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Geochemistry of west Siberian streams and their potential response to permafrost degradation

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[1] Measurements of solute concentrations from previously unstudied watersheds throughout west Siberia suggest that warming and permafrost degradation will likely amplify the transport of dissolved solids to the Kara Sea and adjacent Arctic Ocean. We present concentrations of Ca^{2+}, K^+, Mg^{2+}, Na^+, Si, Cl^-, SO_4^{2-}, HCO_3^-, inferred alkalinity, and total inorganic solutes (TIS) from 94 streams and rivers within the Ob'-Irtysh, Nadym, and Pur river drainage basins. The sampled sites span $\sim 10^6$ km^2, a large climatic gradient ($\sim$55°–68°N), and 39 permafrost-influenced and 55 permafrost-free watersheds. The solute composition of our samples is strongly influenced by carbonate mineral dissolution. Furthermore, our results show that TIS concentrations of waters in permafrost-free watersheds average $\sim$289 mg L^{-1}, in contrast to only $\sim$48 mg L^{-1} in permafrost-influenced watersheds. This sixfold difference likely occurs because permafrost forms a confining barrier that inhibits the infiltration of surface water through deep mineral horizons and restricts mineral-rich subpermafrost groundwater from reaching surface water pathways. A principal components analysis–based end-member mixing analysis supports the premise that mineral-rich groundwater is the primary source of solutes to streams in permafrost-free watersheds, whereas mineral-poor peat surface water is the primary source in permafrost-influenced watersheds. With climate warming and subsequent permafrost thaw this region may transition from a surface water–dominated system to a groundwater-dominated system. Additionally, should permafrost in the region completely disappear, we estimate that TIS export from the west Siberian region to the Kara Sea would increase by $\sim$59% (from its current value of $\sim$46 Tg yr^{-1} to $\sim$73 Tg yr^{-1}). Such an increase in dissolved solid delivery to the Kara Sea could have important implications for future biological productivity in arctic Eurasian shelf waters and the Arctic Ocean basin interior.

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1. Introduction

[2] The Arctic is particularly sensitive to observed and projected shifts in climate and is a harbinger of global change, as average annual arctic temperatures have increased at almost twice the global rate over recent decades and are predicted to increase by an additional 4°–7°C over the next century [e.g., *Arctic Climate Impact Assessment*, 2004]. Continued warming will likely have profound consequences for many systems throughout the region, including permafrost extent, river discharge and stream biogeochemistry [e.g., *Anisimov and Nelson*, 1996; *Peterson et al.*, 2002; *Frey and Smith*, 2005]. Each year, rivers transport $\sim$3300 km^3 of freshwater to the Arctic Ocean, of which $\sim$35% is derived from the Ob' and Yenisey rivers of west Siberia alone [*Aagaard and Carmack*, 1989]. This freshwater delivery exerts considerable influence on Arctic Ocean and global ocean circulation through impacts on North Atlantic Deep Water (NADW) formation, salinity distribution and sea ice formation [*Rahmstorf*, 1995; *Vörösmarty et al.*, 2001]. Furthermore, the river transport of solutes and nutrients to arctic Eurasian shelves and the Arctic Ocean basin interior heavily influences biological production [*Dittmar and Kattner*, 2003, and references therein] and consequently, the drawdown of atmospheric CO_2.

[3] Despite west Siberia's large geographic size ($\sim 2.6 \times 10^6$ km^2) and global significance of potential hydrological change, little is known about stream and river geochemistry in the region. General discussion of the inorganic character of arctic Eurasian rivers is presented by *Telang et al.* [1991] and *Gordeev et al.* [1996]; however, sampling sites are limited to the mouths of major rivers. Similarly, several studies investigating major elements, trace metals, radionuclides, and pesticides confine sampling points either offshore in the Kara Sea or in the main stems of the Ob'-Irtysh or Yenisey rivers [e.g., *Dai and Martin*, 1995; *Bobrovitskaya et al.*, 1997; *Moran and Woods*, 1997;

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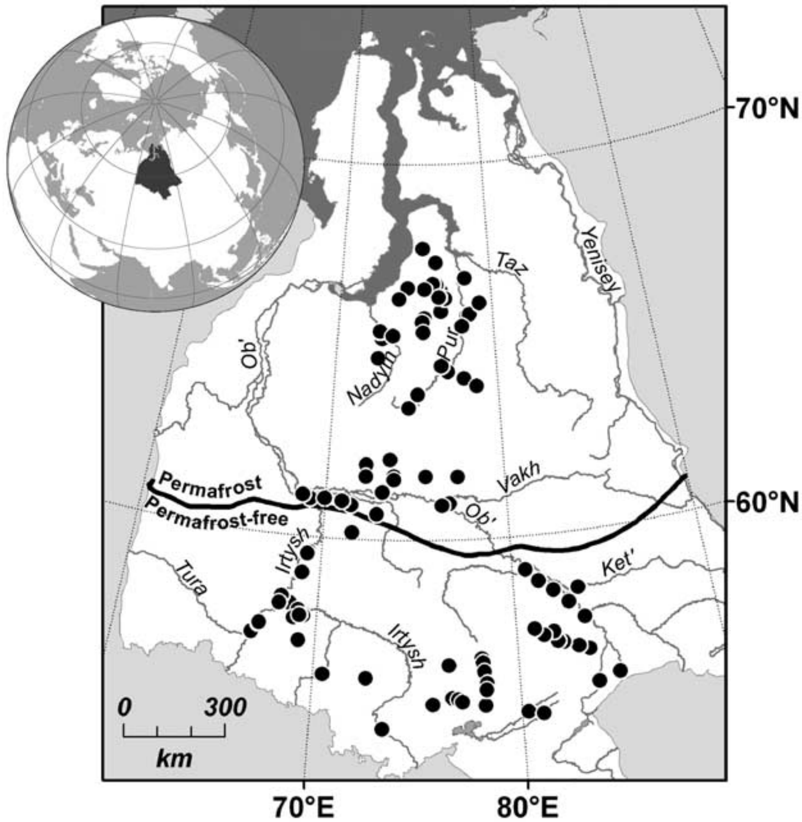

Figure 1. West Siberia and the locations of 94 water samples collected throughout the region. The permafrost limit, based on *Brown et al.* [1997, 1998], is also demarcated.

Cochran et al., 2000; *Alexeeva et al.*, 2001; *Krishnamurthy et al.*, 2001; *Paluszkiewicz et al.*, 2001]. While the solute composition of main stem surface waters in west Siberia provide a general measure of the spatially averaged environmental conditions for the region, additional sampling points from smaller watersheds throughout the region are required to understand solute sources, weathering reactions and potential anthropogenic contamination with higher spatial resolution. This has been accomplished in east Siberia, with extensive sampling of tributaries yielding a thorough assessment of riverine chemistry and weathering environments [e.g., *Gordeev and Sidorov*, 1993; *Martin et al.*, 1993; *Guieu et al.*, 1996; *Huh et al.*, 1998a, 1998b; *Huh and Edmond*, 1999]. Comparison of these results with those in west Siberia lends valuable insight into two potentially dissimilar geochemical regimes at similar latitudes. Most importantly, given the hydrological significance of west Siberian rivers to Eurasian shelf waters and the Arctic Ocean, establishing a comprehensive understanding of the region's current riverine chemistry is critical for assessing its potential role in arctic and global change.

[4] The primary goals of this study are twofold. First, we present an unprecedented comprehensive assessment of the inorganic water chemistry of west Siberian streams and rivers, sufficiently robust to determine regional solute sources and potential anthropogenic contamination in watersheds throughout the region. Second, because the sampled watersheds span a large climatic and permafrost gradient, we seize a unique opportunity to "substitute space for time" in order to predict how inorganic river water chemistry may change under scenarios of continued climate warming and permafrost degradation. These goals are achieved through presentation of Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}, Si, Cl^{-}, SO_4^{2-}, HCO_3^{-}, inferred alkalinity (Alk_{inf}) and total inorganic solutes (TIS) concentrations from 94 streams and rivers located throughout west Siberia (Figure 1). From these data, we develop and utilize an EMMA model that incorporates key solutes to investigate the variability of source waters contributing to streamflow throughout the region. Further, we derive a regional hydrological model in order to calculate an annual flux of solutes from west Siberia. On the basis of these solute fluxes, we can predict the influence that warming and permafrost degradation may have on the river transport of dissolved solids to the Kara Sea shelf waters and adjacent Arctic Ocean.

2. Study Site

[5] West Siberia is the world's largest intracratonic basin [*Peterson and Clarke*, 1991], bounded by the Ural Mountains to the west, the Yenisey and Taymyr ranges to the east, and the Altay-Sayan and Kazakhstan shields to the south. The underlying basement consists of Precambrian and Paleozoic fold systems that include regions of partly metamorphosed Paleozoic carbonate and clastic sediments as well as Paleozoic intrusive rocks [*Energy Information Administration* (*EIA*), 1997]. A 3–10 km thick basin cover of Mesozoic-Cenozoic clastic and sedimentary rocks of marine, nearshore marine, and continental origin lies over these basement rocks [*EIA*, 1997; *Ulmishek*, 2003], thinning out completely toward the basin boundaries. These basin sediments were deposited during at least three major

transgression-regression cycles in an extensive, shallow, inland sea and have experienced little tectonic disturbance since deposition [*Peterson and Clarke*, 1991]. In general, the basin sediments are dominated by sandstone and shale, although limestone and salt diapirs are also present [*Peterson and Clarke*, 1991]. The large basin size and stable depositional history of slow subsidence and basin filling combine to make the West Siberian Basin one of the largest oil and natural gas producing regions in the world [*Peterson and Clarke*, 1991]. As a result of hydrocarbon extraction, surface water and groundwater are sometimes contaminated with oilfield brines (the connate water removed from oil productive geologic formations), which are highly concentrated in dissolved salts [e.g., *Collins*, 1975; *Alexeev et al.*, 2004]. Overlying the basin cover, Quaternary deposits are generally thin (often consisting of sands and other aeolian and fluvial deposits) [*Kremenetski et al.*, 2003] and Tertiary and Cretaceous sediments are commonly exposed in river valleys [*Bleuten and Lapshina*, 2001].

[6] West Siberia occupies $\sim$2.6 $\times$ 10^6 km^2 and owing to its uniformly low topographic relief, is considered the largest flat area on Earth. Cool temperatures, poor drainage and waterlogged conditions have enabled accumulation of $\sim$70.2 Pg of carbon in the region's extensive peatlands over the last $\sim$11,000 years [*Kremenetski et al.*, 2003; *Sheng et al.*, 2004; *Smith et al.*, 2004]. A recent and comprehensive inventory now confirms that the region contains nearly 600,000 km^2 of peatlands, representing a Holocene carbon sink of global significance [*Sheng et al.*, 2004; *Smith et al.*, 2004]. More than half of the region is influenced by permafrost ($\sim$1.4 $\times$ 10^6 km^2 of its $\sim$2.6 $\times$ 10^6 km^2 total land area), with 15% of the region covered with continuous permafrost (northward of $\sim$66°N) and 39% of the region covered with discontinuous, sporadic or isolated patches of permafrost ($\sim$61°–66°N) (Figure 1). The presence of permafrost and the low hydraulic conductivity of peat strongly influence the hydrology of the region, limiting infiltration and producing perched water tables near the land surface. This in turn promotes the existence of tens of thousands of shallow lakes and wetlands throughout the region [*Smith et al.*, 2005]. The two largest rivers draining west Siberia are the Ob' and Yenisey (Figure 1). The $\sim$2,990,000 km^2 watershed area of the Ob' River discharges $\sim$404 km^3 each year and the $\sim$2,580,000 km^2 watershed area of the Yenisey River discharges $\sim$630 km^3 each year [*Kimstach et al.*, 1998].

3. Data and Methods

3.1. Stream and River Sampling

[7] Ninety-four watersheds were sampled during three field campaigns to west Siberia during late summer (mid-July through late August) of 1999, 2000 and 2001 (Figure 1 and Table 1). These combined samples constitute an unprecedented, geographically extensive and temporally synoptic data set for west Siberia that spans $\sim$55°–68°N in latitude and covers $\sim$$10^6$ km^2 in land area Water samples were taken from a broad array of watersheds, with drainage basin areas ranging from $\sim$19 km^2 to $\sim$2.6 $\times$ 10^6 km^2. Furthermore, the sampled sites include 39 permafrost-influenced watersheds and 55 permafrost-free watersheds. This differentiation is made using the southern limit of permafrost as mapped by *Brown et al.* [1997, 1998] and occurs at a latitude of $\sim$61°N (Figure 1).

[8] Water samples were filtered in the field through Osmonics® 0.22 micron mixed-ester membranes and stored in acid-washed high-density polyethylene bottles at 4°C until analysis. Two samples were taken from each location. The first (for analysis of dissolved cations) was acidified with double distilled concentrated nitric acid. The second (for analysis of dissolved anions) was not acidified and was collected without head space to minimize degassing. Ca^{2+}, K^+, Mg^{2+}, Na^+ and Si concentrations were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) at the Cornell University Nutrient and Elemental Analysis Laboratory in the Department of Horticulture. Cl^- and SO_4^{2-} concentrations were measured by ion chromatography (IC) in the Department of Ecology and Systematics at Cornell University. All analyses had accuracy and precision within ±5%. Values of pH were measured in the field using an Oyster® portable pH meter. Inferred alkalinity (Alk_{inf}) was calculated by charge balance. Owing to the high concentrations of dissolved organic carbon (DOC) in these waters [*Frey and Smith*, 2005], we assumed Alk_{inf} to be composed of both carbonate alkalinity and organic anions. As a first approximation, we estimated the organic anion concentration of each sample from its pH and DOC concentration [*Thurman*, 1985]. We attributed the remainder of Alk_{inf} to carbonate alkalinity, which we assumed to be HCO_3^- based on the circumneutrality of the waters (Table 1). We then defined total inorganic solutes (TIS) as the sum of eight solutes (Ca^{2+} + K^+ + Mg^{2+} + Na^+ + Si + Cl^- + HCO_3^- + SO_4^{2-}).

3.2. End-Member Mixing Analysis (EMMA)

[9] A principal components analysis (PCA)-based EMMA, following *Christophersen and Hooper* [1992], was used to determine the proportions of end-members solutions contributing to streamflow for each of our samples. PCA-based EMMA models have been used primarily at a single sample site to identify temporal patterns in end-member contribution to streamflow by separating discharge components of hydrographs that span noteworthy events (e.g., storms, freshet) [*Burns et al.*, 2001; *McHale et al.*, 2002; *Liu et al.*, 2004]. In contrast, for this study we developed a PCA-based EMMA model to identify synoptic spatial patterns in end-member contribution to streams located throughout the west Siberian region. Although we sampled the suite of stream waters during three summers, we consider the assemblage of samples as synoptic because they were all sampled at similar points in their respective hydrographs.

[10] Three end-members were assumed to contribute to streamflow in the 94 sampled watersheds: Peat surface water, groundwater and oilfield brine. Solute concentrations for the three end-members were determined as follows. The peat surface water end-member was calculated as the average of 40 peat surface water samples from sites distributed throughout the region, collected by depressing the peat surface, and filtered and analyzed for solute concentrations just as for our stream samples (as described in section 3.1.). The stream sample with the highest dissolved solids concentration (KF-01-50; Table 1), but without oilfield brine solute indicators (e.g., high concentrations of Cl^-), was used as a first-order approximation of the groundwater end-

Table 1. Solute Concentrations and Watershed Characteristics for the 94 Sample Sites

Sample	River	Date	Latitude, °N	Longitude, °E	Watershed Area, km^2	Discharge, km^3 yr^{-1}	pH	Ca^{2+}, μmol L^{-1}	K^+, μmol L^{-1}	Mg^{2+}, μmol L^{-1}	Na^+, μmol L^{-1}	Si, μmol L^{-1}	Cl^-, μmol L^{-1}	HCO_3^-, μmol L^{-1}	SO_4^{2-}, μmol L^{-1}	Alk_{inf}, μeq L^{-1}	TIS Milligrams per Liter	TIS 10^9 Grams per Year	TIS Grams per Square Meter per Year
Permafrost Influenced																			
KF-99-13	Pyaku-Pur	7/22/1999	63.50	74.60	4336	0.98	6.22	97.8	0.0	59.1	84.1	176.1	15.4	271.7	4.7	373.4	29.8	29.2	6.7
KF-99-2	Trom-Yegan	7/24/1999	62.12	73.55	8311	2.55	6.44	106.9	0.0	52.9	364.7	53.6	345.1	232.6	2.3	253.2	19.5	49.8	6.0
KF-99-17	Mokovaya	7/24/1999	61.67	73.78	530	0.13	6.52	68.1	0.0	38.7	74.7	125.1	31.7	149.4	3.7	335.4	42.1	5.6	10.5
KF-99-16	Unknown	7/25/1999	61.97	72.18	95	0.02	5.99	63.9	9.4	31.7	912.6	49.2	475.9	25.1	14.7	126.8	8.0	0.2	1.6
KF-99-18	Pym	7/25/1999	61.65	72.19	10761	2.83	6.18	26.2	0.0	17.0	48.8	124.4	10.2	506.0	0.7	616.5	75.2	213.0	19.8
KF-99-6	Mokovaya	7/26/1999	61.58	73.78	621	0.16	6.70	127.2	0.0	64.9	425.7	98.9	384.0	319.1	3.5	419.4	52.7	8.2	13.2
KF-99-43	Gun Yegan	8/15/1999	61.65	77.38	56	0.01	6.65	184.6	0.0	96.0	263.2	84.4	285.1	355.7	4.8	531.8	50.4	0.4	8.0
KF-99-30	Agan	8/17/1999	61.68	75.58	28210	7.81	6.74	143.6	0.0	80.5	172.4	155.9	136.8	402.7	3.6	477.5	45.8	357.8	12.7
KF-00-2	Unknown	7/15/2000	66.46	76.68	19	0.00	5.80	33.3	0.0	25.4	81.4	36.8	60.5	0.0	7.5	149.4	7.7	0.0	0.7
KF-00-5	Ngarka-Tabyakha	7/17/2000	66.64	76.68	2671	0.29	6.52	35.2	0.0	31.9	69.3	159.5	12.6	0.0	26.7	144.9	11.3	3.3	1.2
KF-00-6	Tabyakha	7/17/2000	66.81	76.40	1835	0.17	6.38	28.5	0.0	25.1	74.6	135.8	40.2	0.0	20.3	107.8	10.7	1.8	1.0
KF-00-9	Eva-Yakha	7/18/2000	66.09	76.66	1385	0.16	6.15	39.4	0.0	28.1	92.1	126.2	43.1	0.0	46.2	101.2	13.9	2.2	1.6
KF-00-12	Pur	7/21/2000	66.97	78.34	93263	28.66	6.98	92.3	11.1	95.9	284.6	209.4	161.2	245.7	15.5	372.0	32.1	919.2	9.9
KF-00-13	Malaya-Khadyr-Yakha	7/21/2000	65.98	78.36	816	0.11	6.88	98.4	0.0	79.0	92.6	197.0	86.3	384.8	5.2	497.3	49.6	5.6	6.9
KF-00-16	Seyakha	7/23/2000	65.92	75.57	251	0.03	6.41	69.0	0.0	63.1	81.2	196.6	8.7	211.0	20.6	309.7	26.8	0.7	2.8
KF-00-17	Khadetta	7/24/2000	67.41	76.40	4933	0.38	6.65	34.1	0.0	32.8	78.8	92.2	35.4	89.2	18.7	153.3	15.1	5.7	1.2
KF-00-20	Seyakha	7/25/2000	65.81	75.44	51	0.00	6.15	34.5	0.0	31.9	107.6	75.6	11.3	4.7	13.0	214.5	8.7	0.0	0.8
KF-00-22	Unknown	7/26/2000	66.44	76.96	189	0.02	6.34	17.3	0.0	11.6	32.0	101.3	9.9	9.6	14.9	52.4	6.9	0.1	0.7
KF-00-23	Malaya-Khadyr-Yakha	7/27/2000	65.99	78.54	743	0.10	7.42	191.7	20.4	218.0	558.9	345.6	384.3	899.0	25.6	987.2	107.3	11.0	14.8
KF-00-26	Unknown	7/29/2000	66.83	76.17	102	0.01	6.37	146.3	12.6	182.8	485.9	227.3	260.4	77.1	18.4	141.1	18.4	0.1	1.3
KF-00-31	Ngarka-Khadyta-Yakha	7/29/2000	66.29	79.25	568	0.08	7.32	45.5	0.0	38.0	79.7	146.6	72.2	800.3	25.8	892.4	88.2	7.0	12.3
KF-00-33	Unknown	7/30/2000	66.48	76.57	219	0.02	6.67	38.9	0.0	33.9	51.3	248.2	16.8	70.5	37.1	118.9	19.0	0.4	1.9
KF-00-41	Ngarka-Poyolova-Yakha	7/31/2000	67.78	75.51	322	0.02	5.03	94.4	0.0	76.7	58.6	54.1	31.3	252.9	24.9	344.0	27.4	0.6	1.7
KF-00-46	Yagenetta	8/3/2000	65.54	75.50	63	0.01	5.85	98.5	7.8	85.6	94.1	385.3	13.5	387.0	35.8	405.4	46.9	0.3	4.4
KF-00-47	Yamsovey	8/3/2000	66.70	75.59	53	0.00	6.22	108.2	12.1	95.5	157.8	322.2	11.8	482.1	39.5	505.9	53.4	0.2	3.9
KF-00-50	Unknown	8/4/2000	65.69	78.01	4204	0.57	6.10	76.6	11.3	69.0	79.6	239.2	26.3	308.0	14.9	351.8	34.9	19.7	4.7
KF-00-56	Kheygi Yakha	8/10/2000	65.36	72.86	8127	1.32	6.24	124.5	17.9	138.5	1104.0	302.6	27.1	1585.0	11.1	1624.0	141.7	186.4	22.9
KF-00-59	Levaya Khetta	8/13/2000	64.83	72.64	8632	1.59	7.12	84.7	2.7	75.7	106.8	314.1	11.9	397.1	8.7	435.2	42.1	66.9	7.7
KF-00-67	Nadym	8/17/2000	65.55	72.72	46254	14.72	5.79	79.9	4.9	67.7	109.8	230.2	42.9	337.5	8.1	381.2	36.9	543.4	11.7
KF-00-68	Pravaya Khetta	8/17/2000	65.44	73.55	4344	0.54	6.32	111.9	13.0	102.8	105.0	313.6	27.3	454.9	28.4	481.0	50.2	26.9	6.2
KF-00-71	Srednyaya Khadyta	8/18/2000	66.73	74.48	85	0.01	6.30	60.6	0.0	50.9	17.0	130.7	24.6	49.7	20.9	201.0	13.6	0.1	1.0
KF-00-74	Nyda	8/20/2000	66.43	73.91	4398	0.47	7.08	92.7	9.4	85.1	137.5	272.6	29.1	376.1	41.6	400.2	45.0	21.0	4.8
KF-00-77	Pyaku-Pur	8/23/2000	64.47	77.02	24011	5.62	6.87	102.3	3.2	77.0	320.7	258.7	130.4	521.6	5.7	568.1	57.7	324.4	13.5

Table 1. (continued)

Sample	River	Date	Latitude, °N	Longitude, °E	Watershed Area, km^2	Discharge, km^3 yr^{-1}	pH	Ca^{2+}, $\mu mol\ L^{-1}$	K^+, $\mu mol\ L^{-1}$	Mg^{2+}, $\mu mol\ L^{-1}$	Na^+, $\mu mol\ L^{-1}$	Si, $\mu mol\ L^{-1}$	Cl^-, $\mu mol\ L^{-1}$	HCO_3^-, $\mu mol\ L^{-1}$	SO_4^{2-}, $\mu mol\ L^{-1}$	Alk_{inf}, $\mu eq\ L^{-1}$	TIS Milligrams per Liter	TIS 10^9 Grams per Year	TIS Grams per Square Meter per Year
KF-00-83	Kharucheiyakha	8/24/2000	63.86	75.14	855	0.16	6.17	108.5	3.5	83.9	266.8	343.3	260.3	369.6	6.3	414.7	54.7	8.6	10.1
KF-00-85	Purpe	8/25/2000	64.63	76.60	4615	0.80	6.20	72.8	9.6	65.3	2893.9	279.3	14.7	3143.4	4.8	3189.1	272.0	216.3	46.9
KF-00-87	Aivasyedapur	8/26/2000	64.28	77.99	22249	5.56	6.48	134.0	1.0	103.1	103.2	233.1	29.5	509.7	4.2	557.3	49.4	274.7	12.3
KF-00-88	Kharampur	8/26/2000	64.06	78.75	2837	0.61	6.75	230.8	0.0	187.0	151.9	141.4	31.2	881.7	2.8	969.5	76.4	46.5	16.4
KF-00-94	Agan	8/28/2000	61.67	75.58	28210	7.81	6.12	139.5	0.0	80.8	341.2	164.2	196.9	509.1	5.5	601.3	58.6	457.4	16.2
KF-00-96	Vakh	8/29/2000	60.93	76.89	73340	23.72	6.78	263.5	0.0	127.0	149.7	233.9	36.1	855.5	7.1	916.7	77.8	1846.2	25.2
									Permafrost Free										
KF-99-15	Ob’	7/27/1999	61.23	73.14	997422	249.17	6.89	338.1	13.4	115.8	222.9	110.3	148.7	825.9	24.0	949.7	83.1	20700.7	20.8
KF-99-40	Bolshoy-Salym	8/11/1999	60.87	71.43	12607	3.07	7.05	422.4	0.3	179.3	142.1	178.0	24.3	1117.7	5.8	1313.0	99.2	304.1	24.1
KF-00-95	Ob’	8/29/2000	60.88	76.47	889451	210.75	6.80	546.2	1.5	188.9	235.9	139.3	57.0	1513.4	48.7	1562.0	134.9	28432.5	32.0
KF-01-1	Tura	7/27/2001	57.24	66.81	77566	20.14	7.74	1015.8	10.6	436.5	275.0	318.6	71.9	2061.9	24.7	2208.7	222.8	4488.4	57.9
KF-01-2	Iska	7/27/2001	57.48	67.09	2748	0.32	7.33	1010.5	82.1	666.1	1402.8	105.6	935.7	2831.6	432.2	3085.3	244.7	77.3	28.1
KF-01-3	Tobol	7/27/2001	57.51	67.13	320568	28.38	7.53	796.9	46.7	420.5	595.9	87.9	401.5	2895.0	235.6	3040.0	346.5	9832.6	30.7
KF-01-4	Irtysh	7/28/2001	58.12	68.58	1002342	27.71	7.70	706.6	9.9	278.7	198.3	218.5	61.1	2027.8	4.1	2209.7	209.1	5793.1	5.8
KF-01-5	Vagay	7/28/2001	57.95	69.03	27047	2.24	7.60	368.3	0.0	232.1	171.3	39.3	53.4	2666.9	3.2	2961.6	243.4	544.3	20.1
KF-01-6	Agitka	7/28/2001	57.80	69.31	2474	0.22	7.50	884.3	0.0	328.5	224.4	187.9	57.5	1774.8	3.7	2171.2	157.0	34.6	14.0
KF-01-7	Ashlyk	7/28/2001	57.73	68.84	3993	0.43	7.77	784.7	19.1	335.9	611.1	97.2	305.7	1069.1	180.8	1321.9	92.9	39.9	10.0
KF-01-8	Ashlyk	7/28/2001	57.81	69.12	4346	0.47	7.67	938.7	15.3	437.8	515.4	225.8	254.1	2302.8	48.2	2615.2	196.8	92.6	21.3
KF-01-9	Rogalikha	7/29/2001	58.29	68.13	714	0.10	7.10	620.5	0.0	226.9	104.0	268.4	10.6	1362.4	6.0	1473.6	118.1	11.6	16.3
KF-01-10	Suklem	7/29/2001	58.10	68.03	518	0.06	7.19	368.3	0.0	140.3	70.2	101.4	15.5	784.6	6.4	1905.3	122.4	6.9	13.3
KF-01-11	Dem’yanka	7/29/2001	59.54	69.34	33402	6.70	6.06	464.3	12.1	225.6	289.3	111.4	215.2	1630.0	25.8	1104.8	71.7	480.5	14.4
KF-01-12	Bobrovka	7/29/2001	59.49	69.25	625	0.10	7.47	539.2	0.2	257.6	92.9	292.2	25.5	1146.2	1.6	1854.2	140.7	14.4	22.9
KF-01-13	Turtas	7/29/2001	58.96	69.06	10100	1.63	7.83	508.8	0.0	212.5	129.2	135.3	30.6	1207.6	7.6	1583.8	104.1	169.9	16.8
KF-01-15	Bolshoy-Salym	7/30/2001	60.13	71.55	5479	1.24	6.54	307.2	0.0	121.6	68.4	134.6	9.7	666.0	5.1	963.0	62.1	77.3	14.1
KF-01-16	Bolshoy-Salym	7/31/2001	60.87	71.43	12607	3.07	7.02	309.4	0.0	131.6	151.9	158.6	9.4	843.6	4.3	1087.4	75.8	232.3	18.4
KF-01-17	Malyi-Salym	7/31/2001	60.96	70.92	2441	0.55	7.05	518.0	17.0	250.0	410.8	76.7	200.5	1074.7	114.4	1292.0	93.5	51.1	20.9
KF-01-18	Irtysh	7/31/2001	60.98	69.14	1562422	86.15	7.63	390.7	0.0	181.9	121.0	141.6	16.3	1390.6	5.6	1559.1	142.0	12236.7	7.8
KF-01-19	Ob’	7/31/2001	61.07	68.73	2637982	314.62	7.73	347.8	2.0	114.3	124.8	99.8	59.5	840.8	28.8	972.8	78.6	24743.1	9.4
KF-01-23	Shapsha	8/1/2001	61.01	69.95	580	0.13	6.28	589.1	0.0	239.5	60.1	170.3	6.1	1604.8	2.2	1756.7	133.9	17.1	29.4
KF-01-24	Bolshoy-Balyk	8/2/2001	60.64	72.86	1406	0.35	6.68	1443.7	49.9	842.2	1517.2	335.6	1005.4	1138.0	116.2	1365.4	149.0	52.4	37.3
KF-01-25	Balakhlei	8/2/2001	57.13	69.16	1793	0.12	7.22	425.2	3.3	189.9	945.2	179.6	858.3	4683.2	5.9	4904.6	457.1	55.9	31.2
KF-01-26	Ishim	8/4/2001	56.27	70.49	269493	3.24	7.92	1771.0	127.3	1121.6	4971.8	60.9	4377.8	4268.0	1090.1	4326.4	739.6	2397.7	8.9
KF-01-28	Osha	8/4/2001	56.20	72.58	7882	0.50	7.68	1477.9	234.1	1677.4	9421.6	44.4	9431.3	4450.2	943.0	4650.1	1023.5	513.3	65.1
KF-01-29	Irtysh	8/5/2001	54.85	73.43	377431	8.37	8.73	644.5	11.4	228.1	554.6	32.8	194.5	1581.0	255.5	1605.5	173.4	1450.9	3.8
KF-01-30	Om’	8/5/2001	55.51	75.83	48116	2.76	8.24	1087.6	30.1	812.2	2286.2	130.1	1373.6	3389.7	465.0	3817.8	420.9	1162.5	24.2
KF-01-31	Tara	8/5/2001	56.56	76.63	9305	0.89	7.81	932.4	10.2	367.3	458.5	203.2	110.2	2393.0	34.7	2952.0	216.2	191.8	20.6
KF-01-32	Tartas	8/6/2001	55.67	76.77	15373	0.93	7.90	1895.1	99.7	2264.1	8007.9	66.1	8908.7	2709.3	1538.0	3216.2	309.6	288.7	18.8
KF-01-33	Kama	8/6/2001	55.64	77.05	2711	0.10	7.86	1122.3	47.4	1130.2	2858.7	95.3	2021.7	4382.9	795.9	4577.0	591.6	58.7	21.6
KF-01-34	Icha	8/6/2001	55.56	77.24	3481	0.14	7.97	1273.5	55.4	1311.3	3464.1	47.0	3129.8	3542.0	491.3	3798.4	507.0	69.9	20.1

Table 1. (continued)

Sample	River	Date	Latitude, °N	Longitude, °E	Watershed Area, km^2	Discharge, km^3 yr^{-1}	pH	Ca^{2+}, $\mu mol\ L^{-1}$	K^+, $\mu mol\ L^{-1}$	Mg^{2+}, $\mu mol\ L^{-1}$	Na^+, $\mu mol\ L^{-1}$	Si, $\mu mol\ L^{-1}$	Cl^-, $\mu mol\ L^{-1}$	HCO_3^-, $\mu mol\ L^{-1}$	SO_4^{2-}, $\mu mol\ L^{-1}$	Alk_{inf}, $\mu eq\ L^{-1}$	TIS: Milligrams per Liter	TIS: 10^9 Grams per Year	TIS: Grams per Square Meter per Year
KF-01-35	Om'	8/6/2001	55.45	78.34	15044	0.54	7.82	1300.5	55.2	1606.7	7042.3	84.6	5782.0	3123.8	1026.8	3566.9	456.5	246.6	16.4
KF-01-36	Kargat	8/6/2001	55.22	80.34	3833	0.13	7.97	1250.8	36.1	971.0	2343.7	138.9	1888.1	4746.1	687.3	5079.0	850.8	111.2	29.0
KF-01-37	Chulym	8/6/2001	55.14	81.04	2589	0.23	8.44	916.0	7.5	640.6	1441.1	165.7	892.3	4014.7	232.6	4443.9	1029.4	233.1	90.0
KF-01-38	Bol'shaya Icha	8/8/2001	56.72	78.25	1090	0.13	8.01	920.0	0.0	358.0	371.1	185.0	91.5	2375.0	13.4	2896.1	208.7	27.7	25.4
KF-01-39	Tara	8/8/2001	56.61	78.30	3308	0.28	7.90	1035.5	8.3	434.5	609.8	174.1	166.8	2790.9	47.6	3342.6	252.1	71.3	21.6
KF-01-45	Tartas	8/11/2001	56.36	78.34	4405	0.38	6.71	652.0	20.5	790.8	1420.2	114.1	1366.4	2360.2	278.4	2906.6	272.9	104.3	23.7
KF-01-46	Kama	8/11/2001	56.05	78.46	1011	0.02	6.99	523.7	61.6	877.6	2416.3	61.6	2013.6	2506.7	277.5	2713.7	353.0	8.6	8.5
KF-01-47	Icha	8/11/2001	55.87	78.41	2303	0.10	7.16	780.5	0.0	621.3	1287.5	165.7	792.1	2086.4	210.3	2409.5	284.5	27.2	11.8
KF-01-48	Ob'	8/12/2001	55.84	83.84	304369	45.99	8.36	1280.8	0.0	493.3	782.5	148.7	221.3	1749.7	120.9	1776.0	157.3	7232.3	23.8
KF-01-49	Tom'	8/12/2001	56.03	84.89	53159	12.93	8.95	1149.5	3.0	529.9	572.9	125.0	146.3	2364.2	36.6	2391.9	217.1	2807.6	52.8
KF-01-50	Shegarka	8/12/2001	56.74	83.57	8995	1.13	7.82	676.2	8.5	216.1	225.4	59.7	61.2	6414.9	91.6	6570.0	549.6	619.4	68.9
KF-01-51	Iksa	8/12/2001	56.86	83.07	2507	0.18	7.82	1914.5	16.7	889.5	1448.9	203.0	327.9	3156.5	88.5	3755.6	277.0	49.7	19.8
KF-01-52	Bakchar	8/12/2001	57.00	82.34	4073	0.49	7.81	837.6	15.2	328.4	454.6	67.9	108.3	3319.5	150.8	3896.3	307.5	151.3	37.1
KF-01-53	Galka	8/13/2001	57.04	82.07	1457	0.17	6.99	1898.5	1.8	647.2	758.2	283.2	147.1	5491.2	146.6	5797.7	483.7	82.3	56.5
KF-01-54	Andarma	8/13/2001	57.31	81.91	2928	0.35	7.02	1831.9	7.4	651.7	1339.3	220.2	283.3	5064.4	125.7	5460.4	445.6	153.8	52.5
KF-01-55	Parbig	8/13/2001	57.24	81.41	3066	0.37	7.48	1216.6	8.0	464.1	431.6	236.5	139.5	4639.0	38.2	5034.7	391.4	146.0	47.6
KF-01-57	Kenga	8/13/2001	57.43	80.97	4421	0.46	7.07	1737.1	13.5	538.6	520.2	300.9	57.1	3136.2	28.2	3660.3	276.9	127.5	28.8
KF-01-58	Chaya	8/14/2001	58.07	82.82	24890	3.78	7.52	1492.8	8.3	530.3	573.3	251.4	172.1	4114.1	36.4	4447.6	353.9	1336.1	53.7
KF-01-59	Shudelka	8/14/2001	58.43	82.10	4394	0.68	7.63	894.0	0.0	282.2	202.8	246.9	37.6	2068.6	11.3	2319.4	174.4	119.0	27.1
KF-01-60	Parabel	8/14/2001	58.71	81.37	24662	3.65	7.68	790.7	0.0	248.1	152.8	231.0	9.2	2213.1	1.8	2573.7	191.7	699.7	28.4
KF-01-61	Vasyugan	8/14/2001	59.04	80.74	61509	13.77	7.35	440.9	0.0	141.1	129.9	157.8	33.2	1030.7	5.7	1344.3	93.1	1282.5	20.9
KF-01-62	Ket'	8/15/2001	58.43	83.37	72138	19.63	7.52	1724.6	3.8	558.3	297.0	266.5	12.1	1374.1	5.3	1511.2	118.6	2327.9	32.3
KF-01-64	Bolshoy Tatosh	8/15/2001	57.62	83.53	982	0.14	6.90	495.3	0.0	167.8	137.5	241.4	7.7	4689.3	6.0	4854.5	384.2	53.4	54.3
									Average										
Permafrost-influenced							6.43	95.0	3.8	74.6	274.7	189.3	98.3	422.4	15.5	505.7	48.2	12665.5[b]	8.8
Permafrost-free							7.50	920.2	21.4	521.0	1193.9	158.6	893.4	2563.7	193.1	2853.7	288.9	33258.5[b]	27.8
Total west Siberian region							6.92[a]	470.4[a]	11.8[a]	277.7[a]	692.9[a]	175.4[a]	460.0[a]	1396.6[a]	96.3[a]	1590.0[a]	157.7[a]	45924.0[b]	17.5[a]

[a]Values for the total region calculated by linearly weighting permafrost-influenced and permafrost-free values by their respective areas.
[b]Total total inorganic solutes (TIS) flux calculated by multiplying average TIS flux (g m^{-2} yr^{-1}) by the respective area of the region or subregion.

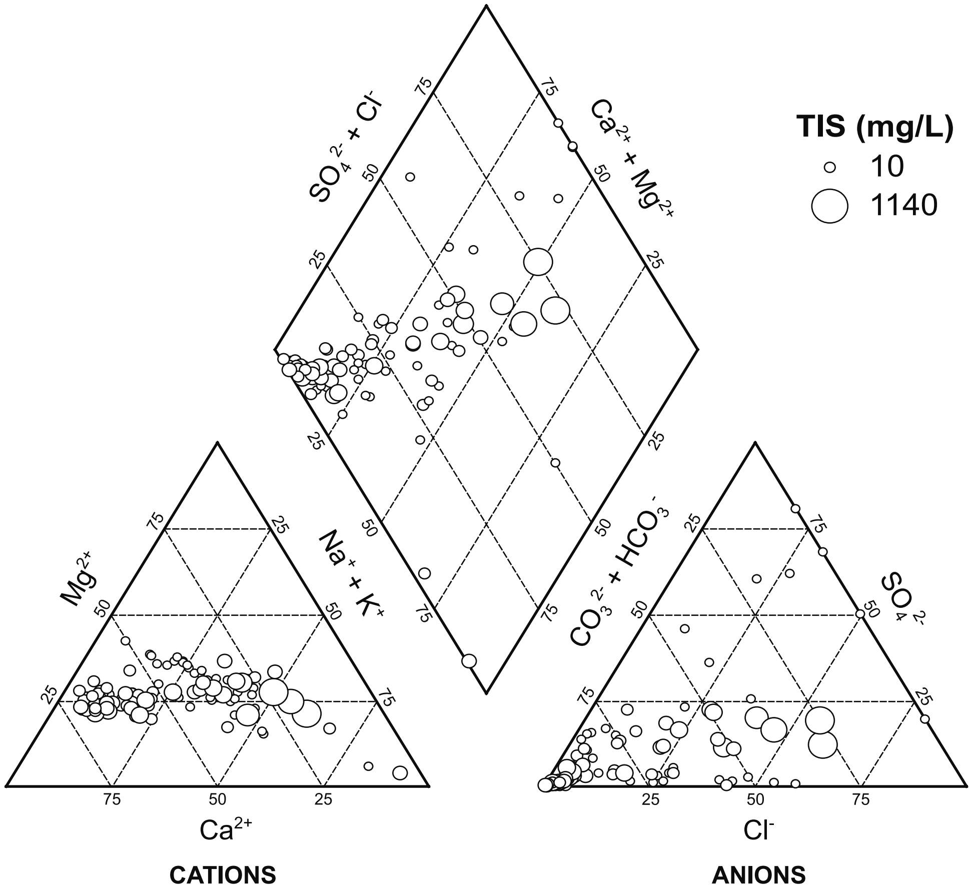

Figure 2. Piper diagram showing the relative concentrations of solutes within each water sample. The size of each point is scaled to the concentration of total inorganic solutes (TIS).

member. Oilfield brine solute concentrations as reported by *Collins* [1975] were used as the oilfield brine end-member, which is nearly identical to that found in the Siberian platform east of west Siberia [*Alexeev et al.*, 2004], yet offers a more complete report of solute concentrations. For our EMMA model, we assumed that the chemical compositions of contributing end-members were constant among all of the samples, thus allowing the sampled watersheds throughout the west Siberian region to be considered as one continuous system.

[11] Chemical constituents were considered acceptable as tracers in the EMMA model if stream water concentrations were bounded by potential end-members, determined by constructing bivariate mixing diagrams of all combinations of measured solutes. Of these solutes (Table 1), four constituents were determined to be satisfactory tracers: Ca^{2+}, Na^{+}, Cl^{-} and Alk_{inf}. Furthermore, these solutes are effectively "nonreactive" in the west Siberian water mixtures. However, sensu stricto, Ca^{2+} and Alk_{inf} can be chemically reactive if solubility limits for carbonate minerals are exceeded (causing mineral precipitation) or if water undersaturated with respect to carbonate minerals dissolves them in contact.

3.3. Discharge Model

[12] In order to estimate solute fluxes for the sampled streams and rivers, we approximated an annual discharge value for each watershed using the regression method for discharge estimation from watershed attributes [*Mosley and McKerchar*, 1993]. Here we utilized discharge (Q), drainage area (A) and watershed mean annual precipitation (P) as input variables. In order to derive the regression equation, Q, A and P were determined as follows: (1) The 154 west Siberian gauging stations and associated discharge data (for years 1961–1990) were identified from the R-ArcticNET data network (available at http://www.r-arcticnet.sr.unh.edu); (2) watershed areas corresponding to each of the 154 gauging stations were delineated with a Lambert Azimuthal Equal Area map projection in the ESRI® ArcGIS™ v. 8.0 Geographic Information System (GIS) using Digital Chart of the World drainage networks, the GTOPO30 digital elevation model, United States Tactical Pilotage Charts, United States Operational Navigation Charts and Russian Oblast maps; and (3) mean annual precipitation over the watersheds was determined in the GIS using gridded climate normals for years 1961–1990 [*New et al.*, 1999]. The resulting derived discharge estimation equation is as follows:

$$Q = 4.38 \times 10^{-20} \cdot A^{1.07} \cdot P^{5.69} \left(r^2 = 0.99\right) \quad (1)$$

where Q is mean annual discharge ($km^3\ yr^{-1}$), A is drainage area (km^2), and P is mean annual precipitation ($mm\ yr^{-1}$). This modeling approach was necessary for flux calculations, as sampling points rarely coincide with gauging stations. Once the regression equation was derived, discharge at each of the 94 sampling locations was calculated by first establishing their respective watershed areas and mean

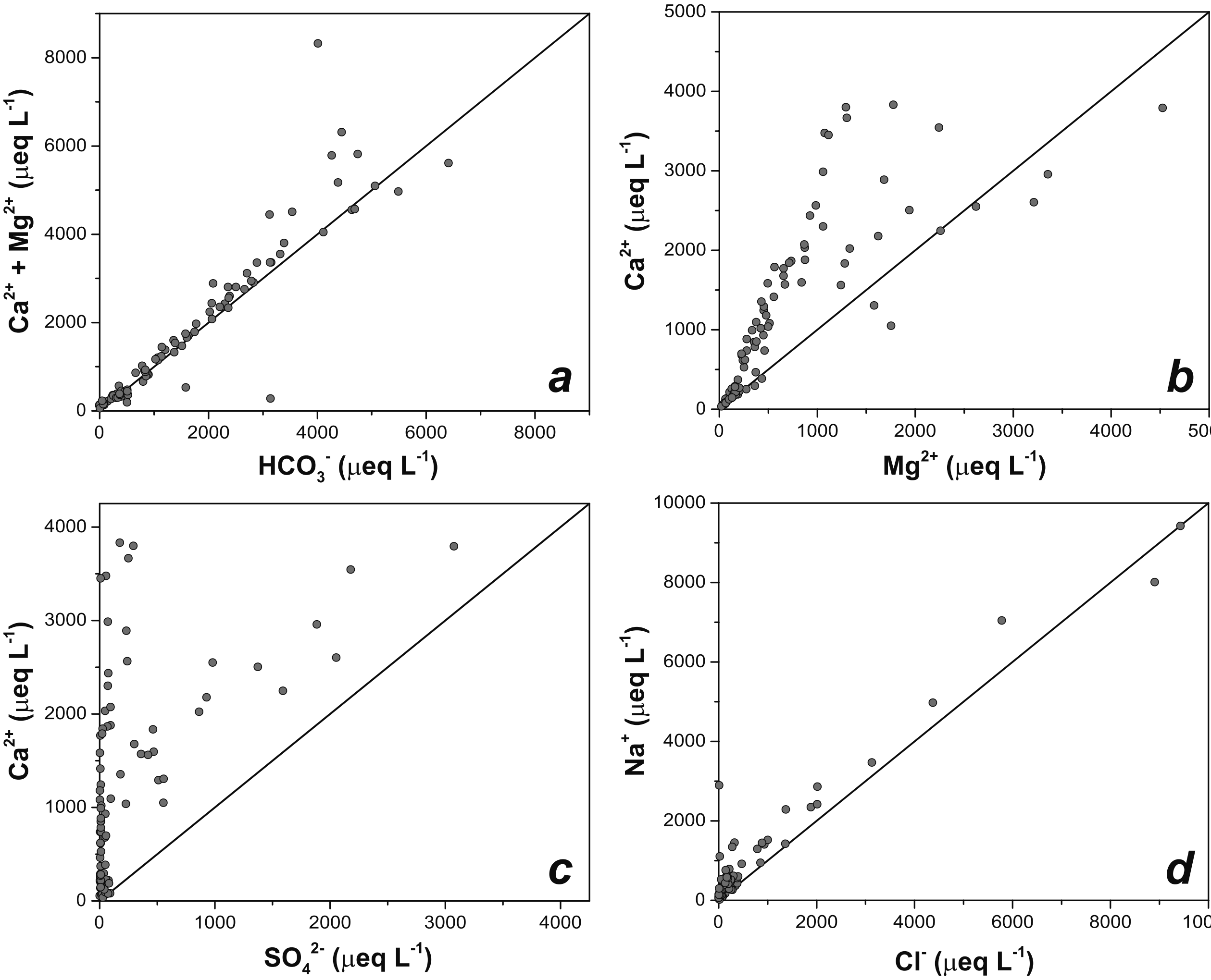

Figure 3. Relationships between (a) $Ca^{2+} + Mg^{2+}$ and HCO_3^-, (b) Ca^{2+} and Mg^{2+}, (c) Ca^{2+} and SO_4^{2-}, and (d) Na^+ and Cl^+. The 1:1 line is shown in each of the four plots.

annual precipitation, as in steps 2 and 3 above. Resulting watershed area and discharge estimates for each of the 94 samples are shown in Table 1. Solute fluxes from the watersheds were then determined by multiplying annual discharge values by respective measured solute concentrations at each of the sampled sites. Although solute concentrations measured during late summer do not necessarily reflect those throughout the entire year, we utilized this approach as a first approximation in the absence of detailed flow-weighted data over the entire annual hydrograph in these remote locations.

4. Results and Interpretation

4.1. Major Solutes

[13] Table 1 presents the chemical compositions of the 94 sampled watersheds (including pH and concentrations of Ca^{2+}, K^+, Mg^{2+}, Na^+, Si, Cl^-, SO_4^{2-}, HCO_3^-, Alk_{inf} and TIS). Waters sampled are generally circumneutral, with a mean pH of 6.9. On average, the least concentrated solutes are K^+, SO_4^{2-}, Si, and Mg^{2+}, whereas Cl^-, Ca^{2+}, Na^+ and HCO_3^- dominate the TIS budget. In addition, all sampled watersheds throughout the region average an Alk_{inf} of ~1590 μeq L^{-1} (ranging from 52 to 3189 μeq L^{-1} and averaging ~506 μeq L^{-1} in permafrost-influenced watersheds, while ranging from 950 to 6570 μeq L^{-1} and averaging ~2854 μeq L^{-1} in permafrost-free watersheds). Furthermore, all sampled watersheds throughout the region average a TIS of ~158 mg L^{-1} (ranging from 7 to 272 mg L^{-1} and averaging ~48 mg L^{-1} in permafrost-influenced watersheds, while ranging from 62 to 1029 mg L^{-1} and averaging ~289 mg L^{-1} in permafrost-free areas).

4.2. Water-Rock Interaction

[14] A Piper diagram (Figure 2) shows the relative concentrations of solutes, with the size of each point scaled to the TIS of each sample. Streams and rivers with the highest TIS concentrations (~1000 mg L^{-1}) are dominated by Na^+ and Cl^-, indicating a significant component of oilfield brine. The remaining samples are Ca-Mg-HCO_3-type waters, reflecting dissolution of carbonate minerals found in the underlying rocks and sandstone cements. The prevalence of carbonate dissolution is supported by the 1:1 relationship between (Ca^{2+} + Mg^{2+}) and HCO_3^- (Figure 3a), consistent with the equation for hydrolysis of carbonate

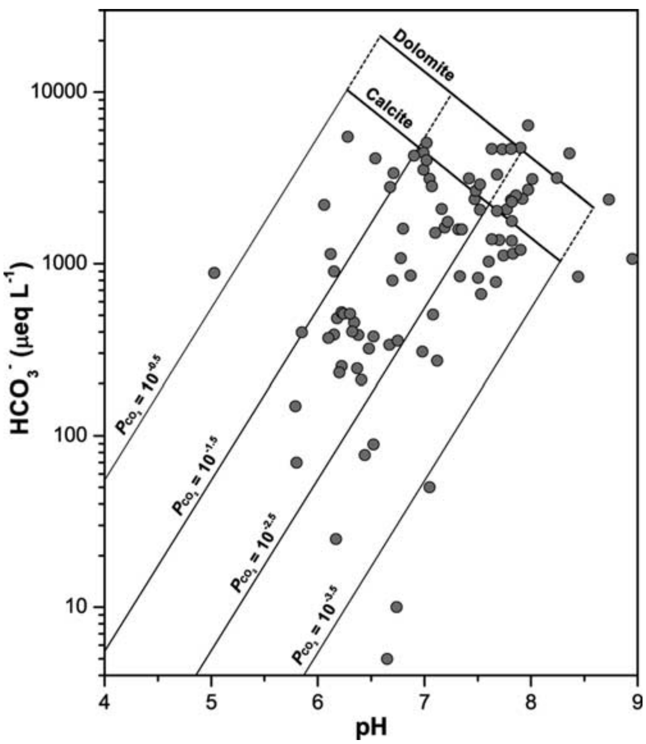

Figure 4. Relationship between HCO_3^- and pH. The isolines of P_{CO_2} define an open system of carbonate dissolution, with P_{CO_2} values found in soils typically higher than those of normal atmospheric concentrations (P_{CO_2} = $10^{-3.5}$). Saturation lines indicating equilibrium with calcite or dolomite are also shown.

minerals by carbonic acid. The correlation between Ca^{2+} and Mg^{2+} (Figure 3b) and the relatively high (~25%) contribution of Mg^{2+} to the cation budget (Figure 2) suggests that a dolomite source rock exists, although samples with Ca^{2+} concentrations falling above the 1:1 line indicate that a noncarbonate Ca^{2+} source (most likely gypsum) is also contributing to stream solutes. The presence of gypsum is supported by the positive correlation between Ca^{2+} and SO_4^{2-} (Figure 3c) in waters with Ca^{2+} concentrations greater than ~1000 μeq L^{-1} (Ca^{2+} concentrations fall above the 1:1 line in Figure 3c because of the additional presence of Ca^{2+} with carbonate dissolution). We can also support the hypothesis that oilfield brines within the sedimentary rocks are impacting the water chemistry of streams at the surface through the observed stoichiometric relationship between Na^+ and Cl^- in our watersheds (Figure 3d). Lastly, one reason carbonate species may dominate the solute composition in west Siberian streams is that carbonate dissolution may be enhanced by the presence of organic peat soils. The plot of HCO_3^- versus pH (Figure 4) indicates that the dissolution of carbonates is occurring somewhere between a P_{CO2} of normal atmospheric concentrations (P_{CO2} = $10^{-3.5}$) and higher values typically found in soils ($P_{CO2} > 10^{-3.5}$), where organic matter is oxidized to CO_2. Therefore oxidation of peat soils in west Siberia undoubtedly enhances carbonate dissolution by providing greater availability of CO_2. Furthermore, the production of organic acids within peat soils may effectively promote silicate weathering as well.

4.3. Latitudinal Contrasts

[15] The solute concentrations of our sampled stream waters show a distinct relationship with latitude (Figures 5 and 6). Stiff diagrams placed at the location of each of the samples (Figure 5) represent both the concentrations and relative abundance of solutes. The shape of the diagrams (denoting the relative abundance of solutes) corroborates the weathering of carbonate rock in many of the sampled watersheds, both north and south of the permafrost limit (~56°–61°N). The surface disposal of oilfield brines may be affecting a small number of streams at the lowest latitudes (55°–57°N), which is apparent in their high concentrations of Na^+ and Cl^-. The size of the Stiff diagrams (denoting the total concentrations of solutes) is strongly dependent on latitude. Solute concentrations north of the permafrost limit (~61°N) are relatively low, whereas concentrations south of the permafrost limit are considerably higher. This relationship is simplified when observing the direct dependence of TIS on latitude (Figure 6). TIS concentrations in permafrost-influenced watersheds (north of ~61°N) are consistently low, but sharply increase south of ~61°N where permafrost disappears from watersheds. On average, concentrations of each solute (except for Si) are significantly higher in southern, permafrost-free watersheds than in northern, permafrost-influenced watersheds (Table 1). To generalize this observation, we note that TIS concentrations average ~289 mg L^{-1} in permafrost-free watersheds, yet only ~48 mg L^{-1} in permafrost-influenced watersheds. Furthermore, permafrost-influenced stream waters are on average slightly more acidic (pH = 6.4) than permafrost-free stream waters (pH = 7.5) (Table 1), possibly driven by the buffering of stream waters at southern latitudes via the discharge of alkaline groundwater or dissolution of carbonates in mineral soils not covered by frozen peat.

4.4. End-Member Mixing Analysis (EMMA)

[16] Results of the principal components analysis of the four tracers used in the EMMA model (Ca^{2+}, Na^+, Cl^- and Alk_{inf}) show that 98% of the variability in west Siberian stream chemistry is accounted for by the first two principal components. On the basis of *Christophersen and Hooper* [1992], our EMMA results show that the three end-members (peat surface water, groundwater and oilfield brine) sufficiently explain the observed variability in stream water solute concentrations in west Siberia. Furthermore, linear regressions between tracer concentrations predicted from the EMMA model and observed tracer concentrations yield r^2 values of 0.98–0.99 and slopes of 0.96–0.97, indicating that the derived EMMA model is a robust means by which to predict proportions of end-member contribution to streamflow throughout west Siberia.

[17] Projecting both the stream water and end-member compositions onto *U* space (as defined by the eigenvector extracted in the PCA) results in a mixing diagram (Figure 7) that shows the variable influence of the end-members on our measured stream samples. Peat surface water and groundwater impact stream composition to a much greater extent than oilfield brine (i.e., note the *x* and *y* axis breaks toward the oilfield brine end-member; Figure 7). Both groundwater and surface peat water contribute a range of 0–100% to streamflow in the region. In contrast, oilfield brine

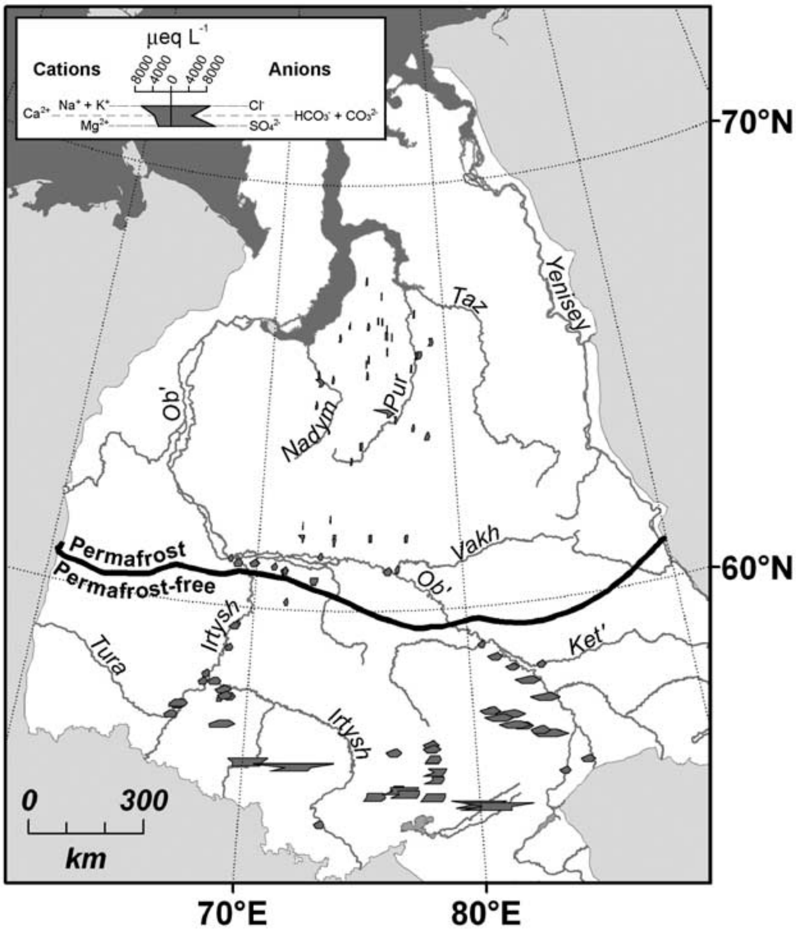

Figure 5. Stiff diagrams representing each of the 94 sampling sites. The size and shape of the diagrams represent the TIS and relative abundance of solutes, respectively. The permafrost limit separates low solute concentrations in the north from high solute concentrations in the south.

contributes only 0–0.6%. The relative impact of peat surface water and groundwater on stream composition is also highly dependent upon the latitude of the sampled stream, with peat surface water the primary contributor to streamflow at higher latitudes (in permafrost-influenced watersheds) and groundwater the primary contributor to streamflow at lower latitudes (in permafrost-free watersheds). On the basis of the results of the EMMA model, we can calculate the relative contribution of groundwater to each watershed as a function of latitude (Figure 8). The groundwater contribution is consistently low in permafrost-influenced watersheds and sharply increases south of ~61°N (when permafrost no longer impacts the watersheds). This observed pattern is nearly identical to the relationship seen between TIS and latitude (Figure 6).

4.5. Flux Estimates of Total Inorganic Solutes

[18] Combining discharge estimates (as determined in section 3.3.) and measured TIS concentrations, we calculate an annual flux of TIS (g yr^{-1}) for each of the sampled watersheds (Table 1) as a first-order approximation for the export of solutes from west Siberian watersheds. Because TIS flux estimates vary as a function of watershed area, an area-normalized TIS flux (in units of g m^{-2} yr^{-1}) is a more meaningful indicator by which to compare watershed solute loads. Our estimates of area-normalized solute loads in the sampled watersheds vary between 0.7 and 90 g m^{-2} yr^{-1} (Table 1). As was seen for TIS concentrations, there is also a strong divergence between solute loads in permafrost-

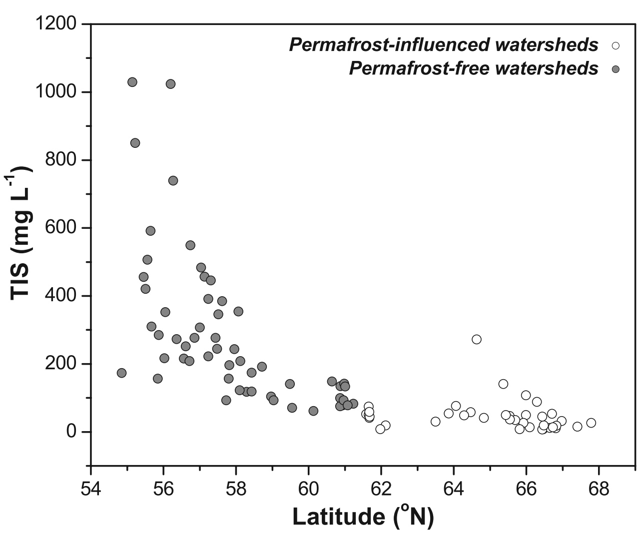

Figure 6. TIS as a function of latitude. TIS rises considerably northward of ~61°N, which is approximately coincident with the permafrost limit.

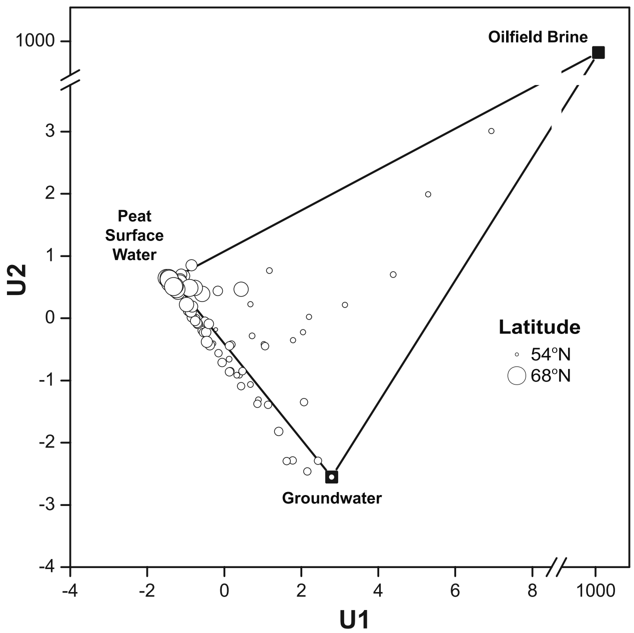

Figure 7. Mixing diagram showing stream water and end-member composition in *U* space. Moving northward in latitude, water samples transition from groundwater-influenced to peat surface water–influenced. This is attributed to the presence of permafrost northward of ~61°N. Also note the small portion of water samples influenced by oilfield brines.

influenced watersheds (averaging ~9 g m^{-2} yr^{-1}) and those in permafrost-free watersheds (averaging ~28 g m^{-2} yr^{-1}). On the basis of these measurements and the areal distribution of permafrost throughout west Siberia, we estimate that the area-normalized flux of solutes from the entire region (~2.6×10^6 km^2) is currently ~18 g m^{-2} yr^{-1} (Table 1).

5. Discussion

[19] The most salient result from this study is the considerably higher solute concentrations found in surface waters from permafrost-free watersheds relative to surface waters from permafrost-influenced watersheds (Table 1 and Figures 5 and 6). Our results are similar to those reported by *Kimstach et al.* [1998], with observations of low TIS (10–30 mg L^{-1}) in northern tundra watersheds and high TIS (200–600 mg L^{-1}) in southern steppe watersheds of the former Soviet Union. In general, the solute composition of stream and river waters in west Siberia is controlled by water-rock interactions in upland areas and below the upper peat layer, biogeochemical processes within the peat column, and hydrology. It is possible that the observed regional divergence in our solute concentrations (e.g., Figures 5 and 6) may be also influenced by variability in surface air temperatures [e.g., *Berner*, 1990; *Bluth and Kump*, 1994], with slow weathering reaction rates in cold, northern watersheds (giving rise to low solute concentrations) and fast reaction rates in warm, southern watersheds (giving rise to high solute concentrations). However, the amount of mineral surface available to dissolution is minimal for frozen ombrotrophic peat (which covers much of the permafrost-influenced region), indicating that temperature gradients are not a primary driver for the observed differences in surface water chemistry. Alternatively, the observed solute divergence may be driven by permafrost-controlled hydrological processes, with permafrost forming a confining barrier that inhibits the infiltration of surface water through deep mineral horizons (limiting water-rock interaction) and restricts mineral-rich subpermafrost groundwater from reaching surface water pathways [*Woo and Winter*, 1993; *Michel and van Everdingen*, 1994; *Woo et al.*, 2000]. This hypothesis is corroborated by *MacLean et al.* [1999], who found that the presence of permafrost significantly reduces the dissolution and transport of dissolved inorganic mineral loads in streams of the Alaskan taiga by confining runoff to upper soil horizons. Our interpretation of permafrost influence on stream solute concentrations in west Siberia is in fact conservative, because low hydraulic conductivity peatlands are thinner in the north and thicker in the south [*Sheng et al.*, 2004].

[20] Measured solute concentrations throughout west Siberia are highly dependent upon permafrost distribution, with solutes more concentrated in waters draining permafrost-free watersheds than those draining permafrost-affected watersheds (Table 1 and Figures 5 and 6). However, we note that Si is the only solute for which permafrost-limited sources appear not to apply. Using a Student's *t* test, we note no difference between Si concentrations for the permafrost-free and permafrost-influenced environments (using an exceedance probability of $p = 0.05$). This independence of Si concentrations from latitude may be caused by the overall low abundance of silicate minerals. A plot of Si/($Na^* + K^+$) (where $Na^* = [Na^+] - [Cl^-]$) indicates that the primary aluminosilicate minerals that are present may be dominated by refractory minerals (i.e., quartz) or alteration products that have lost a significant portion of their soluble cations. Furthermore, diatom formation and dissolution in lakes and rivers are thought to play significant roles in Si systematics in freshwater systems at high latitudes [e.g., *Rouse et al.*, 1997; *Laing and Smol*, 2000], controls that are difficult to evaluate from synoptic sampling.

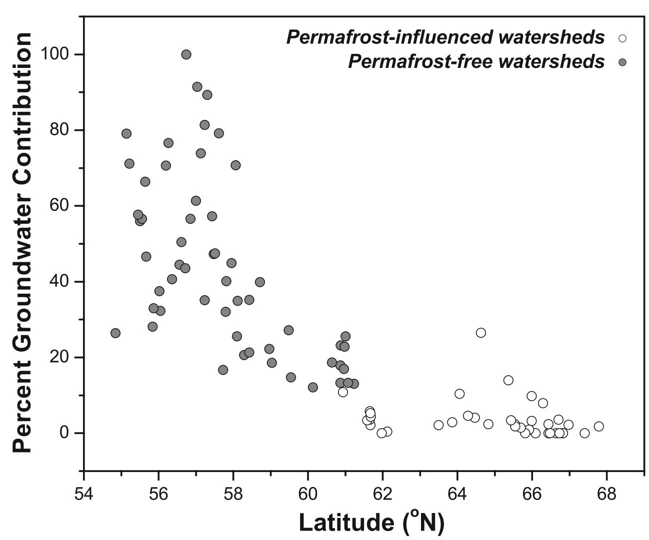

Figure 8. Percent groundwater contribution to streamflow as a function of latitude, calculated through end-member mixing analysis.

[21] A recent suite of studies [*Huh et al.*, 1998a, 1998b; *Huh and Edmond*, 1999] described the inorganic geochemistry of the heavily permafrost-influenced east Siberian rivers (including tributaries of the Lena, Omoloy, Indigirka, Kolyma, Anadyr and Anabar rivers) and investigated the potential influence of climate on weathering and solute fluxes in the various lithologies of the region. However until now, a comparable study has not existed for west Siberia. In east Siberian rivers, overall weathering is dominated by carbonates and evaporates [*Huh et al.*, 1998a, 1998b; *Huh and Edmond*, 1999]. This is generally similar to our results in west Siberia. Furthermore, average area-weighted TIS loads in east Siberian watersheds (which are all permafrost-influenced) range from 13 to 81 g m^{-2} yr^{-1} draining the sedimentary platform of the Siberian Craton [*Huh et al.*, 1998b]; 2 to 20 g m^{-2} yr^{-1} draining the Verkhoyansk and Cherskiy ranges [*Huh et al.*, 1998a]; and 3 to 35 g m^{-2} yr^{-1} draining the basement terrain of the Siberian Craton and the Trans-Baikal Highlands [*Huh and Edmond*, 1999]. In comparison, our measured west Siberian TIS loads range from 1–47 g m^{-2} yr^{-1} in permafrost-affected watersheds and 4–90 g m^{-2} yr^{-1} in permafrost-free watersheds, with a regionally averaged TIS load of ~18 g m^{-2} yr^{-1} for the entire west Siberian area (Table 1). As east Siberian watersheds are generally more heavily influenced by permafrost than those in west Siberia [*Brown et al.*, 1997, 1998], we expect TIS loads to be significantly lower than those found in this study. However, east Siberian watersheds with the highest TIS loads are characterized by remarkably widespread development of marine halite and gypsum in mineral substrates, which play a dominant role in the solute compositions and total concentrations of these waters [*Huh et al.*, 1998b]. Our average value of ~18 g m^{-2} yr^{-1} within west Siberia is similar to solute loads in other high-latitude drainage basins such as the Lena (~11 g m^2 yr^{-1}), Yenisey (~27 g m^2 yr^{-1}) and Mackenzie (~36 g m^2 yr^{-1}), whereas significantly higher loads can be found in lower-latitude rivers such as the Brahmaputra (~104 g m^2 yr^{-1}) and Yangtze (~92 g m^2 yr^{-1}) [*Berner and Berner*, 1996] where weathering rates are high and water-rock interaction is not limited by permafrost. However, solute loads in low-latitude rivers may not always be high: Export from the silicate-dominated Amazon basin (~44 g m^2 yr^{-1}) [*Berner and Berner*, 1996] may be controlled by different weathering regimes or by hydrological transport processes in which a lack of topography causes weathering products to be inefficiently removed, thus allowing thick soils to develop (and further limiting water-rock interaction) [*Stallard and Edmond*, 1987].

[22] Our results show that the permafrost limit in west Siberia marks a clear threshold, with northern, permafrost-influenced watersheds exhibiting low solute concentrations and southern, permafrost-free watersheds exhibiting dramatically higher solute concentrations. A warming arctic climate may thus lead to increased release of solutes to rivers through: (1) surface air temperature impacts on weathering kinetics, with a warming climate enhancing overall reaction rates [e.g., *Berner*, 1990]; or more likely (2) the resulting degradation of permafrost allowing both mineral-rich groundwater to reach surface water pathways and surface water to no longer be solely confined to upper soil horizons [e.g., *Michel and van Everdingen*, 1994; *Rouse et al.*, 1997]. Although *Stendel and Christensen* [2002] predict permafrost will nearly disappear from the west Siberian region by the year 2100, the response of permafrost dynamics to climate warming is highly complex and its expected rate of degradation is largely unknown [e.g., *Zhang et al.*, 2005]. If recently observed air temperature trends in west Siberia continue [*Frey and Smith*, 2003], however, permafrost will undoubtedly thaw dramatically in the coming decades. On the basis of our measured solute concentrations in both permafrost-influenced and permafrost-free watersheds, we estimate that the current regionally averaged TIS export from west Siberia (over ~2.6 × 10^6 km^2) is ~18 g m^{-2} yr^{-1} (Table 1), or ~46 Tg yr^{-1}. This calculated TIS flux is remarkably similar to that of the Ob' basin reported by both *Gordeev et al.* [1996] (~47 Tg yr^{-1}) and *Telang et al.* [1991] (~46 Tg yr^{-1}). If permafrost were to completely disappear from west Siberia (from its current area of ~1.4 × 10^6 km^2), we predict that TIS export will increase to ~28 g m^{-2} yr^{-1} (assuming constant discharge), or ~73 Tg yr^{-1} (a ~59% increase). However, these predictions of total solute loads exported to the Kara Sea and Arctic Ocean may be confounded by uncertainty in the response of river discharge to climate change and anthropogenic drivers [*Berezovskaya et al.*, 2004; *McClelland et al.*, 2004; *Yang et al.*, 2004a, 2004b; *Ye et al.*, 2004]. In addition, although impacts of permafrost thaw are likely the most important drivers of our predicted increases in inorganic solute concentrations, "substituting space for time" inherently incorporates potential ecological or biogeochemical causes of increased solute concentrations that may occur with warming as well.

[23] Concerns about increasing freshwater delivery to the Arctic Ocean have recently emerged [e.g., *Peterson et al.*, 2002; *Dyurgerov and Carter*, 2004; *Arnell*, 2005; *Wu et al.*, 2005], with implications for the cessation of NADW formation (and hence impacting global thermohaline circulation) if an additional 0.06–0.15 Sv of freshwater were to be transported to the Arctic Ocean [e.g., *Clark et al.*, 2002; *Peterson et al.*, 2002; *Rahmstorf*, 2002]. This phenomenon is directly related to increasing the presence of freshwater at convection sites in the Greenland/Iceland and Labrador seas, thus capping the sites with low-salinity waters, inhibiting convection, and slowing or even halting NADW formation [e.g., *Aagaard and Carmack*, 1989]. It is apparent that variability in Siberian river discharge may in fact impact the salinity of adjacent shelf waters [*Steele and Ermold*, 2004]. Our estimates of increasing total solute concentrations (i.e., salinity) of river waters entering Arctic Ocean circulation may therefore plausibly enlarge the predictions of freshwater volume needed to halt NADW formation, thereby tempering the estimates of when NADW may cease to form. However, calculations to determine the impacts on freshwater flux reveal that even while keeping river discharge constant, our predicted increases in solute concentrations will have a minimal impact on convection site processes. This is demonstrated with the following equation:

$$\text{freshwater flux} = \text{volume flux} \cdot \left(S_{ref} - S\right)/S_{ref} \qquad (2)$$

where the freshwater flux can be separated from the total volume flux of water by utilizing S_{ref} (the reference salinity of the Arctic Ocean) and *S* (the salinity of the freshwater mass of interest). Here we assume a S_{ref} of 34.8 ppt and a combined total volume flux of all arctic rivers of 0.1 Sv [*Aagaard and Carmack*, 1989]. From Table 1, using a river salinity (*S*) of 0.16 ppt (assuming this for all arctic rivers) currently and 0.29 ppt (if permafrost were to completely disappear from the Arctic), the freshwater flux to the Arctic Ocean would decrease from 0.0995 Sv to only 0.0992 Sv. Considering the volume of freshwater flux needed to impact NADW formation (0.06–0.15 Sv), this 0.0003 Sv difference caused by potential river salinity differences is minimal.

[24] Although predicted increases in solute loads delivered to the Kara Sea are unlikely to have a physical impact on salinity driven ocean circulation, they could impact biogeochemical processes on the Eurasian shelves and Arctic Ocean basin interior. Our estimate of increasing inorganic solute loads may be used as a proxy indicator of potential increases in micronutrients (e.g., Cu, Co, Fe, Mn, Mo, Ni, Zn) under conditions of degrading permafrost and resulting enhanced water-rock interaction. These micronutrients play an important role in high-latitude marine environments and along with light-restricting sea ice cover, commonly limit primary production and phytoplankton growth [*Harrison and Cota*, 1991; *Grebmeier et al.*, 1995, 1998; *Carmack et al.*, 2004; *Sarthou et al.*, 2005; *Smetacek and Nicol*, 2005]. However, other arctic shelf areas may be so highly productive that zooplankton and microbial consumption cannot deplete the resulting large carbon source, which subsequently may be advected to the Arctic Basin interior through entrainment with dense, briny waters forming as a result of sea ice formation [e.g., *Grebmeier et al.*, 1998]. Although complicated by predictions of rising temperatures and sea ice cover reduction [e.g., *Sarmiento et al.*, 2004], it is important to consider that projected increases in river transport of dissolved solutes to nutrient-limited arctic marine environments may further enhance primary production and consequently, lead to greater sequestration of atmospheric CO_2 in shelf and basin sediments. This could in turn act as a negative feedback to warming and permafrost degradation.

6. Summary and Conclusions

[25] Measurements of inorganic solute concentrations from 94 watersheds in west Siberia indicate strong carbonate dissolution for most of the samples throughout the region. More remarkable is the contrast seen between low solute concentrations found in northern permafrost-influenced watersheds and considerably higher concentrations found in southern permafrost-free watersheds. We attribute this phenomenon to (1) the presence of permafrost constraining mineral-poor peat surface water to be the primary contributor to streamflow in the north and (2) the absence of permafrost allowing mineral-rich groundwater to be the primary contributor to streamflow in the south. With climate warming and subsequent permafrost thaw this region may therefore transition from a surface water–dominated system to a groundwater-dominated system. This premise is confirmed with a PCA-based EMMA model, utilized with an unconventional approach (i.e., to identify spatial patterns in end-member contribution to streams located throughout a region rather than to identify temporal patterns at a single sample site). On the basis of our measurements, we estimate a ~59% increase in TIS export from west Siberia to the Kara Sea should permafrost completely disappear from the region. This potential shift in the river transport of solutes is unlikely to impact ocean convection site processes, but may have critical implications for primary production and carbon cycling on arctic Eurasian shelves and in the Arctic Ocean basin interior.

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