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Nutrient variations in boreal and subarctic Swedish rivers: Landscape control of land–sea fluxes

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Abstract

We examined the hypothesis that the extent of vegetation cover governs the fluxes of nutrients from boreal and subarctic river catchments to the sea. Fluxes of total organic carbon (TOC) and dissolved inorganic nitrogen, phosphorus, and dissolved silicate (DIN, DIP, and DSi, respectively) are described from 19 river catchments and subcatchments (ranging in size from 34 to 40,000 km^2) in northern Sweden with a detailed analysis of the rivers Luleälven and Kalixälven. Fluxes of TOC, DIP, and DSi increase by an order of magnitude with increasing proportion of forest and wetland area, whereas DIN did not follow this pattern but remained constantly low. Principal component analysis on landscape variables showed the importance of almost all land cover and soil type variables associated with vegetation, periglacial environment, soil and bedrock with slow weathering rates, boundary of upper tree line, and percentage of lake area. A cluster analysis of the principal components showed that the river systems could be separated into mountainous headwaters and forest and wetland catchments. This clustering was also valid in relation to river chemistry (TOC, DIP, and DSi) and was confirmed with a redundancy analysis, including river chemistry and principal components as environmental variables. The first axis explains 89% of the variance in river chemistry and almost 100% of the variance in the relation between river chemistry and landscape variables. These results suggest that vegetation change during interglacial periods is likely to have had a major effect on inputs of TOC, DIP, and DSi into the past ocean.

Changes in vegetation cover on land have altered biogeochemical cycles by affecting both silicate weathering rates and carbon sequestration on land (Schwartzman and Volk 1989; Berner 1992). How these altered weathering patterns have been manifested in land–sea fluxes of nutrients is still not clear. Natural changes in river runoff of nutrients might have influenced the primary production regime of the entire ocean environment, and thus the CO_2 concentration of the atmosphere. Both dissolved silicate (DSi) and dissolved inorganic nitrogen (DIN) inputs into the contemporary ocean are estimated to be between 5 and 6 Tmol yr^{-1} (Tréguer et al. 1995; Jaffe 2000). Thus, the Si : N ratio of total annual input (i.e., loads from rivers and the atmosphere, including N fixation) corresponds to the molar uptake demand ratio of diatoms, which is $\sim$1 (Brzezinski 1985). An improved understanding of changes in inputs of DSi will help explain the variation of diatom production over geological timescales. About 90% of the DSi input to the global ocean is estimated to come from rivers. However, in global biogeochemical budgets and models (Tréguer et al. 1995; Tréguer and Pondaven 2000), river inputs to the ocean are still considered as having been constant during the late Quaternary. Instead, it was argued that increased input of aeolian silicate (Tréguer and Pondaven 2000) or fertilizing iron (Falkowski 1997) to the ocean have been responsible for an increased CO_2 uptake via the biological pump during glacial periods.

Today, arctic rivers contribute roughly a sixth (5,500 km^3)

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of the global annual water discharge to the ocean (Shiklomanov et al. 2000). However, during deglaciation periods, these contributions should have been much more significant because of the massive release of melting water over extended areas from about 70°N down to 40°N (Andersen and Borns 1997). A prominent example is the St. Lawrence River, which is supposed to have influenced the entire North Atlantic during the Younger Dryas (Broecker et al. 1989). Still, the biogeochemical significance of glacial periodicity to such river systems is unclear.

Most studies on land indicate an increase of chemical weathering and, thus, of DSi fluxes with an increase in vegetation cover (Berner and Berner 1996), suggesting that the highest weathering rates can be expected during an interglacial period. On the other hand, from analyses of marine sedimentary paleoceanographic records, it has been inferred that during glacial periods, DSi fluxes might have been twice as high as today because of an increase in physical weathering (Froelich et al. 1992).

Vegetation might be a crucial force in the downstream change of nutrients and major elements in boreal watersheds, as indicated by a positive correlation between the two river chemistry variables of total organic carbon (TOC) and DSi found during winter base flow in a recent study of some headwater lakes and streams of northern Sweden (Humborg et al. 2002). Previous field studies in small tropical watersheds (Cochran and Berner 1996; Alexandre et al. 1997; Oliva et al. 1999), and especially in weathering limited environments (sensu Drever 1997), indicate that vascular plant vegetation appears to be a major factor affecting the silica weathering rate (Drever and Zobrist 1992; Drever 1994; Anderson et al. 2000). In contrast, a negative correlation between vegetation cover, dissolved organic carbon (DOC), and weathering products has been reported by Engstrom et al. (2000) for small lakes in a recently deglaciated terrain in Alaska. However, most of these studies investigating the effect of vegetation on weathering are small in scale (i.e., deduced from soil profile analyses or from investigations in watersheds <100 km^2), and differences in weathering patterns might be explained by local geochemical and hydrological conditions. Thus, there is still a lack of large-scale analyses of how river chemistry is related to landscape variables in boreal and subarctic watersheds that have undergone repeated changes in vegetation cover during glacial cycles (Kohfeld and Harrison 2000) and that could potentially have a major impact on land–sea nutrient fluxes globally. Moreover, an evaluation of potential causal mechanisms regulating river chemistry is also missing. The areas of our study catchments ranged from 34 to 40,000 km^2, allowing us to test whether an effect of vegetation cover on weathering rates can be found over various spatial catchment scales and is, therefore, also displayed in nutrient land–sea fluxes. We use physical geographic, hydrological, and biogeochemical information from northern Swedish river catchments to study how land–sea fluxes of nutrients from boreal and subarctic rivers are regulated.

Materials and methods

Investigated area—Our study encompasses the northern Swedish river systems of Torneälven, Kalixälven, Råneälven, Luleälven, Piteälven, Skellefteälven, and Umeälven, which are ideal case studies with sufficient background data for investigating the significance of vegetation cover on nutrient land–sea fluxes. All studied rivers drain into the northern Gulf of Bothnia (Baltic Sea) and have their headwaters in the mountainous area close to the Norwegian border, except Råneälven, which originates in the eastern forested region (Fig. 1A). The investigated catchments are located between 64° and 69°N, several originating above the Arctic Circle. The whole area is sparsely inhabited and can, apart from regulation of the rivers Luleälven, Skellefteälven, and Umeälven, be characterized as relatively unperturbed. In the Scandinavian mountain range (the Scandes), the climate is typically subarctic, with continuous frost from mid-October to May (Ångström 1974). Westerly winds prevail and deliver 1,000 to 2,000 mm yr^{-1} of precipitation to the headwater areas (Carlsson and Sanner 1994). Cold climate favors boreal biomes (taiga, tundra) as typical also for the large Siberian and Canadian rivers (Kohfeld and Harrison 2000). The spatial vegetation gradient found in our investigated watersheds—from essentially unvegetated rock at the top elevations, through alpine pasture and deciduous brushwood/short deciduous forest, to coniferous forest and mires in the river catchments—represents dominating biotopes of environments deglaciated in the Holocene. The upper mountainous headwater areas (summits below 2,200 m above sea level) are sparsely vegetated or even barren (Table 1), generally with thinner soil thickness than in the forested landscape downstream. The tree line is found at 650–800 m above sea level. Two of the rivers, Kalixälven and Luleälven (Fig. 1B), have been studied in greater detail.

Sampling strategy—Since 1970, the rivers of the present study have been routinely monitored (monthly, $n = 360$) for biogeochemical variables at their mouths by the Swedish University of Agricultural Sciences (SLU, Department of Environmental Assessment). Our own field samplings were carried out in 1999–2001 in the rivers Kalixälven ($n = 8$) and Luleälven ($n = 9$), where several subcatchments, including streams as well as inlets and outlets of natural lakes and reservoirs, were investigated in detail. The water discharge of these high-latitude rivers is dominated by the spring flood in late May to early July, when roughly half of the annual water discharge occurs. We therefore used discharge-weighted mean concentrations (Table 1) of the various constituents to evaluate empirical relationships between physical geographical data and concentration records of dissolved constituents. We chose to sample early winter conditions in November and December and late winter conditions in March, April, and May. We also sampled the spring flood from snowmelt in late May to early July. Summer conditions were investigated during August and September. The sampled catchments, streams, rivers, lakes, and reservoirs are indicated in Fig. 1A,B. The mire-draining stream Muddusätno (Fig. 1B) was sampled monthly ($n = 192$) by the SLU.

Analytical methods—We sampled water directly at the water surface using syringes that were prewashed in 0.1 M hydrochloric acid before sampling. The water samples were

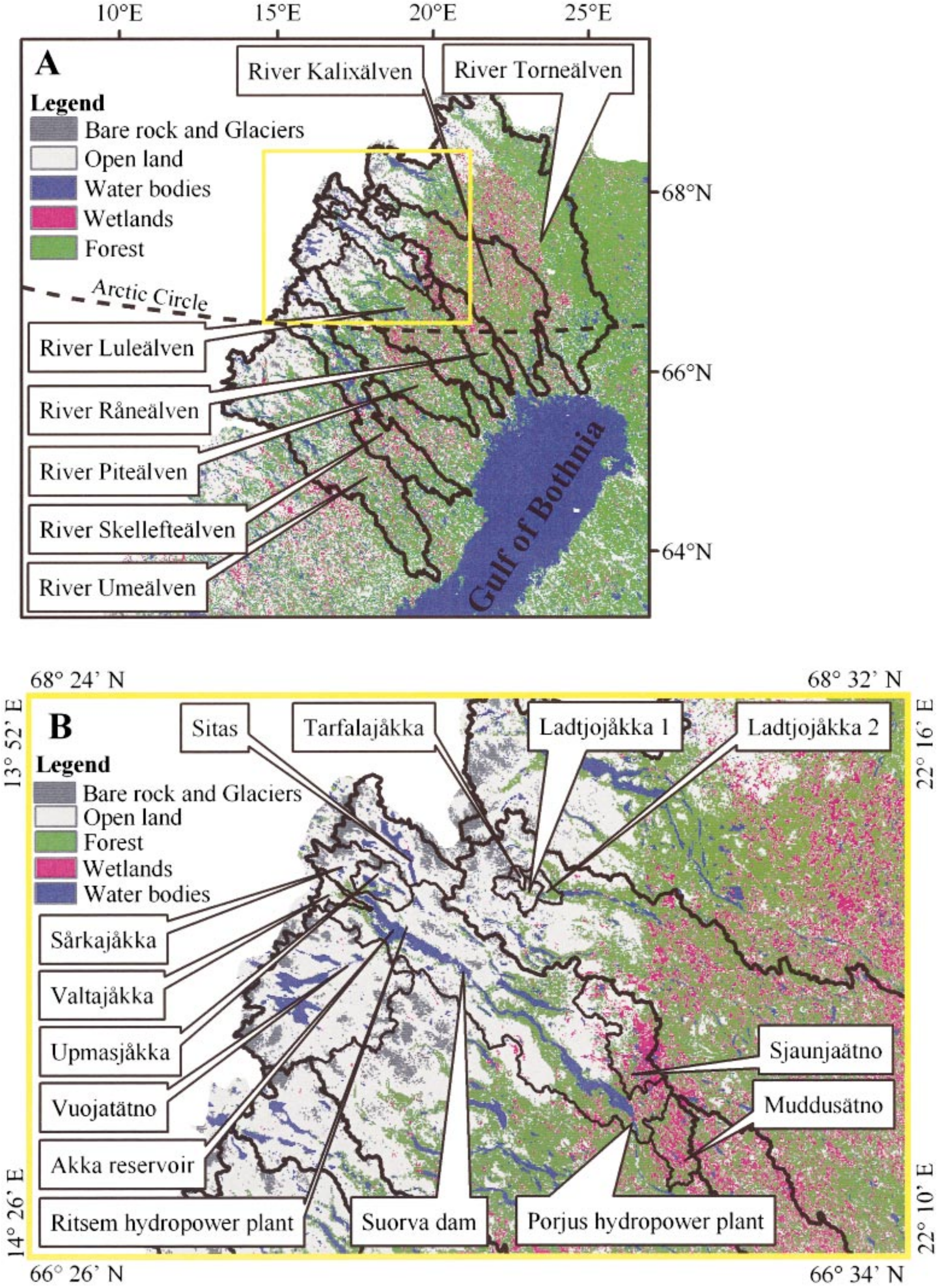

Fig. 1. (A) Catchment areas and land cover characteristics of the investigated major river systems in northern Sweden. (B) Detail of the headwater area of the rivers Kalixälven and Luleälven, showing location of sampling sites, subcatchment areas, and land cover characteristics.

filtered immediately through prewashed cellulose membrane filters (0.45 μm, Millipore®), and the filtrates were collected in carefully cleaned polypropylene and polyethylene tubes and bottles. All containers used for collecting TOC and nutrient samples were prewashed with ultraclean water, and for inductively coupled plasma–optical emission spectrometry (ICP-OES) analysis, they were acid washed. The water samples for ICP analysis were immediately preserved by adding 1 ml suprapur concentrated HNO_3 to each 100 ml of sample. All syringes, tubes, and bottles were precleaned with ultraclean water (ELGA® systems, Maxima Analytica and Spectrum RO1).

The concentration of DIN and dissolved inorganic phosphorus (DIP) was determined colorimetrically by means of flow injection analysis (Lachat®; *see* Ranger 1993) or segmented flow analysis (Flow Solution® IV, Alpkem Corpo-

Table 1. Catchment areas, land cover, water discharge, and discharge-weighted annual mean concentration of total organic carbon (TOC) and dissolved inorganic nutrients (DIN, DIP, DSi; b.d.l., below detection limit) in 19 river systems of northern Sweden. Runoff and river chemistry data from monthly measurements monitored at the river mouths by the Swedish University of Agricultural Sciences, Uppsala, Sweden.

River	Catchment area (km^2)	Wetland (%)	Lake and stream (%)*	Snow and ice (%)*	Unvegetated rock (%)	Open land (%)	Coniferous forest (%)†	Deciduous brushwood/forest (%)‡	Runoff (km^3)	Nutrient (μmol L^{-1})			
										TOC	DIN	DIP	DSi
Torneälven§	39,865	10.3	4.4	1.5	0.3	27.0	41.5	15.0	13.89	540	3.9	0.16	86.5
Kalixälven§	17,994	19.3	2.9	1.4	0.2	21.2	39.5	15.2	10.28	438	6.7	0.15	82.2
Tarfalajåkka	34	0.0	2.0	47.5	2.3	50.2	0.0	0.0	0.02	29	1.8	0.19	22.5
Ladtjojåkka 1	200	0.3	2.8	17.6	2.5	70.6	0.7	5.6	0.12	—	4.5	0.02	53.6
Ladtjojåkka 2	298	0.2	2.9	15.0	3.3	66.1	1.4	11.1	0.17	—	1.9	0.02	66.2
Råneälven§	4,176	26.5	2.8	0.0	0.0	14.1	46.6	9.9	1.47	579	3.0	0.12	97.2
Luleälven§	25,095	8.7	7.8	5.9	0.4	41.5	28.4	7.2	17.50	203	3.1	0.07	39.3
Upmasjåkka	306	0.8	16.1	11.4	0.3	61.5	1.8	8.1	0.31	88	1.9	0.02	17.0
Sårkajåkka	305	0.0	3.6	31.2	0.5	61.4	0.2	3.1	0.36	47	1.6	0.02	9.7
Valtajåkka	147	2.0	0.5	11.5	0.4	70.8	1.1	13.6	0.07	82	1.4	b.d.l.	30.6
Ritsem hydropower plant	973	0.1	9.3	29.0	0.8	60.8	0.0	0.0	1.26	43	2.6	b.d.l.	12.0
Vuojatätno	2,832	0.1	9.4	16.2	0.4	72.9	0.2	0.7	3.43	39	2.6	b.d.l.	15.7
Suorva dam	5,603	0.2	11.8	17.3	0.7	67.0	0.5	2.6	4.86	71	2.3	b.d.l.	13.2
Sjaunjaätno	849	27.7	4.0	0.0	0.0	39.2	21.7	7.4	0.38	360	2.1	0.02	73.2
Porjus hydropower plant	9,828	4.6	11.0	10.5	0.6	59.4	8.8	5.1	8.19	—	1.0	0.02	22.4
Muddusätno‖	450	38.9	2.1	0.0	0.0	6.9	49.5	2.6	0.19	—	3.4	0.08	78.4
Piteälven§	11,221	8.9	6.3	1.3	0.8	32.8	42.3	7.4	5.93	320	3.6	0.09	66.3
Skellefteälven§	11,671	9.4	11.8	1.4	0.4	34.1	34.4	8.2	5.86	321	3.4	0.06	39.9
Umeälven§	26,684	7.9	6.4	1.5	0.4	42.0	32.1	9.5	15.22	325	3.5	0.07	46.8

* Recorded by satellite at the end of June/early July 1999.

† Mainly Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*).

‡ Mainly short deciduous forest/deciduous brushwood of birch (*Betula* spp.) and willow (*Salix* spp.).

§ Runoff and river chemistry data from monthly measurements monitored at the river mouths by the SLU between 1970–2000.

‖ Runoff and river chemistry data from monthly measurements monitored at the river mouths by the SLU between 1988–2000.

ration). DSi was determined by ICP-OES (Varian Vista® Pro Ax). TOC in water samples was determined by a high-temperature combustion technique (Shimadzu® TOC-5000).

Runoff estimates and discharge-weighted mean concentrations—To be able to calculate discharge-weighted TOC and nutrient concentrations, we estimated the water discharge of the various subcatchments of the rivers Kalixälven and Luleälven (Fig. 1B) using a semidistributed conceptual runoff model, the HBV model (Lindström et al. 1997). Here, semidistributed means that a basin can be separated into a number of subbasins and that each one is distributed according to altitude and type of vegetation in the catchment area. Each subbasin can then be further divided into a number of elevation zones, depending on the height variation of the subbasin. The elevation zone was in turn divided into three vegetation classes: forest, open land, and lakes.

The standard routine of the HBV model is based on a degree-day approach involving ambient air temperature as well as water-holding capacity of snow; the latter results in varying delays in the runoff. Primary input data are daily mean values of precipitation, air temperature, and evapotranspiration rate in each subbasin, respectively. The model performance was measured over both a calibration period and a validation period of independent data. The main criterion of the model performance is the R^2 value, calculated according to Nash and Sutclife (1970). The R^2 value was 0.927 for the calibration and 0.890 for the validation periods. The difference in R^2 values reflects a more variable measured flow during the validation period. The high validation R^2 value shows that the HBV model predicts runoff well.

Land cover, soil type, and bedrock—Calculations of percent land cover and of soil and bedrock types for each drainage area were performed by ARC View® 8.1 (ESRI). The drainage basin boundaries were obtained from the Swedish Meteorological and Hydrological Institute. Table 1 summarizes land cover, and Tables 2, 3 soil and bedrock types of the investigated catchments and subcatchments, respectively. The data used for land cover calculations were compiled from satellite images, with a spatial resolution of 150 × 150 m, and various reference data sets provided by Metria Miljöanalys®. Soil and bedrock types have been compiled from geological maps of the Swedish Geological Survey.

Slight differences in lake area percentages between Table 1 and Tables 2, 3 arose because the lake areas given in the land cover and soil type maps were obtained by different methods (i.e., by means of satellite information recorded at the end of June/early July in 1999 [Table 1] and by airplane photography and field mapping of consecutive years [Table 2, 3], respectively). Moreover, different filling stages further resulted in various surface areas of the lakes/reservoirs and

Table 2. Soil types (and percent area of glacier and lake and stream) in the investigated catchments.

River	Catchment area (km^2)	Till below tree line (%)	Till above tree line (%)	Peat (%)	Thin soils and bare rock (%)	Glacio-fluvial sediment (%)	Sand and gravel (%)	Silt and clay (%)	Glacier (%)	Lake and stream (%)
Torneälven§	39,865	34.9	11.8	22.7	12.5	13.1	1.7	0.4	0.1	2.7
Kalixälven§	17,994	45.6	7.4	23.3	9.6	9.7	2.4	0.6	0.2	1.2
Tarfalajåkka	34	0.0	30.4	0.0	43.9	8.4	0.0	0.0	17.3	0.0
Ladtjojåkka 1	200	1.7	41.6	0.0	44.7	1.9	5.9	0.0	4.2	0.0
Ladtjojåkka 2	298	5.3	48.7	0.0	36.4	1.7	5.1	0.0	2.8	0.0
Råneälven	4,176	52.2	0.0	29.0	5.7	8.3	2.5	1.4	0.0	0.8
Luleälven	25,095	35.4	12.6	10.9	25.3	5.6	2.1	1.0	0.7	6.3
Upmasjåkka	306	2.5	19.0	0.0	61.7	0.0	0.0	0.0	0.0	16.7
Sårkajåkka	305	1.9	0.3	0.0	97.6	0.0	0.0	0.0	0.0	0.2
Valtajåkka	147	14.2	4.7	0.8	67.7	9.5	2.6	0.0	0.0	0.5
Ritsem hydropower plant	973	0.0	24.9	0.0	55.7	2.2	0.0	0.0	0.0	17.2
Vuojatätno	2,832	0.9	24.2	0.2	57.8	3.2	1.2	0.0	1.5	11.1
Suorva dam	5,603	1.6	20.7	0.1	59.4	2.2	0.7	0.0	0.9	14.3
Sjaunjaätno	849	47.7	0.6	35.3	6.5	9.8	0.0	0.0	0.0	0.0
Porjus hydropower plant	9,828	16.8	19.5	6.7	40.0	4.2	0.6	1.0	0.6	11.5
Muddusätno	450	40.8	0.0	42.0	4.6	12.7	0.0	0.0	0.0	0.0
Piteälven	11,221	54.9	5.5	7.5	16.6	7.3	2.7	1.3	0.2	4.1
Skellefteälven	11,671	54.4	5.2	10.5	15.0	4.0	1.8	1.5	0.0	7.5
Umeälven	26,684	59.2	12.2	7.5	10.3	4.3	3.1	0.7	0.0	2.7

streams studied (cf. Tables 1–3). ‘‘Snow and ice’’ (Table 1) indicates high-altitude areas of surface draining from snowmelt during summer, whereas ‘‘Glacier’’ (Table 2) indicates strictly glaciated areas, only. Note, that ‘‘Unvegetated rock’’ (Table 1) indicates truly hard rock outcrops, whereas ‘‘Thin soils and bare rock’’ (Table 2) includes soils up to 100 cm thick as well.

The bedrock is usually covered by till (Fredén 1994), sometimes several tens of meters thick. In all, seven soil types were recognized (Table 2). The dominant soil type, till (Table 2; *see* ‘‘Till below tree line’’ and ‘‘Till above tree line,’’ respectively) reflects the regional bedrock composition, which is dominated by minerals like quartz, plagioclase, microcline, micas, and amphiboles.

Bedrock types (Table 3) were grouped according to weathering properties: carbonate rocks and carbonate-rich shale

Table 3. Bedrock types in the investigated catchments. The bedrock types were classified according to their chemical influence on water chemistry (*see text*).

River	Catchment area (km^2)	Shale (%)	Carbonate-rich shale (%)	Carbonate rock (%)	Sandstone (%)	Quartzite (%)	Gneiss (%)	Alkaline rock (%)	Granite and acid volcanic rock (%)	Lake and stream (%)
Torneälven§	39,865	11.6	0.0	0.9	0.4	3.4	23.0	14.6	43.4	2.7
Kalixälven§	17,994	12.3	0.0	0.1	0.1	1.6	3.2	17.6	63.8	1.2
Tarfalajåkka	34	0.0	0.0	0.0	0.0	6.1	23.4	61.5	9.0	0.0
Ladtjojåkka 1	200	0.0	0.0	0.0	0.0	10.1	41.2	40.9	7.8	0.0
Ladtjojåkka 2	298	0.0	0.0	0.0	0.0	7.6	39.7	37.9	14.8	0.0
Råneälven	4,176	12.8	0.0	0.1	0.9	0.0	0.0	13.1	72.3	0.8
Luleälven	25,095	7.0	2.9	1.4	3.2	5.3	11.4	14.2	48.3	6.3
Upmasjåkka	306	24.8	11.3	0.0	0.0	2.6	44.2	0.4	0.0	16.7
Sårkajåkka	305	38.3	15.7	0.0	0.0	1.7	35.0	6.4	2.6	0.2
Valtajåkka	147	2.4	20.8	0.0	0.0	3.3	64.6	0.0	8.4	0.5
Ritsem hydropower plant	973	24.9	9.1	2.0	0.0	15.1	7.9	2.0	21.8	17.2
Vuojatätno	2,832	19.4	16.8	7.2	0.0	3.9	12.4	28.2	1.1	11.1
Suorva dam	5,603	17.8	13.3	4.0	0.0	4.9	25.0	16.8	3.9	14.3
Sjaunjaätno	849	0.3	0.0	0.0	0.0	0.0	0.0	6.6	93.1	0.0
Porjus hydropower plant	9,828	10.2	7.7	2.4	1.4	4.3	18.0	15.9	28.6	11.5
Muddusätno	450	0.6	0.0	0.0	0.0	0.0	0.0	21.9	77.5	0.0
Piteälven	11,221	9.4	0.1	1.0	2.4	9.2	5.0	8.0	60.9	4.1
Skellefteälven	11,671	14.9	0.1	0.5	1.7	10.1	6.9	7.6	50.6	7.5
Umeälven	26,684	23.2	2.6	0.9	0.1	9.7	14.6	6.5	39.7	2.7

Table 4. Results from PCA on landscape variables of 19 river catchments in northern Sweden. Explained variance and loadings for each component and respective landscape variable (Tables 1–3) are reported. Loadings mainly controlling the component (>|0.5|) are marked in bold.

	PC1	PC2	PC3	PC4	PC5
Explained variance (%)	43.2	17.8	11.6	9.3	4.6
Land cover variable					
Wetland	**−0.940**	−0.149	−0.127	−0.003	−0.104
Lake and stream	0.317	−0.358	0.355	−0.170	**0.586**
Snow and ice	**0.635**	0.440	−0.177	−0.576	−0.114
Unvegetated rock	0.435	**0.832**	0.020	0.218	−0.104
Open land	**0.891**	0.113	−0.233	0.060	0.249
Coniferous forest	**−0.847**	−0.206	0.346	0.157	−0.153
Deciduous forest	−0.218	−0.264	0.030	**0.735**	−0.427
Soil type variable					
Till below treeline	**−0.757**	−0.273	0.439	0.233	−0.162
Till above treeline	0.529	**0.721**	−.050	0.231	0.282
Peat	**−0.952**	−0.149	−0.155	0.020	−0.104
Thin soils and bare rock	**0.870**	−0.142	−0.309	−0.282	−0.010
Glaciofluvial sediment	**−0.788**	0.040	−0.210	0.040	−0.312
Sand and gravel	0.128	0.369	0.198	**0.831**	−0.104
Glacier	0.153	**0.796**	−0.050	−0.411	−0.240
Silt and clay	−0.348	−0.211	**0.819**	0.137	−0.050
Bedrock type variable					
Shale	0.412	**−0.617**	0.157	−0.341	0.150
Carbonate-rich shale	**0.640**	−0.498	−0.408	−0.165	0.175
Carbonate rock	0.184	−0.080	−0.080	−0.144	**0.862**
Sandstone	−0.184	−0.119	**0.782**	0.040	0.020
Quartzite	0.436	0.313	**0.563**	0.090	0.196
Gneiss	**0.759**	0.020	−0.363	0.305	−0.342
Alkaline rock	0.020	**0.929**	−0.150	−0.109	0.010
Granite and acid volcanic rock	**−0.924**	−0.134	0.204	0.080	−0.107

(high weathering rate); shale and alkaline rocks (intermediate weathering rate); gneiss, granite, and acid volcanic rock and sandstone (low weathering rate); and quartzite (very low weathering rate). Sandstone and quartzite were chosen as two separate classes because of the higher content of feldspar (plagioclase and microcline) in the sandstone (Björklund 1989) and the higher weathering resistance of the quartzite. Some of the rock types can also contain weathering-resistant clay minerals, especially the shales, which might affect weathering. However, the weathering rates of clay minerals are much less known than those of primary silicate minerals.

Statistical analysis—We used principal components analysis (PCA) and cluster analysis to distinguish landscape characteristics (land cover, types of soil and bedrock) of the river catchments. In addition, multiple linear regression and redundancy analysis (RDA) were performed to statistically test the relationship between river chemistry (TOC and dissolved inorganic nutrients) and landscape variables.

PCA is a common multivariate technique used for data reduction. It ordinates a number of correlated variables along orthogonal principal components, in which the principal components describe the variation within the original data in descending order. In practice, this commonly means that only the first few principal components are needed to describe the major part of the original variation. Each of these principal components is a weighted linear combination of all variables, in which the weight of a variable is called loading. These loadings indicate which variables are primarily responsible for describing the principal components (i.e., those with largest positive or negative loadings have a larger influence than those with small ones; Table 4). Principal scores for each river catchment were calculated as the sum of individual variable loadings (Table 4) multiplied by the area percentage of the corresponding variables in the river catchments (Tables 1–3). Thus, a principal score was calculated for each river catchment and principal component.

Cluster analysis was used to divide river catchments into clusters on the basis of their similarity in terms of all landscape variables. For this study, a hierarchical method, Ward's minimum variance clustering algorithm (Ward 1963), was used. At each iterative step, the clustering routine joins the two clusters that minimize the variance within the cluster and simultaneously maximize the variance between clusters. Clustering was performed on the resulting principal components, similar to that conducted for other environmental data (Danielsson et al. 1999).

We used two independent approaches to statistically test the role of vegetation in regulating river chemistry: multiple linear regression and RDA. Multicollinearity among environmental variables is a common problem in these types of analyses and could cause unstable regression and canonical coefficients. With the use of the orthogonal principal components of the landscape variables, this problem is avoided. Multiple linear regression analysis offers the opportunity to test the linear relationship between a single river chemistry variable (TOC, DSi, DIP, and DIN) and the principal components. RDA is an ordination method applied for multivariate classification, which analyzes linear relationships between several river chemistry variables and principal components (derived from a PCA on landscape variables) simultaneously. Linearity between these variables was tested prior to RDA with the use of detrended canonical correspondence analysis.

The significance of each RDA ordination axis is statistically tested by unrestricted Monte Carlo permutations with forward selection to identify which principal components explained significant ($P < 0.05$) amounts of variation in river chemistry (Ter Braak 1986). The final result is presented in an ordination diagram in which the main pattern of variation in river chemistry and principal components (derived from a PCA on landscape variables) are presented as arrows, together with the distribution of river catchments. Rivers found near the head of an arrow are strongly and positively correlated with that variable (and vice versa). All analyses were made in CANOCO (vers. 4.5; Ter Braak 1990). Some DIP values below the detection limit (*see Table 1*) were replaced by half their detection limit (0.008 μmol L^{-1}) in order to permit their use in the statistical analysis.

Results

PCA and cluster analysis on landscape variables—The landscape characteristics were highly correlated, with 86.5% of the variance explained along the first five principal components (PCs). Table 4 reports the loadings for the various landscape variables within the five PCs. PC1, which describes 43% of the data variance, is characterized by high loadings of peat, wetland, granite and acid volcanic rock, coniferous forest, glaciofluvial sediment, and till below the tree line, but low loadings of snow and ice area, carbonate-rich shale, gneiss, thin soils and bare rock, and open land area (Table 4). Thus, almost all land cover and soil type variables associated with vegetation are linked to PC1, and a high negative score for this component corresponds to catchments with high cover of vegetation. The second principal component (PC2), which describes 18% of the data variance, is described by high loadings of alkaline rock, unvegetated rock, glacier, and till above the tree line, as is typical for periglacial environments in the area. PC3, which describes 12% of the data variance, is described by high loadings of silt and clay, sandstone, and quartzite (i.e., dominated by soil and bedrock types that have low weathering rates). Sand and gravel and deciduous brushwood/forest are the major constituents of PC4, which describes 9% of the data variance, is interpreted as typical for the upper tree line in northern Sweden that consists of short birch (*Betula pubescens tortuosa*). Finally, PC5, which describes 5% of the data variance, holds high loadings for carbonate rock and lake and stream areas.

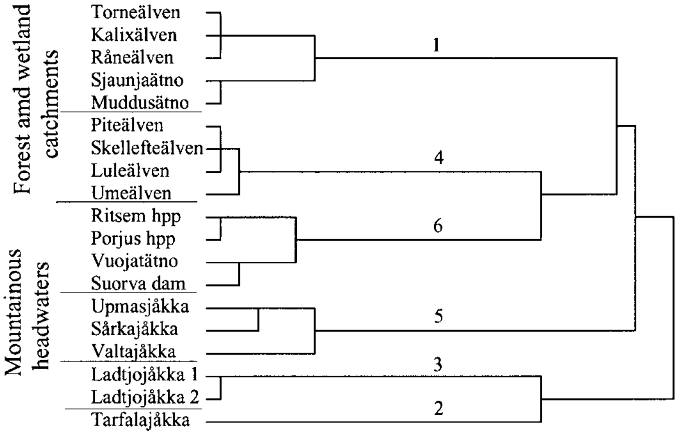

Fig. 2. Dendrogram from Ward's minimum variance clustering with the use of the principal scores of individual river catchments from the five principal components (based on landscape variables) as input variables. The river catchments can be divided in two major groups: mountainous headwaters (four clusters) and forest and wetland catchments (two clusters). The main characteristics are: 2, glacier; 3, alpine area and subalpine birch forest; 5, alpine area (open highland); 6, large lakes/reservoirs. Both forest and wetland clusters have high vegetation cover, whereas cluster 1 is richer in area of wetland and coniferous forest than cluster 4.

The cluster analyses of the five principal components distributed the 19 river catchments into six groups (Fig. 2), which can be further summarized into two major groups: mountainous headwaters versus forest and wetland catchments. The river headwaters have in common that most of their catchments are located above the tree line (i.e., <15% of the catchment area is covered by forest; Table 1). Figure 3 shows the score distribution of the five principal components for headwaters, as well as forest and wetland catchments, respectively. Statistically, the catchments of headwaters, as well as forest and wetland catchments, only differed significantly in terms of land cover and soil type variables associated with vegetation (PC1).

Within the mountainous headwaters, four clusters appeared (Fig. 2). In the first, the headwater of river Kalixälven, with its uppermost glacier stream, Tarfalajåkka, was found (cluster 2). This catchment showed a very high PC2 score and low scores for PC4 and PC5 (i.e., an alpine environment with glaciers and low percentage of lake area). The watercourses Ladtjojåkka 1 and 2, the two downstream stations of the Kalixälven headwater, are located below the tree line. Their catchments were high in scores PC2 and PC4 (i.e., consisted both of alpine environments and subalpine birch forest; cluster 3). The three minor streams discharging into the northwestern part of the Akka reservoir (Upmasjåkka, Sårkajåkka, and Valtajåkka) formed cluster 5, with a highly positive PC1 score and highly negative PC2 score. They all represent open highlands (i.e., alpine environments with low and little vegetation but, in contrast to clusters 2 and 3, with low percentage of snow- and ice-covered areas). Cluster 6 consists of the major inputs to the Akka reservoir (Vuojatätno and Ritsem hydropower plant) and the outlets of the major reservoirs (Suorva dam and Porjus hydropower plant). These catchments are mainly characterized by highly

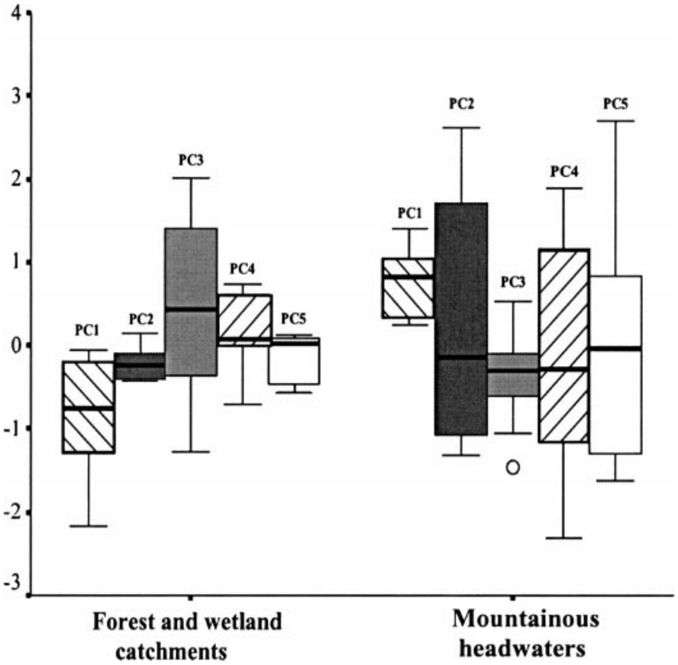

Fig. 3. Box plot of scores for each principal component (PC1–PC5) separated into the two main groups: mountainous headwaters (<15% forest) and forest and wetland catchments. The boxes indicate the 25th and 75th percentiles, the bold line the median value, and whiskers the largest and smallest observations, respectively. One outlier (circle) is excluded.

positive PC5 scores, namely, headwater catchments with a high percentage of lake/reservoir area.

The wetland catchments (Sjuanjaätno and Muddusätno; first-order tributaries) are most similar to the relatively unperturbed river systems Torneälven, Kalixälven, and Råneälven (cluster 1) and are characterized by a high percentage of vegetation (negative PC1 scores). The rivers of Luleälven, Piteälven, Skellefteälven, and Umeälven form the second group of forest and wetland catchments (cluster 4), with slightly negative scores for PC1, related to less vegetation cover (Table 1) compared with cluster 1, but high scores of PC3 from certain occurrence of silica-rich soils and bedrock (Tables 2, 3) with low weathering rates.

River chemistry classified by landscape clusters—A clear relationship appeared when relating the six clusters (based on the landscape variables identified with PCA) to our chemistry data set. The various clusters reappear clearly in the positive relationships between DIP/DSi (Fig. 4A), DIP/TOC (Fig. 4B), and DSi/TOC (Fig. 4C). Highest concentrations of TOC, DIP, and DSi were found in the unperturbed forest and wetland catchments (cluster 1), with lower concentra-

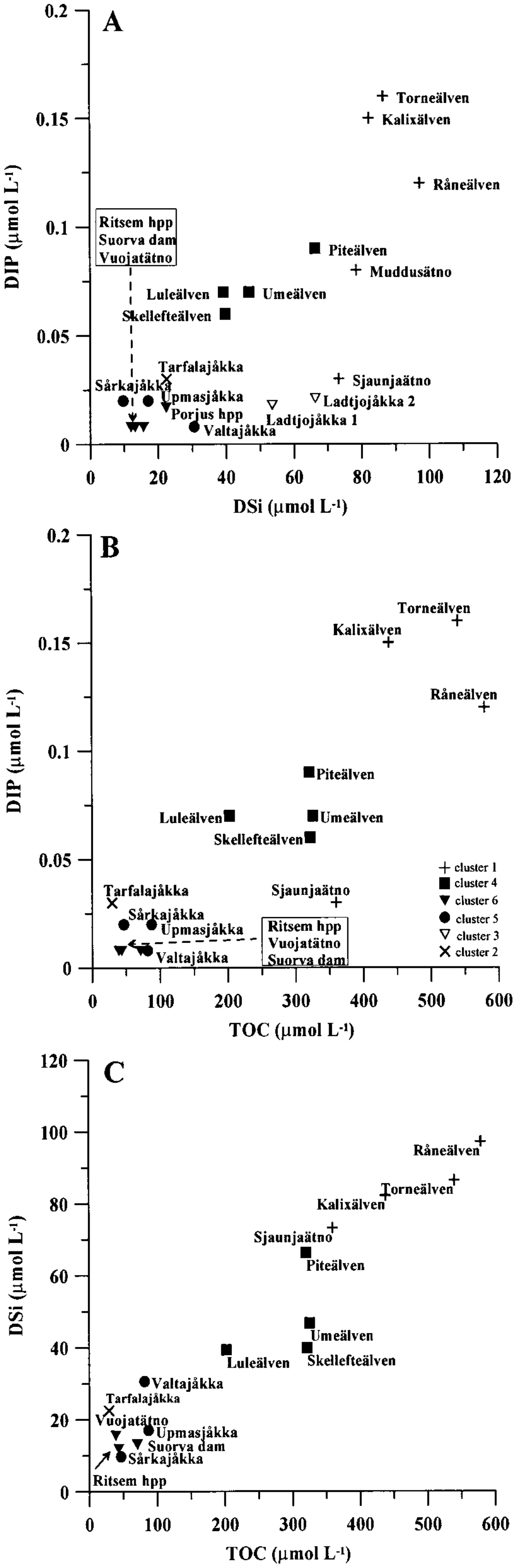

Fig. 4. Relationships of long-term river water chemistry variables (discharge-weighted annual mean concentrations). (A) DIP versus DSi, (B) DIP versus TOC, and (C) DSi versus TOC. River catchments are classified according to cluster identity of Fig. 2; cluster 3 is not shown in Fig. 4B,C because of the lack of TOC measurements. The main characteristics of the headwater clusters are: 2, glacier; 3, alpine area and subalpine birch forest; 5, alpine area (open highland); 6, large lakes/reservoirs. Both forest and wetland clusters have high vegetation cover, whereas cluster 1 is richer in area of wetland and coniferous forest than cluster 4. hpp, hydropower plant.

tions in the rivers of cluster 4, and lowest concentrations in all mountainous headwaters (clusters 2, 3, 5, and 6). TOC, DIP, and DSi concentrations (mean ± SD, μmol L^{-1}) were significantly (Kruskal–Wallis test, $\alpha = 0.05$) lower in headwaters (TOC = 57 ± 23, DIP = 0.021 ± 0.005, DSi = 26 ± 19) than in the forest and wetland catchments (TOC = 580 ± 126, DIP = 0.092 ± 0.043, DSi = 68 ± 21).

The DIN concentration pattern (not shown) differed from that of the other nutrients. Whereas TOC, DIP, and DSi concentrations ranged over about one order of magnitude from the headwaters to the river mouth, DIN concentrations remained rather low, about 2.1 ± 1.0 μmol L^{-1}, regardless of whether the lotic waters originated from catchments dominated by barren ground, forest, or wetland (Table 1). Consequently, DIN concentrations did not change between the clusters, but remained fairly constant.

River chemistry versus landscape variables by multiple linear regression analysis and RDA—Given that the first five principal components explained such a large proportion (87%) of the variation in landscape variables, the relationships of the individual river chemistry variables to the principal components were further analyzed. Ordinary stepwise regression (with the use of partial F-test with criteria entry $p = 0.05$ and removal $p = 0.10$) and with principal components as independent variables and TOC, DIP, DSi, and DIN as dependent variables, resulted in the following statistically significant ($\alpha = 0.05$) relationships.

$$\mathrm{TOC} = 221.2 - 192.2 \cdot \mathrm{PC1} - 65.6 \cdot \mathrm{PC2} \qquad (r^2_{\mathrm{adj}} = 0.80)$$

$$\mathrm{DIP} = 0.05 - 0.03 \cdot \mathrm{PC1} \qquad (r^2_{\mathrm{adj}} = 0.43)$$

$$\mathrm{DSi} = 45.9 - 22.6 \cdot \mathrm{PC1} + 13.4 \cdot \mathrm{PC4} - 7.3 \cdot \mathrm{PC5} \qquad (r^2_{\mathrm{adj}} = 0.87)$$

For DIN, none of the principal components were significant.

As for TOC, DIP, and DSi, the first component was significant throughout. In other words, the higher the percentage of land cover and soil type variables associated with vegetation, the higher the concentrations of TOC, DIP, and DSi. For DSi, PC4 and PC5 also make a significant contribution, with a higher percentage of deciduous brushwood/forest or of sand and gravel relating to higher DSi concentration, whereas percentages of both lake and carbonate rock are linked to lower concentrations. TOC was also negatively associated with the periglacial environment.

RDA was used to statistically determine the relationship between the set of river chemistry variables and the set of principal components. DIN was excluded because in the multiple linear regression analysis, it was not found to correlate to any of the landscape variables studied. Therefore, the following results are restricted to TOC, DIP, and DSi as river chemistry variables. Only PC1 explained significant ($p = 0.002$) amounts of variation in river chemistry. All in all, the principal components explained 89% of the variance in river chemistry, and 74% was related to PC1.

The angles between the arrows of the river chemistry variables (TOC, DIP, and DSi) in the ordination diagram are all small (Fig. 5), indicating high intercorrelation. Both river chemistry variables and river catchments of cluster 1 are highly, negatively correlated to PC1. This is in accord with the results reported above; the river catchments with high percentages of vegetation were negatively related to PC1 (Table 4) and showed highest concentrations of TOC, DIP, and DSi. The rivers of clusters 5 and 6 are found on the negative side of the first axis, together with the arrow of PC1 because both are related to snow and ice, open land, unvegetated rock, till above the tree line and thin soils (Table 4). The arrow of PC4 is located at the positive site of the first axis, indicating that deciduous brushwood/forest also might be related to river chemistry variables. The first axis also explains 99.9% of the variance in the relation between river chemistry and landscape variables.

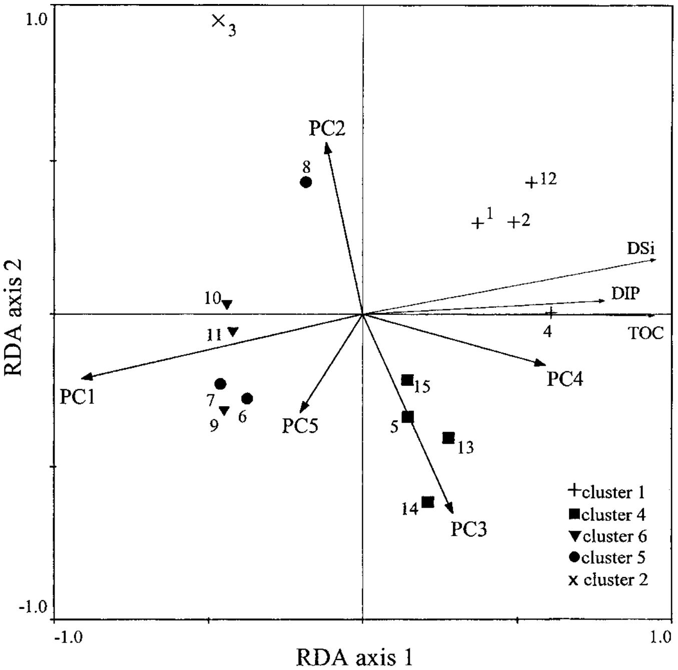

Fig. 5. Redundancy analysis (RDA) ordination diagram. River chemistry (TOC, DIP, and DSi) and landscape variables (PC1–PC5) are shown as arrows. The river catchments are presented according to cluster identity of Fig. 2. The river catchments are: 1, Torneälven; 2, Kalixälven; 3, Tarfalajåkka; 4, Råneälven; 5, Luleälven; 6, Upmasjåkka; 7, Sårkkajåkka; 8, Valtajåkka; 9, Ritsem hydroelectric power plant; 10, Vuojatätno; 11, Suorva dam; 12, Sjaunjaätno; 13, Piteälven; 14, Skellefteälven; 15, Umeälven.

Discussion

Our study of entire landscapes in northern Sweden suggests that the effects of vegetation cover on weathering processes also are found at larger scales. This is indicated by the clusters of landscape variables related to TOC, DIP, and DSi concentrations, irrespective of catchment scale (Figs. 4A–C, 5). Thus, the presence of coniferous forest and wetland/peat, in combination with glaciofluvial sediments and till below the tree line overlying granite and acid volcanic bedrocks (Table 4), coincides with high TOC, DIP, and DSi concentrations in the boreal and subarctic river catchments studied. In contrast, the DIN concentrations were not significantly correlated to landscape characteristics. Possibly, this

DIN might emanate from atmospheric deposition and biological (diazotrophic) fixation, whereas TOC, DIP, and DSi contribute to or result from weathering processes. A major implication from this study is that changes in landscape characteristics during glacial cycles might have affected land–sea fluxes of TOC, DIP, and DSi significantly.

Vegetation control versus temperature and physical weathering—The evaluation of potential causal mechanisms regulating river chemistry in boreal and subarctic watersheds revealed a clear response. PC1 is negatively associated with landscape variables that are typical for deglaciated environments (i.e., mainly by coniferous trees and wetlands and soil types of peat, glaciofluvial sediments, and till below the tree line). The river systems with the lowest scores for PC1 had the highest TOC, DIP, and DSi concentrations (cluster 1; *see Fig. 2; Table 1*). The RDA analysis demonstrated a significant relation between river chemistry and landscape variables (Fig. 5), in which all land cover and soil type variables associated with vegetation (PC1 and PC4; *see Table 4*) contribute strongly in describing the variation in TOC, DIP, and DSi.

A large effect of temperature on river chemistry can be ruled out because the temperature differences between the mountainous headwaters and the river mouths are quite small. In the Luleälven River, for example, the mean annual temperature is -0.1°C in the headwaters (Ritsem), -0.3°C at a station located in the middle of the catchment (Porjus), and $+2.5$°C at the river mouth. The weathering rate increases by about 6% for each degree C as calculated for plagioclase (by the Arrhenius equation and an activation energy of 10 kcal mol^{-1}; *see* Lasaga 1998). Thus, a catchment-integrated increase in weathering in the investigation area because of temperature is probably $<10\%$. Moreover, landscape characteristics associated with periglacial environments (i.e., snow and ice, unvegetated rock, thin soils and bare rock, as well as till above tree line) appear to have little influence on biogeochemical dynamics, in contrast to what has been previously suggested (Froelich et al. 1992).

Low concentrations of TOC and dissolved inorganic nutrients that resemble that of rain and proglacial meltwater (Humborg et al. 2002; Thillman 2003) were found both in pristine systems, such as Tarfalajåkka (cluster 2; *see Fig. 2*) and the headwaters of the Akka reservoir (cluster 5; *see Fig. 2*), as well as in the major inputs to and outlets from the major reservoirs of the Luleälven headwaters (cluster 6; *see Fig. 2*). In all these, water has had essentially no contact with vegetated soils. In the uppermost headwater of the Kalixälven River, sparsely vegetated rock matter or alpine pastures with a thin soil layer dominate the landscape. In the Luleälven River system, 95% of the water running into the Akka reservoir is from areas above the tree line. Thus, the biogeochemistry of the water systems above the tree line is spatially and temporally uniform, although freshly weathered rock matter is continuously produced, for instance, by glaciers. When deciduous brushwood/forest appears, concentrations of dissolved constituents increase, as demonstrated in the Ladtjojåkka 1 and 2 streams (cluster 3; *see Fig. 2*), which showed higher DSi concentrations than the other headwaters, presumably as a result of a combination of weathered soils and the appearance of more vegetation.

Damming strongly affects the land–sea fluxes of TOC and nutrients (Humborg et al. 2002). In the mountainous headwater of the Luleälven River, damming has inundated the river valley, causing major losses of vegetated soil. In total, 15 major dams are located along the Luleälven River. Hard rock fragments and organic matter in the littoral zone of these reservoirs are easily washed away. In reaches between the reservoirs, underground headrace channeling of water in combination with a reduction of water level fluctuations has further decreased soil–water contact and, consequently, lowered the weathering rates. Therefore, the river biogeochemistry of the Luleälven River is uniform in space (Table 1) and time and resembles that of periglacial systems with sparse vegetation and low weathering regimes (Humborg et al. 2002). The somewhat higher nutrient concentration at the river mouth can be explained by tributaries draining wetlands (i.e., Sjaunjaätno and Muddusätno; Table 1). However, the rivers of Piteälven, Skellefteälven, Luleälven, and Umeälven form a distinct group of their own (cluster 4; *see Fig. 2*). In fact, they have low scores for all components except PC3 (Table 4), described by high loadings for silt and clay, sandstone, and quartzite. However, it is not very likely that the presence of the latter soil and bedrock types (*see area percentages in Tables 2, 3*) will affect river biogeochemistry. More important, the transformations of wetlands and forests into lake (reservoir) areas have certainly resulted in reduced scores for PC1 (Table 4) in the three regulated rivers of Luleälven, Skellefteälven, and Umeälven.

TOC as a large-scale proxy for organic degradation and chemical weathering—Our multivariate statistical analyses on landscape variables and river biogeochemistry integrate small-scale interactions between bedrock, soil, pore water, and biota (from microbes to vascular plants) and provide evidence that they also are significant on a larger scale in weathering-limited environments, such as the studied boreal and subarctic watersheds. On the basis of laboratory studies, it is well known that chemical weathering rates of silicate minerals in acid solutions are related to temperature and pH (Brantley and Stillings 1996; Lasaga 1998), as well as the presence of organic (ligand/acid) compounds (Amrhein and Suarez 1988). It has also been argued that the concentration of such organic compounds under normal soil conditions seems too low to significantly increase the weathering rate (Drever and Stillings 1997) and that weathering products even decrease with increasing vegetation and soil cover (Engstrom et al. 2000). However, the latter study was performed in an area rich in carbonate, where calcium fluxes decreased when the formerly exposed (easily weathered) bedrock was covered with soil and vegetation. This contrasts with our findings and previous field studies in deglaciated terrain dominated by bedrock rich in feldspar and quartz covered with till (Drever and Zobrist 1992; Anderson et al. 2000) that show that vascular plant vegetation appears to be a major factor in increasing the weathering rate of silica and phosphorus.

Among plausible chemical mechanisms by which vascular plants might enhance the weathering rate, three main processes are discussed in the literature: root exudation of organic acids (Grayston et al. 1997), the activity of ectomycorrhizal fungi (van Breemen et al. 2000; Landeweert et al. 2001), and associated mineral dissolution by bacteria (Bennett et al. 2001). In high-latitude river systems, TOC often consists of >80% DOC (cf. Wetzel 2001) and can be regarded as a proxy for various organic acids and ligands formed. The positive correlation between TOC and both DIP and DSi is striking (Fig. 4B,C). That DOC is a function of forest cover has also been reported for subarctic lakes in Canada (Pienitz and Vincent 2000). Intriguingly, the area of deciduous brushwood/forest in our studied catchments (Table 1; PC4 in Table 4) appeared less significant for river biogeochemistry than that of coniferous forest or wetland (PC1; *see Table 4*). Moreover, in our investigated area, the biomass per unit area of deciduous brushwood/forest (i.e., mainly birch, *Betula* spp., and willow, *Salix* spp.) is often less than that in wetland or coniferous forest, the latter dominated by Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*). In support of our findings, a long-term field study in France has reported that coniferous species enhance the weathering rate on feldspar, compared with broad-leaved deciduous trees (Augusto et al. 2000).

Northern Swedish rivers as model systems for high-latitude areas—Mean global concentrations of TOC, DIN, DIP, and DSi for recent unperturbed subarctic and boreal rivers are estimated at 750, 6, 0.1, and 110 μmol L^{-1}, respectively (Meybeck 1979, 1982). The investigated Swedish rivers, and especially the unperturbed forest and wetland catchments (cluster 1), represent these conditions reasonably well (Table 1). Most riverine nutrient inputs to the Arctic Ocean come from Russia, and an extensive data set has recently been intercalibrated (Holmes et al. 2001). DIN values reported from the three largest Siberian rivers, Ob, Lena and Yenisey, respectively (Holmes et al. 2000), show low concentrations comparable to the studied rivers of Northern Sweden (Table 1). Time series of DIP from the rivers Lena and Yenisey indicate concentrations between 0.1 and 0.3 μmol L^{-1}, respectively (Holmes et al. 2000, 2001). Concentrations of TOC and DSi in the major Siberian rivers likewise resemble our records (Table 1; Fig. 4). Mean TOC and DSi concentrations of major Siberian rivers, including the Lena, Ob, Yenesey, and Onega, are 615 and 95 μmol L^{-1}, respectively (Gordeev 2000). Thus, the fragmented data sets of major arctic Siberian rivers indicate that their nutrient concentrations and dynamics are similar to those presented here for the northern Swedish rivers. Also, a recent study in the Mackenzie River Basin, Canada, reported mean DOC and DSi concentrations of 1,088 and 78 μmol L^{-1}, respectively, and positive relationships between DOC and DSi concentrations, as well as DOC concentrations and weathering rate estimates (Millot et al. 2003).

Similar patterns in river chemistry appear even in the Southern Hemisphere. Stream chemistry data from unpolluted primary forests in temperate South America exhibiting a broad range of environmental factors that influence ecosystem nutrient cycles showed a remarkably consistent pattern of low nitrogen loss from all forests. As in our study, stream nitrate concentrations were exceedingly low, and dissolved organic nitrogen was the main fraction of nitrogen loss from these forests (Perakis and Hedin 2002). Assuming our findings to be general for high-latitude areas, we suggest that changes in type and cover of vegetation from glacial to interglacial periods might increase TOC, DIP, and DSi fluxes to the sea by an order of magnitude, in contrast to DIN fluxes, which might have remained constantly low.

The potential effect of such variations in river chemistry is challenging, for instance, when considering the melting of the North American Laurentide Ice Sheet in the Younger Dryas. During this period, the river discharge of the St. Lawrence increased to 2×10^5 m^3 s^{-1} (Clark et al. 2001), and simultaneously the vegetation along the ice edge changed from polar desert or tundra to coniferous and broad-leaved forest (Kohfeld and Harrison 2000). Given that much of this water had passed through the forested landscapes, this single river could then have transported about 0.6 Tmol DSi into the North Atlantic each year, which is more than 10% of the total present annual supply to the ocean (Tréguer et al. 1995). In contrast, DIN and DIP concentrations in high-latitude rivers were presumably low throughout glacial cycles, and even lower than in the recent Arctic Ocean, North Atlantic, and North Pacific (Levitus et al. 1993). Thus, much of the nitrogen supply to the northern marine environments might have come from biological nitrogen fixation in the warmer areas of the ocean, which has been assumed to be highest in glacial periods (Falkowski 1997). During glacial periods, the low DSi supply to the northern seas presumably slowed the biological pump (Dugdale et al. 1995), whereas during periods of active deglaciation, the DSi supply to the northern marine environments has probably been maximal. The biological pump is most sensitive to diatom production, and hence DSi variations. It can be estimated from global ocean carbon and DSi budgets (Tréguer et al. 1995; Falkowski et al. 1998) that diatom sedimentation is responsible for more than half of the carbon export production of the contemporary ocean.

The biogeochemistry of high-latitude rivers is greatly influenced by vegetation cover and soil types such as peat. Thus, vegetation changes during the deglaciation process are likely to have had major effects on river biogeochemistry and land–sea fluxes. For instance, inputs of TOC and DSi to the ocean from formerly glaciated areas could have increased by an order of magnitude after deglaciation, judging from the spatial vegetation gradient in our study and vegetation change between glacial and interglacial periods. This would have had crucial effects on coastal environments (Humborg et al. 1997, 2000; Ittekkot et al. 2000) and possibly even in midlatitude areas of the North Atlantic, where DSi at present is often found in low concentrations after the spring bloom (Levitus et al. 1993). A lower input might even lead to Si limitation in the North Atlantic or elsewhere as reported for some of the high nitrate–low chlorophyll areas in contemporary upwelling Pacific water, where DSi set the upper limit on the total possible biological utilization of dissolved inorganic carbon (Dugdale and Wilkerson 1998). Finally, because global warming is believed to be especially pronounced at high latitudes in the Northern Hemisphere (IPCC 2001), a change in structure and cover of vegetation could quite rapidly alter the biogeochemistry of river catchments and land–ocean interactions along the coasts of the Arctic Ocean.

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