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Weathering rates and origin of inorganic carbon as influenced by river regulation in the boreal sub-arctic region of Sweden

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Abstract

Major environmental stressors of boreal and sub-arctic rivers are hydrological changes and global warming and both factors will significantly influence the future evolution of the river chemistry in high latitudes. We tested the hypothesis whether lower concentrations of dissolved constituents observed in regulated rivers come along with lower weathering rates, though specific discharge as a major force for physical erosion and weathering is often higher in regulated river systems. In this study the river chemistry, weathering rates and related carbon dioxide consumption in two large watersheds in the sub arctic region of Sweden, one regulated river (Lule River) and one unregulated river (Kalix River), was investigated. Weathering rates of silicates in the two watersheds are shown to be different; the silicate weathering rate in Kalix River catchment is almost 30% higher than in the Lule River catchment. This is most likely a result of constructing large reservoirs in the former river valleys inundating the alluvial deposits and thus decreasing soil/water contact resulting in lower weathering rates. Furthermore, the difference observed in weathering rates between lowland regions and headwaters suggests that weathering in sub arctic boreal climates is controlled by the residence time for soil water rock interactions followed by lithology. The chemistry in the two rivers shows weathering of silicates as the origin for 68% of the inorganic carbon in the Lule River and 74% for Kalix River.

The study clearly shows that river regulation significantly decreases alkalinity export to the sea because lower weathering rates gives less carbon dioxide ending up as DIC. By considering sources for inorganic carbon we here report that the inorganic carbon load that originates from respiration of organic matter in soils makes up of 30% and 35% of the total C export for the watersheds of the Kalix River and Lule River, respectively. Therefore, both the inorganic (i.e. the origin of carbon in DIC) and organic carbon load carbon must be considered when studying climate changes on the organic carbon load since effects from increased degradation of organic matter may lead to more weathering (higher production of DIC).

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1 Introduction

River exports of dissolved solids (Si, Ca, Mg, Na, K, HCO$_3$) are closely linked to weathering rates of silicate and carbonate minerals (Berner and Berner, 1996; Humborg et al., 1997), and river chemistry supply and retention reflect the processes in soils and
5 along the aquatic continuum. The chemical weathering rate of silicate minerals is controlled by a proton promoted part and a ligand promoted part (Amrhein and Suarez, 1988). The most important proton source is carbonic acid originating from either (*i*) atmospheric CO_2 that is dissolved in water, or (*ii*) respiratory formed CO_2 originating from the degradation of organic matter. Other significant factors controlling the weath-
10 ering regime in a river catchment is temperature, specific runoff (Berner and Berner, 1996) and physical erosion (Gaillardet et al., 1999).

Comparisons between regulated and non-regulated rivers have often shown that regulated rivers have lower concentrations of major elements (Humborg et al., 2000, 2004) and it has been argued that the lower concentrations in boreal watersheds of northern
15 Sweden are an effect of "less" weathering in the regulated watersheds (Humborg et al., 2004). However, lower concentrations of dissolved constituents in regulated rivers may also be related to a high specific discharge, i.e. a dilution effect, since rivers with a higher specific discharge are preferentially regulated due to higher energy gains. Thus, the main aim of this study was to compare specific weathering yields (mol km^{-2} yr^{-1})
20 between a regulated and an unperturbed watershed, since these can be directly related to possible differences in mass fluxes of major dissolved constituents such as Si and alkalinity. Special emphasis on these weathering related constituents have been given, since the Si export influences diatom production in coastal seas and the alkalinity export (mainly as HCO$_3^-$) is a significant variable for regional carbon budgets (Raymond
25 and Cole, 2003).

River geochemistry has, in many studies since the pioneering work of Garrels and Mackenzie (1971), given important information about denudation rates of biogeochemical elements and the related consumption of atmospheric CO_2. Several different ap-

proaches have been applied for these calculations ranging from studies of small rivers draining one rock type under a given climate condition (Amiotte-Suchet and Probst, 1993; Bluth and Kump, 1994; White and Blum, 1995) to a more global perspective, studying the very large rivers' geochemistry (Berner et al., 1983; Gaillardet et al., 1997; Holland, 1978). One such study is of the Amazon River by Gaillardet et al. (1999) and Mortatti and Probst (2003). It stressed the importance of physical erosion and its relation to chemical weathering. Similar relations have also been observed in small catchments of the Canadian Shield that is comparable to our investigation area (Millot et al., 2002). In this study we have used a method presented by Mortatti and Probst (2003), to compare (*i*) river chemistry, (*ii*) weathering rates and (*iii*) consumption/sequestration of CO_2 during weathering of primary minerals between two boreal sub arctic rivers, Lule River (heavily regulated) and Kalix River (unregulated).

2 Material and methods

2.1 Study area

The Lule and Kalix River basins are located in the sub arctic boreal climate zone of northern Sweden. In total, the two drainage basins cover an area of nearly $50\,000\,\mathrm{km}^2$ (Lule River: $25\,225\,\mathrm{km}^2$ and Kalix River: $23\,846\,\mathrm{km}^2$). The rivers have their headwaters in northwest, close to the Norwegian border in the Scandinavian Caledonides, and they flow southward to southeast into the foothills and the boreal forested lowland of the Precambrian basement. They finally drain into the Bothnian Bay (Northern part of the Baltic Sea). Lule River has been regulated since the early 1900s with the latest regulation in the 1970s. In 1923 the Akkajaure reservoir, sometimes also called the Suorva dam, (Fig. 1) was erected, today with water level amplitude of $33\,\mathrm{m}$ and an active storage capacity of $5.9\,\mathrm{km}^3$ of water. Except for the water regulation of Lule River, the two rivers can be considered as relatively unperturbed due to the sparse population. Therefore, these two rivers are optimal for investigations of controlling weathering

factors in a sub arctic boreal environment. The rivers drain through similar geological settings, which make them an excellent investigation area to study the effects of hydrological alterations on river biogeochemistry as such.

The mean water discharge for Lule River and Kalix River is 17.6 km^3 yr^{-1} and 9.3 km^3 yr^{-1} respectively, and the mean annual precipitation for the basins is 698 mm and 544 mm, respectively. Westerly winds from the Atlantic Ocean are prevailing delivering high precipitation in the headwater of Lule River, with mean precipitation of 1200 mm yr^{-1}. Rain shadow in the headwater of Kalix River gives a mean annual precipitation of only half of that observed in headwater of Lule River (Table 1). Most of the precipitation is accumulated as snow; this accumulation starts normally in October and ends in June. The snow melts during early summer, which results in high discharge during a short time period (May to July). The cold climate with annual mean air temperatures close to –2°C in the headwaters and about +1°C at the river mouths (Table 1), also leads to high runoff ratios as seen for headwaters in Table 1. The overall hydrology is presented in Table 1.

In the headwater areas above the tree line (about 650–800 m a.s.l.), the vegetation cover is mainly alpine heath. Barren lands, with no soil layer, and glaciers are also found. In the forested lowland the soil thickness becomes greater. The soils are dominated by till containing minerals like Quartz, K-feldspar, K-mica and Plagioclase with a minor percentage of mafic minerals, like Amphibole, Clorite, Epidote and Pyroxene. Alluvial deposits are found along the main river valleys where soil thickness is found several times larger than in the upstream catchments; this is especially true for the headwaters. The forested lowland is vegetated with shrub and brushwood, deciduous and coniferous forests but also mires. Muddus River is a good example of a lowland tributary to Lule River. It is a typical boreal river influenced by its large amount (42%) of mires (Humborg et al., 2004).

2.2 Geological settings

The Swedish Caledonides are divided into five main tectonic units; the uppermost thrust rocks, the upper thrust rocks, the middle thrust rocks, the lower thrust rocks and the autochthonous sedimentary series in the easterly marginal zone of the Caledonian thrust succession. These sedimentary series consist of phanerozoic sediments, mainly sandstone and shale (Gee and Zachrisson, 1979; Kulling, 1964, 1972, 1982).

The Akkajaure reservoir is situated in a U-shaped valley, surrounded by the middle thrust rocks, the Akkajaure Nappe Complex, which is the dominant tectonic unit in the headwater of Lule River (Gee and Zachrisson, 1979; Kulling, 1964, 1982). Precambrian gneissic granitoids, gneissic granites, granites and syenites, dominate the Precambrian acid igneous rocks of the middle thrust rocks within the headwater of the Akkajaure reservoir (Björklund, 1985; Kulling, 1964). In the catchment of Vuojatätno, located in the southwestern part of the basin, the uppermost and upper thrust rocks dominate, here consisting of minerals like mica-schist, calcareous mica-schist, marbles and minor occurrences of amphibolites (Björklund, 1985; Kulling, 1964). Calcite and Dolomite occur frequently (Kulling, 1982).

In Sweden the highest mountains are located within the upper thrust complex, e.g. the massif of Akka (2010 m a.s.l.), in the headwater of Lule River, and the Kebnekaise Mountains (2103 m a.s.l.), in the headwater of Kalix River (Kulling, 1964). The upper thrust rocks are dominating in the headwater of Kalix River. Andreasson and Gee (1989) have identified three major tectonic units in the area: the Tarfala amphibolite, the Storglaciären gneiss and the Kebne dyke complex. The dyke complex consists of mafic rocks with subordinated metasediment. The mafic rocks of the highest mountains have been referred to as amphibolites by Kulling (1964). However, Andreasson and Gee (1989) suggested that the Kebnekaise massif might be dominated by dolerite. At lower altitudes in the downward succession, the Storglaciären gneiss is exposed consisting of mylonitic granitoids. Below this rock there is the Tarfala amphibolite. These rock successions are probably similar for the surrounding mountains i.e. Ladtjovagge val-

ley. The Precambrian crystalline basement is visible in the valley of Tarfalavagge and Ladtjovagge. The percent of main bedrock type in each investigated catchment, except for Killingi in Kaitum River, is presented in Table 2.

3 Sampling and methodology

In the headwaters of the Lule River catchment all main tributaries to the Akkajaure reservoir were sampled; additionally, depth profiles in the reservoir itself were also taken. In the Kalix River Basin samples were taken in the Ladtjo River at the inlet of Lake Paijtas (Fig. 1). The sampling period was from June 2000 to April 2001. Samples were taken at three yearly hydrological events: base flow (winter flow) in April, spring flood in June and summer/autumn flow in September/October.

The water samples were collected directly at the surface by syringes or with a Teflon coated Ruttner-type sampler (Limnos), pre-washed in 0.1 M hydrochloric acid and carefully rinsed with ultra-clean water. The water samples analyzed for dissolved elements were filtrated through pre-washed cellulose membrane filters (0.45 um Millipore) and collected in acid washed polyethylene bottles. For conservation of cations, one ml of SUPRAPURE nitric acid (65%) (MERCK 1.00441.100) was added for every 100 ml of water in the field. Dissolved element concentrations were analysed with ICP-OES (inductively coupled plasma-optical emission spectrometer) Varian Vista Pro Ax, with an analytical precision of better than 4% (typically less than 2%), based on measurements of certified standards. The anions were analysed with IC (Ion Chromatography, Dionex DX-300 system equipped with an AS14 column and using electric suppression). The analytical precision for IC analysis was also better than 4% (but typically lower), based on measurements of certified standards.

Alkalinity of filtrated water samples was determined by a modified back titration method (Almgren et al., 1983), using an automatic titration unit equipped with; a Metrohm 632 pH-Meter and a reference electrode, Metrohm 6.0219.100, a Metrohm 655 Dosimat and a Metrohm 614 Impulsomat. The samples were weighted and titrated

with acid in room temperature down to pH 4.0, with 0.1M hydrochloric acid (Titrisol, MERCK). The alkalinity (as HCO_3^-) was calculated from the difference between the amount of acid added and the excess acid present. The excess acid was determined by adding 0.1M sodium hydroxide (Titrisol, MERCK) to pH 5.6.

5   Total organic carbon, TOC, was determined on unfiltrated water samples using a Shimadzu TOC-5000-analyzer (fluid injection, catalytic combustion).

Selected water samples were analyzed for their mass ratio of $^{87}Sr/^{86}Sr$. This was done after filtration of the water samples and an ion-exchange to enrich the Sr concentration. Thereafter the collected Sr was coated on wire filaments. The Sr isotope

10   composition was analyzed by using a thermal ionisation (solid source) mass spectrometer (TIMS, Finnigan Mat 262) at IFE, Oslo, Norway. The precision was better than ±0.000001.

3.1   Calculation of water discharge and precipitation volume

The flow discharge and precipitation volume, for water mass balance calculations has

15   been quantified with a hydrological model, called the HBV model. The model was developed at the Swedish Meteorological and Hydrological Institute (SMHI) in the early 1970s (Bergström and Forsman, 1973) for runoff simulation and hydrological forecasting. The model has been modified many times since then, but the main modelling philosophy has been unchanged. Details of its application on the Akkajaure catchment

20   are found in Sahlberg (2004).

3.2   Precipitation chemistry and calculation of fluxes

To be able to calculate weathering rates good estimates of water fluxes (precipitation and runoff) are essential. When watersheds are located in areas where precipitation is not strongly acidic, the chemical weathering can be considered as a function of:

25   Chemical weathering = element fluxes – deposition

This type of approach does not consider cation exchange or biomass uptake, which

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are considered to be in steady state (Drever and Clow, 1995). The major difficulty is to get valid deposition figures for the whole catchment. This simplified relation is realistic only if the deposition encompasses all atmospheric inputs including bulk precipitation, dry deposition and throughfall.

5 The element concentrations in the precipitation (bulk deposition), from nearby meteorological stations were used to calculate the deposition (Table 3). The headwater precipitation concentrations in Lule River are mean values from three different stations, one situated in Norway, the European Monitoring and Evaluation Programme (EMEP)-station Trustervatn (http://www.emep.int/), which is situated at 65°50′ N and

10 13°55′ E, near the Atlantic coast at an altitude of 439 meters above sea level. The other two are situated in Sweden; the Swedish Programme for Environmental Monitoring (PMK)-station Abisko (http://www.ivl.se/miljo/), 68°21′ N and 19°03′ E, and the EMEP-station Ammarnäs (http://www.emep.int/), 65°58′ N and 16°12′ E. Abisko was used for the headwaters in Kalix River, and the PMK-station Pålkem (http://www.ivl.se/miljo/),

15 66°26′ N and 20°38′ E, for the river mouth of Kalix River and Muddus River in the lowland of Lule River.

Due to the large drainage area of the Lule River, ranging from the west near the Atlantic coast to the west coast of the Bothnian Bay (Baltic Sea), spatial variations in rain water composition make it difficult to calculate the mean elemental deposition

20 for the whole area (i.e. at the river mouth) without separating the area into smaller regions. We divided the area in a headwater area, contributing to nearly half of the total runoff in the basin, and a lowland region, contributing the other half. For the elemental deposition of the Lule River basin, a mean value has been taken between the precipitation chemistry at the PMK-station Pålkem, here representing the lowland

25 region of Lule River basin and the headwater elemental concentration in rainwater. The main difference between the used precipitation chemistry stations are caused by the distance to the Atlantic and the sea salt contribution. The high concentrations of nutrients (NO_3 and NH_4) and sulphate (SO_4) in rainwater close to the Bothnian Bay coast are probably caused by anthropogenic pollution.

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3.3 Weathering rates and CO_2 consumption

River geochemistry contains information about both the supply of ions to the liquid phase, i.e., by the lithology, and the retention of ions, i.e., removal of ions during formation of clay minerals for example. The procedure for calculation of total atmospheric/soil CO_2 consumed by rock weathering of carbonates and silicates, as well as alkalinity (HCO_3^-) follows the hypothesis outlined by Mortatti and Probst (2003). The consumed atmospheric/soil CO_2 is as follows (for an explanation of used abbreviations see Table 4);

$$CO_{2atm} = Na_{sil} + K_{sil} + 2Ca_{sil} + 2Mg_{sil} + Mg_{carb} + Ca_{carb} \qquad (1)$$

and the produced alkalinity/HCO_3^-;

$$HCO_{3total} = Na_{sil} + K_{sil} + 2Ca_{sil} + 2Mg_{sil} + 2Mg_{carb} + 2Ca_{carb} \qquad (2)$$

The difficulty with this approach is to distinguish the Ca and Mg silicate contribution of the total fluxes of Ca and Mg. Attempts have been made; by using the ion ratio (Na+K)/(Ca+Mg) in stream water draining only silicate rocks (Probst et al., 1994), or by using the average ratio Ca/Na and Mg/Na of runoff water draining a granite shield basement (Drever, 1997). We have used the ion ratios Ca/Na=1.10 and Mg/Na=0.43, calculated for Råne River, which drains an area in between Lule- and Kalix River Basins where the bedrock consists mainly of Precambrian silicate rocks (Humborg et al., 2004). The Ca/Na and Mg/Na ratios multiplied by the sodium concentration at the different locations represent the Ca and Mg derived from silicates.

All HCO_3^- produced by silicate weathering (see Reaction 3–5 below) is of atmospheric/soil origin, whereas for carbonate weathering (Reaction 6) only half of bicarbonate released is of atmospheric/soil CO_2 origin. This can be summarized in the following reactions;

– incongruent weathering of albite to kaolinite

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$$NaAlSi_3O_8 + 2CO_2 + 11H_2O \Rightarrow Al_2Si_2O_5(OH)_4 + 2HCO_3^- + 2Na^+ + 4H_4SiO_4 \qquad (3)$$

– incongruent dissolution of K-feldspar to kaolinte

$$2KAlSi_3O_8 + 2CO_2 + 11H_2O \Rightarrow Al_2Si_2O_5(OH)_4 + 2HCO_3^- + 2K^+ + 4H_4SiO_4 \qquad (4)$$

– incongruent dissolution of Ca-plagioclase to kaolinte:

$$CaAl_2Si_2O_8 + 2CO_2 + 3H_2O \Rightarrow Al_2Si_2O_5(OH)_4 + 2HCO_3^- + Ca_2^+ \qquad (5)$$

– calcite dissolution:

$$CaCO_3 + CO_2 + H_2O \Rightarrow Ca_2^+ + 2HCO_3^- \qquad (6)$$

To get the chemical weathering rate, the specific fluxes (in mol km^{-2} yr^{-1}), are related to the drainage area (here the rate is given for the cationic silicate fluxes):

$$F_{cationic}sil=(Na_{sil} + K_{sil} + 2Ca_{sil} + 2Mg_{sil})/drainagearea \qquad (7)$$

$$F_{cationic}carb=(Ca_{carb} + Mg_{carb})/drainagearea \qquad (8)$$

3.3.1 CO_2 consumption during weathering of minerals

The mass budget of CO_2 consumption due to rock weathering (silicate and carbonate rock weathering) becomes:

$$CO_{2atm}=Na_{sil} + K_{sil} + 2Ca_{sil} + 2Mg_{sil} + Mg_{carb} + Ca_{carb} \qquad (9)$$

and the mass budget of CO_2 consumption and formation from silicate rock weathering:

$$CO_{2sil}=Na_{sil} + K_{sil} + 2Ca_{sil} + 2Mg_{sil} \qquad (10)$$

The CO_{2x} Eq. (9) to (10) relate the stoichiometry for the weathering reactions 3 to 6, where cations are "produced" from reactions with protons that originates from carbonic acid (that has its origin from atmospheric/soil CO_2).

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In Table 5 physical parameters, major element concentrations, TOC, Sr isotope ratios for the dissolved load of each tributary, the Akkajaure reservoir and the river mouths of Kalix River and Lule River, are presented. Three different hydrological events are shown; spring flow in May/June, summer flow in August/September and base flow in November to April. Water chemistry of Muddus River, Kaitum River and the Lule and Kalix River mouths are presented with yearly mean values for the period 1985 to 2003. The average charge balance (in μeq) between total dissolved cations (Σ cations= Na^+ + K^+ + $2Ca^{2+}$ + $2Mg^{2+}$) and total dissolved anions (Σanions = Cl^- + $2SO_4^{2-}$ + HCO_3^-) was better than 10% (see Table 5). The ionic strength of all investigated waters is very low.

4   Results

On average, Ca^{2+} is the most abundant major cation in all streams, ranging from 37–112 umol L^{-1}, followed by Na^+ (24–85 umol L^{-1}), Mg^{2+} (9–48 umol L^{-1}) and K^+ (9–31 umol L^{-1}), except for Valtajåkka in the headwater of Lule River which is dominated by Na^+(51 umol L^1), followed by Ca^{2+} (37 umol L^{-1}), Mg^{2+} (19 umol L^{-1}) and K^+ (13.3 umol L^{-1}). For anions the most abundant anion is HCO_3^- in both Kalix River and Lule River Basin. In Kalix River basin SO_4^{2-} dominates over Cl^- and vice versa in Lule River basin. The high concentration of Cl^- and Na^+ in headwater of Lule River basin compared to headwater concentration of Kalix River basin (almost half of the concentration of Na^+ and Cl^- compared to Lule River), reflect the contribution from precipitation (see Table 3). The highest major element concentrations are observed during winter (baseflow) when the discharge is low.

The highest Ca^{2+} concentration is measured at the River mouth of Kalix River (112.1 umol L^{-1}). Vuojatätno in the headwater of Lule River basin has a similar concentration of Ca^{2+}, 105.7 umol L^{-1}. The lowest average Ca^{2+} concentration is observed in Valtajåkka (37.4 umol L^{-1}). Valtajåkka also has the lowest average concentration of HCO_3^-. Under winter base flow Valtajåkka has the highest measured silica concentra-

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tion in Lule River headwater, 71 umol L^{-1}. The lowest average molar concentration of silica is observed in Sitas and Vuojatätno, followed by Akkajaure reservoir (15 umol L^{-1}) and Lule River mouth (40 umol L^{-1}). The silica concentration is generally doubled in Kalix River Basin, at the river mouth about 100 umol L^{-1}. The highest average molar

5 concentration of silica is in Muddus River (114 umol L^{-1}), which also have the highest TOC concentration of 5.5 mg L^{-1} or 0.46 mmol L^{-1}. Previous reported studies of river chemistry and the relation between silica and TOC (Humborg et al., 2004) is also valid in the investigated streams (Fig. 2) and thus DOC/TOC can be used as a proxy for soil/water contact resulting in elevated silica concentrations.

10 The ternary diagrams (Figs. 3a–b) show the overall dominance of calcite in the headwater streams relative to the cations derived from silicates, despite the very small proportions of carbonates relative to silicate bedrock in the studied areas (Table 2). The carbonate chemistry dominance observed in the Akkajaure reservoir is a reflection of the river chemistry in Vuojatätno, which contributes to about 70% of the water in Akka-

15 jaure reservoir (Table 1).

In the Na normalized mixing diagrams (Figs. 4b and c) the tributaries, Akkajaure reservoir and River mouth is plotted. The used end members ratios for carbonates in this study are estimated using data on small rivers draining one single lithology (carbonates, silicates and evaporites). These end member ratios are taken from Gaillardet et

20 al. (1997); the silicate end member ratio for Ca/Na is 0.35 ±0.25, Mg/Na = 0.24±0.16, Sr/Na = 3±1×10^{-3}, HCO$_3$/Na = 1±1 and ^{87}Sr/^{86}Sr = 0.73±0.01. The used end member ratios for carbonates in this study are Ca/Na = 45±25, Mg/Na = 15±10, Sr/Na = 40±20×10^{-3}, HCO$_3$/Na = 90±40 and ^{87}Sr/^{86}Sr = 0.7075±0.0005, and the evaporite end member ratios are Ca/Na = 0.17±0.09, Mg/Na = 0.02±0.01, Sr/Na = 3±2×10^{-3},

25 HCO$_3$/Na = 0.3±0.3and ^{87}Sr/^{86}Sr = 0.7081±0.0005.

The Sr isotope ratio plotted vs. the molar Ca/Sr ratio in Fig. 4a demonstrates the mixing in Vuojatätno between old silicate rock, with ^{87}Sr/^{86}Sr ratios >0.73 and carbonates (limestone), with ^{87}Sr/^{86}Sr ratios around 0.709, also the present value in oceans (Dickin, 1997). Valtajåkka is draining the old granitic Precambrian basement resulting

in higher Sr isotope ratios >0.74 (Faure, 1986). Vuojatätno also shows very homogenous Sr-isotope ratios over the year, which is probably due to an increasing weathering intensity of isotopic homogenous bedrock and soil layers with increasing discharge but is also influenced by two major lakes upstream of the outlet of Voujatätno in the Akkajaure reservoir, Virihaure (4.4 km^3) and Vastenjaure (3.0 km^3). In Valtajåkka the Sr isotope ratios varies with discharge, although the variation is small. The highest Sr isotope ratio is observed during winter, possibly showing a combination of deeper groundwater percolation near the old Precambrian basement, with higher Sr-isotope values and small dilution effects of the bedrock strontium signal due to low rain water discharge during winter.

In Table 6 the element mass budgets, weathering rates and the consumed CO_2 for the investigated different sources are presented, i.e. carbonates, silicates, evaporites and rain, and atmosphere, silicate and carbonate, respectively. The silicate weathering rate is specified as a flux (mass budget/total drainage basin) and specific fluxes (mass budget/silicate outcrop in the drainage basin) and the specific weathering of lowland areas (total river load-headwater load)/(total catchment area-headwater area). The different flux estimates show that cations released from weathering of silicates and the amount of carbon dioxide used for silicate weathering dominates unregulated lowland rivers such as Muddus River (unregulated tributary to Lule River) and the river mouth of Kalix and Kaitum Rivers in the headwater of Kalix River. The silicate weathering rates for these rivers showed almost the same value; 45.1×10^3 mol km^{-2} yr^{-1} for Muddus River, 46.7×10^3 mol km^{-2} yr^{-1} for Killingi and 47.4×10^3 mol km^{-2} yr^{-1} for the river mouth of Kalix River. At the river mouth of Lule River this value is 27.7×10^3 mol km^{-2} yr^{-1}. In the headwaters of Lule River these numbers are, Valtajåkka 27.9×10^3 mol km^{-2} yr^{-1}, Vuojatätno 24.7×10^3 mol km^{-2} yr^{-1}, Akkajaure 26.0×10^3 mol km^{-2} yr^{-1} and Sitas 16.4×10^3 mol km^{-2} yr^{-1} showing the slowest silicate weathering rate (Table 6, $F_{cationic}$ sil). To get a more "true" value for the silicate weathering rate, it is possible to relate the rate to the specific outcrop of silicate rock in the drainage area. Here presented as $F_{cationic}$ sil specific outcrop (mol/specific

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outcrop of silicate rock in km^2/year). The calculated specific cationic silicate denudation rates, $F_{cationic}$sil specific outcrop, for Vuojatätno, Valtajåkka, Lule River mouth, and Sitas are; 38.0×, 35.4×, 32.1×, and 22.9×10^3 mol km^{-2} yr^{-1}, respectively.

5 Discussion

On a large scale many variables control the chemical denudation of continents, such as lithology, runoff, temperature, relief and vegetation. The importance of bedrock on chemical denudation rates was identified early (Garrels and Mackenzie, 1971; Meybeck, 1987). Studies have shown that the silicate chemical weathering rates are 2 to 3 times higher for silicate rocks in the Andean mountain basins compared to the lowland basins (Gaillardet et al., 1997). The largest difference of almost a factor 40 is shown for the River Solimoes, draining the Andes, compared to the Rio Negro (Guayana shield, highly weathered Precambrian shield) in the lowland. In another study on the 60 largest rivers of the world, Gaillardet et al. (1999) concluded that the possible controlling variables for modern silicate weathering rates is a combined effect of runoff-temperature and physical denudation. These parameters which are related to both climate (e.g., temperature, precipitation, and runoff) and tectonics (e.g., physical denudation, sediment transport, landscape surface age, and bedrock exhumation) are the main principal factors controlling physical and chemical weathering over geological time scale (i.e. transport-limited or weathering-limited regime). Recent studies have also shown the importance of DOC/TOC (Humborg et al., 2004; Millot et al., 2003) for Si concentration in rivers and thereby silicate weathering rates.

Our detailed analyses on weathering rates in boreal and sub arctic systems shows that although much higher specific discharge and steeper slope angel, i.e. higher physical erosion, the weathering rates are less in a regulated river compared to an unregulated river, i.e., lower concentrations of dissolved solids can not only be explained by a dilution effect; there is indeed less weathering occurring. Moreover, weathering rates are higher in the lowlands compared to the headwaters in both systems. This suggest

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that in this cold and weathering limited system the role of vegetation and soil thickness is much more evident for weathering rates than in warmer and wetter climates elsewhere. However, about 5% of the total land cover within the watershed of the Lule River has been converted into water area (reservoirs) and this occurred especially along the river valleys of the headwaters where alluvial sediment was continuously deposited leading to a formerly riparian zone with a rich vegetation cover. The effect of this % change in land cover is therefore much higher than what is revealed with number on how much land is converted into water area. Although we can not quantify yet the role of these alluvial deposits for overall weathering rates we hypothesize here that the drowning of these areas that came along with river regulation explain to a significant extent the lower weathering rates observed in the Lule River compared to the Kalix River. The effect from much smaller water level fluctuations in the river valley not affected by damming should also be considered as an important factor (reduced water/soil interactions in the riparian zone).

5.1 Weathering sources, major dissolved components, TOC and end member mixing

The silicate dominated Precambrian basement in the lowland of the Kalix and Lule River shifts the river mouths chemistry more toward the Si corner in the ternary diagram (Fig. 3), compared to the more carbonate dominated headwaters (especially Vuojatätno and Sitas which represent catchments with large lakes). This silicate weathering signal is also observed in the mixing diagram for Muddus River, Kaitum River (Killingi) and Valtajåkka (Fig. 4), where the sodium normalized values are lower than the tributaries to the Akka system with carbonate weathering dominance.

In the pristine catchment Kalix River, and in the unregulated Valtajåkka and Muddus River in Lule River Basin, the major element concentrations vary seasonally (Table 5). Vuojatätno, Sitas and the river mouth of Lule River show very small dilution effects (i.e. melt water diluting the ground water signal), which probably can be attributed to the lithology in Vuojatätno (and large lakes upstream) and regulation effects for Sitas and Lule River (large reservoirs). The seasonality, with spring peak discharge and

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low winter base flow is flattened out on yearly basis compared to the Kalix River, as well as the differences in concentration of major element. Vuojatätno is dominated by carbonate rock weathering (see Figs. 3 and 4), which under high discharge may lead to an increase in weathering (Berner and Berner, 1996). The same effect may also

5 be important for the weathering of silicates, when fresh silicate mineral surfaces are exposed to the increasing physical erosion caused by high runoff (but only to a certain degree where dilution may become important again).

This inverse relationship between Ca^{2+} and Na^{+}, is unusual in fresh waters, and may be a result of dominating rainwater contribution to stream water (sea salt), halite

10 dissolution, silicate dominating weathering (Na-plagioclase) over Calcite, or biomass uptake of Ca^{2+}. In small river catchments it can be difficult to quantify the mean annual concentrations when studies have been done with only a few samples. Short-term climatic and biotic fluctuations can be omitted or in some cases dominate the data, principally due to the role of flood events in small watersheds. Salt and nutrients are

15 stored in the unsaturated zones and washed out during events of high discharge (Drever, 1997). Each flood influences significantly the annual mass balance of elements and discharge and can be hard to capture in small watersheds with a fast response to rainfall/snowmelt and thereby showing large fluctuations in runoff during the year.

In Vuojatätno where carbonate sedimentary rocks are present, the Ca^{2+} concentra-

20 tion exceeds $100 \, \mu$mol L^{-1} and alkalinity (as HCO_3^-) reaches values around $200 \, \mu$eq L^{-1}. The highest dissolved Si concentration in the headwater of Lule River was observed in Valtajåkka as shown by Humborg et al. (2004) to be caused by vegetated soil (in Valtajåkka the land cover consists of 1.13% coniferous forest, mainly spruce and 13.62% deciduous forest, mainly birch), and it is very likely that vegetation plays

25 an important role for weathering of silicates (Moulton and Berner, 1998; Moulton et al., 2000), especially in a weathering rate limited environment (Anderson et al., 2000; Drever, 1994; Drever and Zobrist, 1992; Millot et al., 2002). Jacobson et al. (2003) stress the importance of geomorphic control on silicate weathering in the Southern Alps, New Zealand, which support our result of silicate weathering rates (Table 7) from

the headwater of Lule and Kalix River. In these weathering limited regimes, with steep topography, rapid discharges (short mean residence times for water), and small vegetated flood plains, water-rock interaction times are limited. Under these conditions, chemical weathering is selective and favours highly soluble minerals with rapid disso-
5   lution rates like calcite instead of silicate minerals. The low silicate weathering rates in the uppermost part of the headwater of Kalix River and Lule River, can therefore be explained by this geomorphic/water-rock interaction theory.

5.2   Weathering rates

The calculated weathering rates for the investigated rivers show higher rates for
10 the Kalix River system compared to the Lule River system (Table 6). Furthermore, the silicate weathering rate is the highest in the lowland part, with rates of $48 \times 10^3 \, \text{mol km}^{-2} \, \text{yr}^{-1}$ and $45 \times 10^3 \, \text{mol km}^{-2} \, \text{yr}^{-1}$, in the Kalix and Lule River respectively. In the headwaters these numbers are $47 \times 10^3 \, \text{mol km}^{-2} \, \text{yr}^{-1}$ calculated for Killingi in the Kalix River basin and $38 \times 10^3 \, \text{mol km}^{-2} \, \text{yr}^{-1}$ calculated for Vuojatätno, in the Lule
15 River Basin. This difference in rates suggests that silicate weathering in sub-arctic boreal climates is controlled by the residence time for water rock interactions followed by lithology. Dam constructions have shown to be a sink for nutrients, due to the increase of water residence time, which produces the pre condition for photosynthesis and algal growth in the reservoirs (Humborg et al., 2000, 1997). Previous studies have, however,
20 concluded that biological uptake of dissolved Si by diatoms is not significant in the Lule River basin and it can therefore be ruled out that this is a major sink for Si (Humborg et al., 2004).
    In the headwater, were we have steep topography and higher runoff like in Vuojatätno the lithology is of major importance, given the highest silicate weathering rate
25 for Vuojatätno, were we have more weatherable minerals compared to the other headwater rivers at the same altitude and with similar runoff. Killingi in Kaitum river is draining an area in size comparable to Vuojatätno's with a similar landscape cover, i.e. glacier, barren land, unvegetated and vegetated soil, but is reaching to a lower ele-

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vation (from about 400–2000 m a.s.l.) compared to Vuojatätno, where more vegetated soils increase water rock interaction time, making the weathering less selective and optimizing weathering of silicates compared to highly soluble calcite.

This study and the study of the sub-arctic Mackenzie River basin by Millot et al. (2003), reports (in comparison with the global average river) low silicate weathering rates. The silicate fluxes (as cationic silicate weathering rates) calculated for Lule River Basin and Kalix River Basin, range from 0.92 to 1.61 $t\,km^{-2}\,yr^{-1}$, respectively, and for Mackenzie River basin from 0.13 to 4.33 $t\,km^{-2}\,yr^{-1}$. Land and Ohlander (2000) have estimate the chemical weathering rates (as base cation flux) of granitic till in a small catchment (9.4 km^2) in Kalix River Basin to 0.356–0.553 $keq\,ha^{-1}\,yr^{-1}$, which is slightly lower than our estimation for Lule River and Kalix River basin of 0.415 and 0.727 $keq\,ha^{-1}\,yr^{-1}$, respectively.

The difference in weathering rates for Kalix and Lule River is most likely caused by the inundations of the river valleys in Lule River in order to regulate the water (building dams and reservoirs) and generate electricity. The river valleys contain the alluvial deposits and therefore even small changes in the landscape in these areas will have a significant impact on the soil/water contact and water residence time in the soil. This can be seen as a decrease of the active area of minerals exposed to chemical weathering resulting in lower weathering rates and concentrations of weathering products in the river.

5.3 CO_2 consumption (sequestration of C) and weathering rates

Globally about 64 % (or near 2/3) of the dissolved inorganic carbon (DIC, mainly as HCO_3^-) in natural waters is derived from the reaction between carbonic acid and minerals (Berner and Berner, 1996; Meybeck, 1987). The production of HCO_3^- is a result of the consumption/sequestration of atmospheric/soil CO_2 during weathering of silicate and carbonate rocks (Reactions 3–6). The relative distribution between silicate and carbonate rock origin of DIC varies, largely because of the much higher weathering rates for the dissolution of carbonate rocks. The contribution of silicate rock in DIC

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is from the carbonate rich drainage areas of Sitas and Vuojatätno 57% and 55%, respectively, and for the silicate dominated drainage areas of Valtajåkka 63%, Muddus River 82%, river mouth of Lule River 68%, headwater of Kalix River 72% and at river mouth of Kalix River 74% (Table 6). The total alkalinity calculated from the stoichiometry with the used model in this study overestimates the alkalinity with nearly 20 to 30%, showing that other proton sources than carbonic acid may be important, i.e. for example pyrite weathering and DOC. The CO_2 consumption/sequestration estimated during weathering are in this study based on the assumption that the only proton source for rock weathering is carbonic acid.

The organic transport of carbon to the sea includes also most of the inorganic carbon since a large part of the inorganic carbon originates from degradation of organic matter, i.e. from soil respiration. For the Kalix River (1990–2000) the mean for TOC (expressed as C) was $4.9\,\mathrm{mg\,L^{-1}}$ and for Lule River (1990–2000) $2.4\,\mathrm{mg\,L^{-1}}$ (Nilsson, 2006). Taking the alkalinity value as approximately the bicarbonate concentration (and all inorganic carbon, this assumption will underestimate the inorganic carbon) the inorganic C that originates from organic C is for the Kalix River $1.9\,\mathrm{mg\,L^{-1}}$ (from Table 5, $0.216\times12\times0.74$) and for Lule River $1.2\,\mathrm{mg\,L^{-1}}$ (from Table 5, $0.149\times12\times0.68$). This means that the organic carbon load for Kalix River is underestimated by 30% and for Lule River by almost 35%. This shows that if climate effects are investigated and only using TOC/DOC as a proxy for increased degradation of organic matter changes in the total carbon load may occur but not necessarily detected in the TOC/DOC fraction (i.e. leads to more weathering and production of more DIC). The total carbon load, inorganic and organic, must therefore be considered if trends for carbon balances in boreal sub arctic watersheds are investigated. In conclusion not only dissolved solids as Si, Ca and Mg will decrease with regulation (Humborg et al., 2000, 1997), a destruction of soil layers due to damming or erosion will decrease alkalinity export fluxes and therefore also influence regional C budgets.

6 Conclusions

The difference in chemical weathering rates between lowland regions and headwaters suggests that silicate weathering in sub arctic boreal climates is controlled by the residence time for soil water rock interactions followed by lithology.

The calculated weathering rates for the investigated rivers show higher rates for the Kalix River system compared to the Lule River system by 30%. The difference in weathering rates for Kalix and Lule River is most likely caused by the inundations of the river valleys in Lule River where the alluvial deposits are "drowned" in the reservoirs causing water to have shorter residence in soils/rocks (see above on the importance of residence time vs. lithology).

The contribution in DIC from weathering of silicate rocks (sequestration of C), i.e. silicate origin of DIC, varies from 55% in the carbonate rich basins to about 80% in basins with high silicate rock domination. At river mouth these numbers are; Lule River, 68% and Kalix River, 74%. The actual organic carbon load leaving these rivers is therefore higher, since the carbon in DIC generated by weathering of silicate rocks origins from degradation of organic matter in soils. This means that the organic carbon load for Kalix River is underestimated by 30% and for Lule River by almost 35%. If climate effects are investigated and only using TOC/DOC as a proxy for increased degradation of organic matter, changes in the total carbon load may occur, but not necessarily detected in the TOC/DOC fraction. The total carbon load, inorganic and organic, must therefore be considered if trends for carbon balances in boreal sub arctic watersheds are investigated.

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Table 1. Hydrology for Lule River and Kalix River and headwater tributaries. The runoff ratio is the ratio of average river runoff (per unit area) to average rainfall (per unit area).

	Lule River Headwater Valldajåkka	Voujaätno	Sitas	Akkajaure reservoir	Lowland Muddusätno	River mouth	Kalix River Headwater Inlet to Pajtas	Killingi	Lowland River mouth
Catchment (km^2)	147	2842	977	4651	452	25225	299	2346	23846
Mean precipitation (mm)	1290	1332	1067	1180	583	698	623	630	544
Men Temperature (˚C)	–2	–2	–2	–2	–1	1	–2	–1.5	1
Mean runoff (m^3 s^{-1})	5.4	109	40.0	154	5.7	447	4.8	38.1	296
Specific discharge (L m^{-2} yr^{-1})	1160	1208	1292	1045	400	559	504	512	391
Runoff Volume (*10^{12} L yr^{-1})	0.2	3.4	0.9	4.9	0.2	17.6	0.2	1.2	9.3
% water discharge to River mouth	1.1	21.5	5.9	30.4	1.0	100.0	1.6	12.9	100.0
% water discharge to Akka system	3.51	70.61	19.31						
Runoff ratio	0.90	0.91	0.90	0.89	0.69	0.80	0.81	0.81	0.72

Lule River:

*Mean precipitation and runoff from the period; 1985 to 2003 for Muddusätno and at river mouth.

*Mean precipitation and runoff from the period; 1998 to 2000 for the headwater area.

Kalix River:

*Mean precipitation and runoff from the period; 1985 to 2003.

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Table 2. Element concentration in rainwater.

River	Location	pH	Conductivity $\mu S\ cm^{-1}$	SO_4^{2-} $\mu mol\ L^{-1}$	Cl^-	NO_3^-	NH_4^+	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	CB %
Lule	Headwater	5.08	10.43	7.39	29.93	3.39	6.51	7.35	1.87	2.98	25.07	2.13	2.69
	Muddusätno	4.69	12.34	13.02	5.15	12.61	12.20	21.95	2.40	1.10	4.82	2.98	5.56
	River mouth	4.82	11.31	10.46	18.84	8.97	9.72	16.91	2.29	2.14	16.44	2.38	5.43
Kalix	Headwater	4.92	8.01	7.42	9.50	4.32	5.71	13.40	1.27	1.10	8.08	1.00	6.92
	River mouth	4.69	12.34	13.02	5.15	12.61	12.20	21.95	2.40	1.10	4.82	2.98	5.56

Lule River:

*The element concentrations in Headwater area are mean values from the EMEP station, Trustervatn in Norway, 1977–2003 (http://www.NILU.no), and the PMK stations Abisko and Ammarnäs in Sweden, 1983–2004 (http://www.IVL.se).

*The element concentrations in rainwater for Muddusätno are mean values from the PMK stations, Pålkem in Gällivare district, 1983-2004 (http://www.IVL.se).

*The element concentrations in rainwater for River mouth is a weigthted mean value from the PMK stations, Pålkem in Gällivare district and Reivo in Arvidsjaur district (IVL), and the concentration in precipitation from headwater.

Kalix River:

*The element concentrations in Headwater area are mean values from the PMK station Abisko in Sweden, 1983–2004 (http://www.IVL.se).

*The element concentrations in rainwater for River mouth is mean value from the PMK station, Pålkem in Gällivare district, 1983–2004 (http://www.IVL.se).

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Table 3. The areal percent of major bedrock types, and the specific silicate and carbonate outcrop in the investigated catchments.

River		Location	Carbonate rock	Carbonate rich shale	Shale	Basic Rock	Gneiss	Granite and acid volcanic rock	Quartzite	Carbonates	Silicates outcrop	Silicate outcrop	Carbonate
			%	%	%	%	%	%	%	%	%	km^2	km^2
Lule	Headwater	Vuojatätno	7.2	16.8	19.4	28.2	12.4	1.1	3.9	24.0	64.9	1843	683
		Valldajåkka	0.0	20.8	2.4	0.0	64.6	8.4	3.3	20.8	78.7	116	31
		Sitas	2.0	9.1	24.9	2.0	7.9	21.8	15.1	11.1	71.7	701	108
		Akkajaure reservoir	4.1	13.3	17.8	16.8	25.0	3.9	4.9	17.3	68.4	3180	806
	Lowland	Muddusätno	0.0	0.0	0.6	21.9	0.0	77.5	0.0	0.0	77.5	450	0
		River mouth	1.4	2.9	7.0	14.2	11.4	48.3	5.3	4.3	86.2	21749	1073
Kalix	Headwater	Inlet to Pajtas	0.0	0.0	0.0	37.9	39.7	14.8	7.6	0.0	100.0	299	0
		Killingi	–	–	–	–	–	–	–	–	–		
	Lowland	River mouth	0.1	0.0	12.3	17.6	3.2	63.8	1.6	0.1	98.5	23488	2

Table 4. Chemical analyses for Lule River and Kalix River and headwater tributaries. CB refers to the ionic charge balance.

River	Location		Date	Season	pH	Cond $\mu S\ cm^{-1}$	Alk $\mu eqv\ L^{-1}$	SO_4^{2-} $\mu mol\ L^{-1}$	Cl^-	NO_3+NO_2	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	Si	Sr^{2+}	TOC ppm	$^{87}Sr/^{86}Sr$	CB %
Lule	Headwater	Akkajaure reservoir	2000 06 14	Spring	6.7	21.2	164.4	22.7	54.9	2.4	0.1	66.4	23.6	45.8	11.0	14.4	0.1	0.5	0.7251	−6.05
			2000 09 08	Summer	6.8	19.7	134.0	20.7	53.9	1.2	0.3	64.7	23.7	45.6	10.3	14.1	0.1	0.7	0.7233	0.52
			2001 04 02	Winter	6.8	23.4	151.8	25.0	66.0	2.5	0.5	73.2	26.5	51.1	12.1	17.2	0.1	0.6	0.7239	−1.38
			Mean		6.8	21.4	150.1	22.8	58.3	2.1	0.3	68.1	24.6	47.5	11.1	15.3	0.1	0.6	0.7241	−2.36
																15.3				
		Voujatätno	2000 06 14	Spring	7.0	27.8	226.0	23.5	63.8	2.3	0.1	98.2	35.4	45.1	7.2	12.7	0.2	0.4	0.7155	−2.97
			2000 09 08	Summer	6.3	28.1	216.0	29.9	58.4	1.6	0.0	107.5	34.0	47.4	8.3	12.5	0.2	0.5	0.7165	0.44
			2001 04 02	Winter	6.7	35.1	227.6	28.8	69.9	3.7	0.3	111.3	37.8	47.8	12.2	15.1	0.2	0.4	0.7159	−0.03
			Mean		6.6	30.3	223.2	27.4	64.0	2.5	0.1	105.7	35.8	46.8	9.2	13.4	0.2	0.4	0.7160	−0.82
		Valldajåkka	2000 06 14	Spring	6.7	11.3	52.1	10.6	48.7	1.0	0.1	21.6	13.8	43.6	5.5	11.8	0.0	0.7	0.7402	−1.36
			2000 09 08	Summer	6.2	10.4	48.3	14.1	47.1	0.0	0.0	30.0	15.8	39.4	5.8	17.0	0.0	1.4	0.7441	5.16
			2001 04 02	Winter	7.0	23.5	120.6	24.6	71.7	3.6	0.2	60.5	26.7	70.7	28.7	70.7	0.1	0.5	0.7467	5.58
			Mean		6.7	15.1	73.7	16.4	55.8	1.6	0.1	37.4	18.8	51.2	13.3	33.2	0.1	0.9	0.7437	3.83
		Sitas	2000 06 14	Spring	6.5	19.0	138.7	23.2	55.2	2.5	0.2	59.8	20.2	44.1	11.8	13.5	0.1	0.5	0.7314	−5.84
			2000 09 08	Summer	7.1	17.1	107.5	23.5	46.5	1.5	0.1	58.0	17.3	39.2	10.9	11.7	0.1	0.4	0.7316	−0.43
			Mean		6.8	18.1	123.1	23.3	50.8	2.0	0.1	58.9	18.7	41.6	11.4	12.6	0.1	0.5	0.7315	−3.1
	Lowland	Muddusätno	1985–2003		7.0		201.1	19.5	20.5	3.5	1.8	87.9	30.8	61.9	11.6	113.9		5.5		
		River mouth	1985–2003		6.9	29.3	149.2	22.1	48.0	2.1	1.1	70.6	27.9	61.3	11.2	40.1		2.8		5.28
Kalix	Headwater	inlet to Pajtas	1999 04 25	Winter		30.0				2.0	0.2	81.3	9.9	27.0	38.8	92.9	0.1			
			1999 12 08	Winter		31.3	136.6	41.5	19.6	3.2	0.3	69.2	8.2	22.7	37.0	93.4	0.1			−6.12
			2000 05 08	Winter			52.1		31.6	1.2	0.2	69.7	11.8	27.2	29.4	90.1	0.1			
			2000 08 18	Summer	6.9	11.0	88.4	20.1	15.1	0.2	0.1	43.9	4.1	13.3	17.5	42.9	0.1	0.9	0.74229	−6.28
			2001 04 04	Winter	6.3	23.3	146.0	42.0	19.1	5.8	0.2	81.8	9.6	27.3	35.5	110.9	0.1	0.5	0.752553	−1.87
			Mean		6.6	23.9	123.7	38.9	21.3	2.5	0.2	69.2	8.7	23.5	31.6	86.0	0.1	0.7	0.74742	−3.30
		Killingi	1985–2003		6.8		223.9	37.6	14.6	3.3	1.6	102.7	36.7	59.0	12.6	78.6		2.1		5.02
	Lowland	River mouth	1985–2003		6.8		216.1	51.1	45.9	6.9	2.5	112.1	47.5	84.9	16.6	100.3		5.1		6.27

*The concentrations are not corrected for atmospheric inputs (see Table 2 for mean rainwater concentrations)

*CB = ((Σcations − Σanions)/(Σcations + Σanions))*100

Table 5. Calculations for each reservoirs element budget (μmol) and their contributions in percent. The silicate flux F (as cationic) is presented as $*10^3$ mol km^{-2} yr^{-1}. The percent for the CO_2 atm (CO_2 used for rock weathering of silicates and carbonates), CO_2 carb (CO_2 used for carbonate weathering) and CO_2 sil (CO_2 used for silicate weathering).

Budgets	Lule River Headwater Vuojätätno μmol	%	Valldajåkka	%	Sitas	%	Akkajaure reservoir	%	Lowland Muddus	%	River mouth	%	Kalix River Headwater Inlet to Pajtas	%	Killingi	%	Lowland River mouth	%
Ca^{2+} sil	1.84E+13	5	1.02E+12	15	3.06E+12	5.2	3.44E+13	10	8.29E+12	52	2.52E+14	25	3.60E+12	32	4.17E+13	34	4.34E+14	38
Ca^{2+} carb	3.13E+14	92	5.54E+12	80	5.35E+13	91	2.96E+14	87	6.98E+12	44	7.03E+14	71	7.19E+12	65	7.99E+13	65	6.71E+14	59
Ca^{2+} rain	7.08E+12	2	3.55E+11	5	1.95E+12	3	1.03E+13	3	6.33E+11	4	4.04E+13	4	3.11E+11	3	1.82E+12	1	3.11E+13	3
Mg^{2+} sil	7.16E+12	6	3.95E+11	11	1.19E+12	7	1.34E+13	11	3.22E+12	58	9.82E+13	25	1.40E+12	37	1.62E+13	37	1.69E+14	37
Mg^{2+} carb	9.89E+13	84	2.53E+12	72	1.35E+13	76	8.79E+13	75	2.06E+12	37	2.58E+14	66	2.11E+12	56	2.64E+13	60	2.77E+14	60
Mg^{2+} rain	1.13E+13	10	5.65E+11	16	3.11E+12	18	1.64E+13	14	2.90E+11	5	3.77E+13	10	2.87E+11	8	1.48E+12	3	1.43E+13	3
K$^+$ sil	2.77E+13	77	1.76E+12	81	9.04E+12	80	4.16E+13	78	1.31E+12	63	1.17E+14	74	1.19E+12	84	1.38E+13	91	1.32E+14	78
K$^+$ rain	8.06E+12	23	4.04E+11	19	2.22E+12	20	1.17E+13	22	7.84E+11	37	4.18E+13	26	2.24E+11	16	1.42E+12	9	3.84E+13	22
Na$^+$ sil	1.68E+13	10	9.28E+11	11	2.79E+12	7	3.14E+13	15	7.56E+12	68	2.30E+14	27	3.28E+12	54	3.80E+13	54	3.96E+14	45
Na$^+$ rain	9.49E+13	56	4.76E+12	57	2.62E+13	66	1.38E+14	67	1.27E+12	11	2.89E+14	33	2.37E+12	39	1.16E+13	16	6.23E+13	7
Na$^+$ eva	5.89E+13	35	2.72E+12	32	1.04E+13	27	3.74E+13	18	2.36E+12	21	3.45E+14	40	4.26E+11	7	2.12E+13	30	4.13E+14	47
*HCO$_3^-$ total	9.19E+14		2.16E+13		1.54E+14		9.37E+14		5.00E+13		2.97E+15		3.30E+13		3.80E+14		3.63E+15	
CO$_2$ sil	9.57E+13	19	5.52E+12	41	2.03E+13	23	1.69E+14	30	3.19E+13	78	1.05E+15	52	1.45E+13	61	1.68E+14	61	1.73E+15	65
CO$_2$ carb	4.12E+14	81	8.07E+12	59	6.69E+13	77	3.84E+14	70	9.04E+12	22	9.61E+14	48	9.29E+12	39	1.06E+14	39	9.48E+14	35
CO$_2$ atm	5.07E+14	55	1.36E+13	63	8.73E+13	57	5.53E+14	59	4.09E+13	82	2.01E+15	68	2.38E+13	72	2.74E+14	72	2.68E+15	74
Fluxes	$*10^3$ mol km^{-2} yr^{-1}																	
F CO$_2$ sil	33.7		37.5		20.8		36.2		70.6		41.6		48.4		71.4		72.6	
F cationic carb	144.8		54.9		68.5		86.7		20.0		42.8		31.1		45.3		39.7	
F cationic sil	24.7		27.9		16.4		26.0		45.1		27.7		31.7		46.7		47.4	
F cationic sil spec. outcrop	38.0		35.4		22.9		38.0		45.3		32.1		31.7				48.1	
cat. sil (Tonns yr-1)	2194		127		478		3838		702		23343		320		3712		38347	
cat. sil (μmol yr-1)	7.01E+13		4.10E+12		1.61E+13		1.21E+14		2.04E+13		6.98E+14		9.47E+12		1.10E+14		1.13E+15	

*HCO$_3^-$ total = Na$^+$ sil + K$^+$ sil + 2Mg^{2+} carb + 2Ca^{2+} sil + 2Mg^{2+} sil + 2Ca^{2+} carb; equation from Mortatti and Probst (2003).

*To distinguish between the contribution of Ca^{2+} and Mg^{2+} from silicate and carbonate weathering in the investigated rivers (Lule River and Kalix River) the ionic ratio Ca/Na= 1.096 and Mg/Na=0.426 were used from a nearby river (Råne River) which only has a silicate bedrock (see text for more information).

*Weathering mass budget = mean element concentration * runoff volume - mean concentration in rain * precipitation volume.

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Table 6. Explanations of used abbreviations in formulas and text.

Abbreviation	=
F_{Na} sil	specific flux of sodium released by silicate weathering
F_{K} sil	specific flux of potassium released by silicate weathering
F_{Ca} sil	specific flux of calcium released by silicate weathering
$F_{cationic}$sil	specific flux of cations released by silicate weathering
F_{Ca}carb	specific flux of calcium released by carbonate weathering
F_{Mg}carb	specific flux of magnesium released by carbonate weathering
$F_{cationic}$carb	specific flux of cations released by carbonate weathering
F_{HCO3}sil	specific flux of HCO_3 released by silicate weathering
F_{HCO3}carb	specific flux of HCO_3 released by carbonate weathering
F_{HCO3}rock weathering	specific flux of HCO_3 released by carbonate and silicate weathering

Fig. 1. Map over the investigated area.

Fig. 2. Dissolved silicate (DSi) concentrations vs. Total organic carbon (TOC) concentrations in headwater tributaries, Akkajaure reservoir, Muddosätno and at river mouth of the Lule and Kalix River. Shown concentrations are yearly mean values.

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Fig. 3. Plots are showing ternary diagrams over the water chemistry at sampled sites.

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Fig. 4. Mixing diagrams for the main tributaries to the Akkajaure reservoir, Akkajaure reservoir and at the river mouth of Lule River, and the headwater and river mouth of Kalix River. The molar ratios are corrected for the atmospheric input. Voujaätno have a strong carbonate signature and is strongly influencing the water chemistry of the Akkajaure reservoir (70% of the water in the Akkajaure reservoir is coming from Voujaätno). At the river mouth of Lule River the water has a more silicate weathering signature, like Kalix River, due to the weathering of Precambrian silicate rich basement in the forested lowland.