt to decrease the complexities of measuring permafrost-active layer dynamics, metals (e.g., strontium (Sr), Fe, Mn, and Al) have been employed as geochemical tracers to infer changes within Arctic watersheds and scale to the landscape watershed scale (Rember and Trefry 2004; Keller et al. 2010; Barker et al. 2014; Lehn et al. 2017).

Riverine sediment environments are a unique chemical setting for trace metal studies, particularly in Arctic ecosystems. Riverine sediments are composed of fine-grained materials that offer excellent surface capacity for metals to chemically and physically sorb or bind, including clay minerals (Ilgen and Trainor 2011; Cai et al. 2014), colloids (Pachana et al. 2010), organic matter (humic and fulvic acids; Sklodowski et al. 2006; Clemens and Ma 2016), Fe oxides (Yin et al. 2016), and Mn oxides (Gunawardana et al. 2015). Unlike surface water and soil systems, sediment environments tend to be more reducing and contain lesser amounts of dissolved oxygen (Morford and Emerson 1999). As a result, metal speciation, mobility, and accumulation are affected by deposition, burial, interaction, and re-suspension in aquatic sediment systems. In particular, metal(loid)s have been shown to accumulate in reducing environments (Kimbrough et al. 1999; Barker et al. 2014; Ilgen et al. 2014) and sediments have been shown to stabilize reduced metals (Miao et al. 2006). Mobilization of sediment as a result of natural disruption events (i.e., snowmelt, wind, rain events, increased turbidity), can result in the transport of metals to the water column and subsequent migration downstream (Kaplan et al. 1995; Pachana et al. 2010). As a result, riverine fate and transport of metals are often controlled by sediment acting as a source, a sink, and a reaction surface for environmental systems. This can have both positive and negative effects on Arctic ecosystems since certain metals (e.g., copper, chromium, and zinc) provide essential nutrients for in-country foods (Horowitz and Elrick 1987; Kabata-Pendias 2010), while others (i.e., mercury (Hg) and cadmium) are toxic even in trace amounts (Schuster et al. 2018). Within the context of Arctic ecosystem processes outlined above, we discuss the role and response of metals in Arctic C cycle processes. We focus on Fe, Sr, uranium (U), and Hg because they represent a ubiquitous element in earth's crust (Fe), a tracer used to distinguish between silicate and carbonate weathering reactions in soils (Sr), a long-lived radioactive element (U), and a toxic metal of concern because it bioaccumulates in the environment (Hg).

11.3.4.1 Iron and the Arctic Carbon Cycle

Fe is the most abundant element on Earth and the fourth most abundant element in the Earth's crust, by mass. As such, Fe has significant importance to life and plays an integral role in biogeochemical reactions. Fe exists in multiple valence states, ranging from -2 to +6, but in the near-surface, it is found primarily as divalent Fe (Fe(II)) or trivalent Fe ((Fe(III)). Fe(II) and Fe(III) readily form complexes with other species, which can act as catalysts in biogeochemical reactions, sinks for organic C, and facilitate electron transfer (Williams and Scherer 2004; Lalonde et al. 2012; Frey and Reed 2012; Page et al. 2013; Trusiak et al. 2018). Fe redox cycling is complex and is intricately tied to the presence of organic C and microbial activity and can vary even within one watershed since reduced Fe tends to accumulate at the permafrost-active layer boundary and oxidized Fe found generally in near-surface environments (Barker et al. 2014; Fig. 11.10).

In the Arctic, the C cycle is a significantly important process due to the abundance of C stored currently frozen in permafrost (Tarnocai et al. 2009; Hugelius et al. 2014) and the risk of CO_2 and CH_4 release if air temperatures continue to increase and permafrost thaws and degrades (Vincent et al. 2017). Fe plays a role in the overall Arctic C cycle, contributing both positive and negative permafrost-C feedbacks to the climate. Fe acts as a sink for organic C due to its reactivity and large surface area (Salvadó et al. 2015), thereby stabilizing C in soil and decreasing the potential for degradation and release of CO_2 (Lalonde et al. 2012; Yang et al. 2017). However, various microbial communities active in Arctic soil systems have been shown to use Fe(II) or Fe(III) as energy sources depending on the community composition (Emerson et al. 2015), leading to substantial positive feedback to climate change by the direct release of CO_2 and potentially CH_4 into the atmosphere (Yang et al. 2017). Additionally, two recent studies have focused on the chemical oxidation of DOC mediated by reduced Fe in anoxic soil waters in the Arctic through the production of hydroxyl radical (•OH), which is a highly reactive oxidant (Page et al. 2013; Trusiak et al. 2018). Therefore, the presence of Fe in soils and soil waters contributes to both the production and consumption of CO_2. A simplified schematic showing the overall role of Fe in the Arctic C cycle is shown in Fig. 11.11. Fe can act as a sink for organic C, energy source for microbial reduction and oxidation, and contribute to the formation of •OH thereby oxidizing organic C. Investigating Fe redox cycling is critical to understanding the fate of C in the Arctic, particularly with projected warming and thawing of permafrost soils.

The chemical speciation of Fe and thus its fate and transport from streams/rivers to the Arctic Ocean are also related to permafrost and C dynamics. Stolpe et al. (2013) have shown that during spring freshet when DOM and Fe abundance is the highest, dissolved Fe is mostly complexed with DOM and present almost exclusively in the form of nanocolloids or the <4 nm size fractions in small Alaska rivers. In contrast, during late summer/early fall when DOM is low in abundance, the molecular size spectra of dissolved Fe show two peaks: one associated with nanocolloids derived from the complexation of Fe with and DOM, and the other with large sized colloids ranging from 10 to 50 nm derived from the formation of Fe oxide/hydroxide which could be removed through coagulation from the

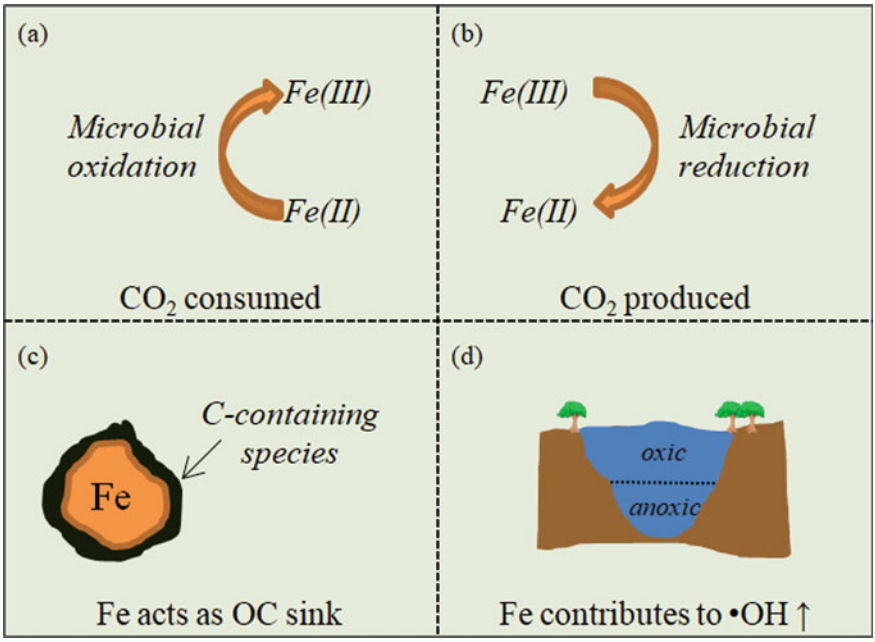

Fig. 11.11 A simplified schematic diagram showing the roles of Fe in the C cycle of Arctic soils and soil pore waters **a** CO_2 is consumed during microbial oxidation of Fe, **b** CO_2 is produced during microbial reduction of Fe, **c** Fe can act as a sink with organic C through precipitation, complexation, and sorption reactions, and **d** reduced Fe plays a role in the formation of hydroxyl radical in anoxic soil waters, which is a highly reactive oxidant for C or metals oxidation

dissolved phase. Similar metal size spectra were also observed for Cr and other trace elements in small Alaska rivers based on the analysis using flow field-flow fraction coupled online with ICP-MS (Stolpe et al. 2013). In addition, Pokrovsky et al (2018) found freeze–thaw cycles of Arctic thaw ponds remove colloidal metals and generate low-molecular weight organic matter in boreal rivers in Siberia.

11.3.4.2 Sr and U Isotopes as Geochemical Tracers

The use of isotopes as environmental tracers for biogeochemical processes in the Arctic has become increasingly popular in recent years to determine trace element dynamics, quantify variations between varied source materials, monitor active layer deepening, and characterize seasonal changes in geochemical processes in watersheds. Since these processes are also the main drivers of C-cycle processes in soils and watersheds isotope studies can be used to infer C cycle processes. Specifically, radiogenic isotopes of Sr (^{87}Sr and ^{86}Sr; Guo et al. 2004b; Bagard et al. 2013; Douglas et al. 2013; Stevenson et al. 2016, 2018; Lehn et al. 2017) and U (^{238}U and ^{234}U) (Koch et al. 2013; Ewing et al. 2015; 2016; Hindshaw et al. 2018) have been applied to understand seasonal geochemical weathering reactions and rates in

permafrost environments. Radiogenic Sr ratios are a function of their source in the near-surface environment resulting from weathering of primary materials and, as such, they are useful for predicting preferential weathering and hydrological flow paths (Stevenson et al. 2016; Keller et al. 2010; Douglas et al. 2013). Conversely, U isotope activity ratios ($^{234}U/^{238}U$) tend to be a function of water residence times (e.g., groundwater versus surface water) and studies have shown that longer water residence times translate to higher $^{234}U/^{238}U$ activity ratios. Permafrost systems can complicate this measurement because uranium isotopic enrichment can also be affected by ice residence time in addition to water residence time (Hindshaw et al. 2018). A study by Ewing et al. (2015) showed that $^{234}U/^{238}U$ ratios were higher for waters sourced from older permafrost thawing compared to younger permafrost. This established U isotope ratios as tracers for identifying the likely sources of soil and organic materials in watersheds.

11.3.4.3 Mercury Bioaccumulation and Release in the Arctic

Hg is a naturally occurring toxic element that is of increasing concern in Arctic ecosystems due to the large stocks of Hg currently stored in the northern permafrost region, and the sensitivity of permafrost Hg to thaw and mobilization (Ci et al. 2018; Schuster et al. 2018). Hg can bioaccumulate in terrestrial and aquatic food webs and has been found in foods across the Arctic region (Jæger et al. 2009). Hg can accumulate in Arctic snow and is present in snowmelt runoff due to the long-range atmospheric transport, oxidation, and subsequent deposition onto the snow surface (Douglas and Sturm 2004; Douglas et al. 2005, 2017; Driscoll et al. 2013; Agnan et al. 2018). The interaction of Hg and organic matter can drive the production of methylmercury (MeHg), which is a neurotoxin that strongly bioaccumulates and biomagnifies in nature (Schartup et al. 2013). MeHg is highly mobile in aquatic systems and is relatively lipid-soluble, making it an ideal species to accumulate in bio (Rice et al. 2014). Since MeHg production, retention, and mobilization are largely controlled by the presence of organic species in soils or water Hg is intimately associated with the C cycle.

Projected future permafrost degradation, particularly the dramatic loss of near-surface permafrost over the next decades (Pastick et al. 2015), will expose soil organic C that is currently bound to Hg and stored frozen. Once exposed, microbial activity can decompose organic matter, releasing CO_2 in the process. Any Hg bound to the soil organic matter is also expected to be released into the environment during permafrost thaw and organic matter liberation (Schuster et al. 2018). Once released, the Hg can interact with both DOM and soil organic matter and form MeHg in watersheds (French et al. 2014). Similar observations in Arctic and sub-Arctic permafrost thaw ponds have already been reported by MacMillan et al. (2015) showing that high MeHg concentrations were correlated with high inputs of organic matter and microbial activity. Organic C affects Hg cycling and bioaccumulation in the environment and permafrost degradation is expected to impact the fate of Hg. However, the magnitude of that impact on the environment remains to be determined and further work is needed to quantify potential human health concerns.

11.4 Conclusions and Knowledge Gaps

Despite the growing body of literature documenting the response of Arctic stream and river biogeochemistry to warming and disturbance, there are still many challenges and uncertainties for the scientific community. In this chapter, we discuss some of these uncertainties and directions for future research, including (1) thermokarst effects (2) changing seasonality, (3) altered watershed hydrology, and (4) timing and magnitude of changes across Arctic landscapes.

The effects of thermokarst and thermal erosional processes on stream and river biogeochemistry represent a critical uncertainty for Arctic researchers. Much of the uncertainty regarding thermokarst is due to the complex, three-dimensional nature of the problem, and the difficulty in predicting the initiation and extent of thermokarst features across the landscape. Whereas many land surface models can now simulate one-dimensional permafrost thaw via active layer thickening, measuring and modeling thermokarst represents a true challenge to the scientific community. Thermokarst can develop across a variety of landscape types and in a variety of modes, including thaw slumps, slope failures, pits, scarps, gullies, and expanding lake margins. Some evidence indicates thermokarst and thermal erosion features may function as a large source of C and nutrients to streams. Other studies have documented that permafrost degradation via thermokarst can enhance riverine fluxes of water, sediment, organic C, nutrients, and trace metals. Still, the persistence and spatial extent of these thermokarst impacts are not clear and require more long-term monitoring and intensive research to better constrain.

As noted above, Arctic streams and rivers exhibit strong seasonal patterns with respect to flows and chemical composition. Under a warming Arctic, changing seasonality represents another key uncertainty that could impact hydrologic and biogeochemical processes in stream and river ecosystems. Evidence indicates many components of northern watersheds are already changing, including the timing and magnitude of snowmelt, the extent of the ice-free season, increase groundwater discharge to surface water (Lamontagne-Halle et al. 2018). In some cases, perennial streams may shift to ephemeral states in response to changing water balance and longer open-water seasons. Tracking the impacts of changing seasonality on river biogeochemical processes will take a considerable, multidisciplinary effort, linking remote sensing, field-based, and modeling approaches.

Changing watershed and subsurface hydrology in Arctic regions represents another key uncertainty and an important area of current and future research. The timing and magnitude of precipitation are likely to change, which may alter runoff to surface water and thawing rates in near-surface soils. Warming and disturbance (wildfire, permafrost thaw) can dramatically alter watershed hydrology and the delivery of water and solutes to stream and river channels. Spatial differences in permafrost characteristics across watersheds, including ground ice content, hydraulic properties, and lithology, all influence the hydrologic and biogeochemical response to warming and thawing. Recent advances in airborne and ground-based geophysical techniques have improved characterizations of subsurface properties in permafrost

landscapes. Groundwater models have also been improved in recent years through the incorporation of freeze–thaw processes. Still, much work is still needed to establish conceptual and quantitative linkages between changing hydrologic conditions, permafrost dynamics, and biogeochemical responses in surface waters.

Predicting the timing and magnitude of change represents yet another key uncertainty and knowledge gap for Arctic river systems. The response of the biogeochemistry of C species, nutrients, and trace elements in Arctic aquatic ecosystems to warming and permafrost thaw should have different extents and time-dependent features, and thus different impacts on ecosystems. In addition, changes in river biogeochemistry are also distinct across Arctic rivers that draining different watershed types (O'Donnell et al. 2016; Lung et al. 2018). Therefore, comprehensive time-series observations in different watersheds across different latitudes are needed to better understand the evolution in C, nutrients, and trace elements biogeochemistry in Arctic rivers in a changing climate. Further, a more process-based understanding of biogeochemical processes that span the terrestrial–aquatic interface will strengthen our understanding of the mechanisms driving change. Large-scale studies of river biogeochemistry and the seasonality of flows and fluxes form the basis for statistical models of the export of DOC, other nutrients, major elements, and trace metals, but for predictions, we need physically based models, and these require an understanding of snow and chemical processes that occur at a much smaller scales.

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Dr. Jonathan O'Donnell is an Ecologist with the National Park Service's Arctic Inventory and Monitoring Network in Anchorage, Alaska. His research focuses on carbon cycling in terrestrial and aquatic ecosystems in Arctic and boreal regions, and how climate and disturbance may alter the fate of carbon. He received his Doctoral and Master's degrees from the Department of Biology & Wildlife at the University of Alaska Fairbanks.

Dr. Thomas A. Douglas is a Senior Scientist and Research Geochemist at the U.S. Army's Cold Regions Research and Engineering Laboratory in Fairbanks, Alaska. He uses geochemical tracers to investigate environmental processes occurring in the snowpack, on sea ice, and in cold regions soil and water. Many of his current projects are focused on predicting the response of permafrost to climate warming and the biogeochemical processes occurring in permafrost soils. This work combines remote sensing, geophysics, extensive site measurements, coring and laboratory measurements, and geospatial analyses to link terrain properties with soil and vegetation characteristics. He holds a Master's degree in Geology from the University of Alaska Fairbanks and a Ph.D. in Earth Sciences from Dartmouth College and is an Affiliate Faculty Member in the Department of Chemistry and Biochemistry at the University of Alaska Fairbanks.

Dr. Amanda Barker is a Research Chemist in the Biogeochemical Sciences Branch at the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) in Fairbanks, Alaska, USA. Her research interests include fate and transport of elements in the environment, permafrost-active layer dynamics, and analytical tools for bulk- and micro-scale geochemical characterization. He received her Doctoral degree in Environmental Chemistry at the University of Alaska Fairbanks.

Dr. Laodong Guo is a Professor in the School of Freshwater Sciences at the University of Wisconsin Milwaukee. His major research focus is on the biogeochemical cycling of carbon, nutrients (N, P, and Si), and trace elements (also radionuclides) in aquatic environments including high-latitude rivers. He received his Doctoral degree in Chemical Oceanography at Texas A&M University, College Station. Before coming to UWM, he was a faculty member at the University of Southern Mississippi (2005–2012) and University of Alaska Fairbanks (2000–2005).