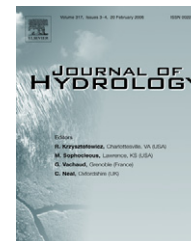




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Hydrochemical patterns of a small lake and a stream in an uplifting area proposed as a repository site for spent nuclear fuel, Forsmark, Sweden

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Received 6 March 2007; received in revised form 13 July 2007; accepted 31 July 2007

KEYWORDS

Boreal;
Stream;
Lake;
Hydrochemistry;
Seasonality;
Water discharge

Summary The overall aim of this study was to increase the understanding of the chemical dynamics of small catchments. The focus was on a small oligotrophic lake and its major inflow stream in an uplifting area in eastern Sweden (Forsmark) proposed as a repository site for spent nuclear fuel. The hydrochemical sampling campaign lasted for nearly 4 years with sample collection monthly to semi-monthly, and continuous flow measurements carried out over the last 20 months. All this was done as part of the Swedish Nuclear Fuel and Waste Management Company's (SKBs) Site Investigation Programme. The major findings were: (1) as a result of the calcareous overburden caused by redistributed Paleozoic deposits, pH and the Ca and HCO_3^- concentrations were relatively high in both the stream and lake throughout the period, (2) limnic primary production resulted in decreased concentrations of Ca, HCO_3^- , NH_4^+ , NO_3^- and Si, and increased pH and concentrations of chlorophyll *a*, O_2 , DON, POC, PON and POP in the lake in summer, while in other seasons (in winter in particular) when the production was minimal or non-existent the concentrations in the lake and the inflow stream were similar, (3) intrusion of brackish-water resulted in moderately to strongly increased concentrations of Cl^- , Na, Mg, Br^- , SO_4^{2-} , K and Sr in the lake: the ratio versus Cl^- were for Na and Br^- always similar to those in sea water, for Mg and SO_4^{2-} similar to those in sea water at elevated Cl^- concentrations ($>3 \text{ mM}$), while K and Sr always occurred in relative excess as compared to sea water, (4) high U concentrations in both the stream and the lake was derived most likely from reduced U-minerals in the overburden and was predicted to be carried to $>90\%$ in the form of calcium uranyl carbonate, in a model in which colloidal Fe and Al oxyhydroxides were not considered, (5) the rare earth elements (REEs) had similar concentrations and fractionation patterns in the stream and lake, unlike those found in the overburden groundwaters, and was predicted to be carried as organic complexes, (6) in terms of the area being chosen as a site for

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bedrock disposal of spent nuclear fuel, of particular importance is further investigations into the sources and mechanisms of the high U concentrations in the surface waters and confirmation of the importance of the calcium uranyl carbonate complex in the surface transport of this metal, and (7) the abundance of dissolved humic acids, predicted to carry the REEs, which consist of analogues for several actinides, deserve special attention in a safety assessment perspective focusing on radionuclide contamination.

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Introduction

A unique feature that strongly increases the complexity of fresh-water chemistry is seasonal variations, which are found across a wide range of catchments with contrasting climate, geology and type of ecosystem. In the boreal zone, the major hydrological event in catchments is the melt-water discharge in spring (April–June depending on the latitude). For example, most rivers discharging into the Arctic Ocean carry 40–80% of their annual volume of water during spring discharge (Gordeev et al., 1996; Rember and Trefry, 2004). The same pattern has been observed for the Kalix River in northern Sweden, which is a major unregulated pristine boreal river system (Ingri et al., 2005). During melt-water discharge, the concentrations of dissolved organic carbon (DOC) and several trace elements commonly increase in contrast to most major elements that are commonly diluted (Ponter et al., 1992; Ingri et al., 2000). Stream-water chemistry also fluctuates widely during storm events when changes in hydrologic flow paths and flow rates affect the amount of water originating from various sources. For example, in two small temperate catchments in Maryland, USA, soil-solution chemistry was found to control stream-water chemistry during periods of high flow and when the water table dropped below the rock–soil interface during summer the stream-water chemistry became controlled by solutes derived from bedrock (Rice and Bricker, 1995). Biogeochemical processes are highly dynamic over an annual climatic cycle including several seasons, and nutrient concentrations in stream water thus often show a strong pattern related to seasonal growth of both terrestrial and aquatic vegetation (Dahlgren and Driscoll, 1994; Holloway and Dahlgren, 2001).

The northern parts of the Baltic Sea and its terrestrial surroundings consist of a unique environment due to the still active land uplift (up to 8–9 mm/year) and the brackish-water. The land uplift is caused by the approximately 3-km-thick Pleistocene ice sheet that retreated c. 10000 years ago. The brackish-water is due to the small inflow of Atlantic water through the narrow Danish straits (475 km³/year) as compared to the outflow (950 km³/year) combined with the relatively high fresh-water discharge (660 km³/year) from the catchment of 1.6 million km² including the Caledonian uplands in Sweden and Norway (Björck, 1995). These two features plus the northern location mean that the small near-coastal catchments are affected by melt-water discharge in spring, huge increase in biological activity during the short but bright summer months, strongly developed seasonality, sporadic intrusions of brackish-waters, and young relatively unweathered soils that may include both trapped sea salts and sedimentary sulphides.

This region and its small catchments thus consist of an area of significant scientific interest in terms of providing knowledge of causal relationships among contrasting parameters affecting surface water chemistry.

The overall aim of this study was to increase the understanding of the chemical dynamics of small catchments within the northern Baltic region. In detail the aims were to: (1) characterise the hydrochemistry of near-coastal catchments in this region, (2) examine the chemical, physical and biological factors affecting the hydrochemistry, (3) compare the hydrochemistry of a small oligotrophic lake to the hydrochemistry of its major inflow stream in a multi-year-perspective and (4) as the study area is located on a site proposed as a deep repository of spent nuclear fuel (Swedish programme), assess the catchment properties and hydrochemical features in relation to the potential threats of such waste.

Material and methods

Site description

The studied catchment is located on the Baltic Sea coast in the municipality of Östhammar approximately 120 km north of the Swedish capital Stockholm (Fig. 1). The area belongs to the boreal forest region characterised by an annual climatic cycle with winter, spring, summer and autumn. During 4 months, December to March, the area is normally covered by snow, while the growing season extends from May to September. Summers are commonly fairly dry with low runoff, a typical autumn is moist/wet, and the characteristic feature of spring is snow melting causing large increases in runoff. The mean annual precipitation is approximately 600–650 mm/year and the annual runoff has been estimated to approximately 200 mm/year (Johansson et al., 2005).

The underlying crystalline Proterozoic bedrock is dominated by c. 1.9 Ga old meta-granitoids, mainly granites and granodiorites affected by ductile deformation (Stephens et al., 2004). Most of the area has recently (during the last 1500 years) risen above the Baltic sea level as a result of the ongoing isostatic uplift of the region (at present 6 mm/year). The topography is flat and ranges from coastal sea level to about 20 m above mean sea level (Johansson et al., 2005). Quaternary deposits cover c. 84% of the land area with till (sandy, clayey) being the most common type followed by minor occurrences of peat, glacial and postglacial clay, and wave-washed sand (Sohlenius et al., 2004). The till is characterised by calcium carbonate concentrations of 10–30% which is about 30 times higher

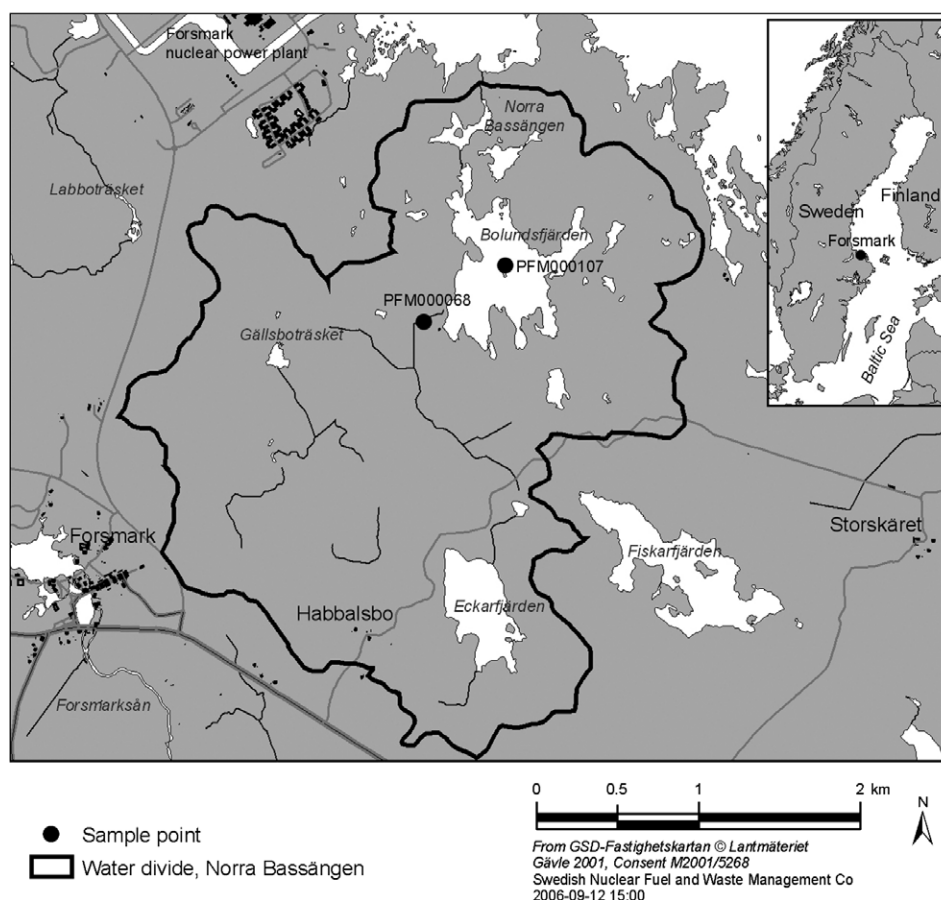


Figure 1 Map over the catchment area with sampling sites identified by codes (PFM000107 = Lake Bolundsfjärden and PFM000068 = Kungsträsket stream which is at the same location as the water discharge station PFM005764) and distribution of streams indicated with black lines and lakes/Baltic Sea as white areas (names given for the major lakes). The location/names of villages, a nuclear power plant and roads are also indicated.

than the Swedish reference data (Lundin et al., 2004; Tröjbom and Söderbäck, 2006). Its origin are Palaeozoic limestone deposits at the bottom of the Baltic Sea northwards (Ingemar and Moreborg, 1976), transported to the area by the Pleistocene ice sheet. Also the Sr concentration is elevated (27–175 ppm; Tröjbom and Söderbäck, 2006), most likely as a result of Sr accumulation in the calcium carbonate. The soils are young and thus poorly developed, but are nutrient-rich due to the influence of the calcareous material (Lundin et al., 2004).

The entire catchment area (outlined in Fig. 1) is 8.67 km² large and mainly covered by coniferous forest (67%) with the remaining part consisting of (c. 10% each) clear-cut forest, open wetland and water surfaces (Brunberg et al., 2004). The central lake is Bolundsfjärden, which receives water from one major and two smaller inlet streams and has one outlet stream entering to Lake Norra Bassängen which empties into the Baltic Sea (Fig. 1). The Lake Bolundsfjärden is 0.61 km² and has a mean depth of 0.6 m and maximum depth of 1.8 m (Brunberg et al., 2004). The lakes in the area are characterised as small and shallow oligotrophic hard-water lakes, due to the low total phosphorous level and high amount of dissolved ions including Ca, Mg, K, Cl⁻ and SO₄²⁻ (Sonesten, 2005).

Water sampling and analysis

The sampling sites were located in Lake Bolundsfjärden (referred to as PFM000107) and in the major inflow to this lake, i.e. the Kungsträsket stream (referred to as PFM000068) (Fig. 1). These sites are integrated in the Swedish Nuclear Fuel and Waste Management Company's (SKB) Site investigation programme (SKB, 2005). All the data collected at these sites are stored in the SICADA database, which is owned and quality checked by SKB. The data used in this study was retrieved from that database on February 27, 2006 (F51P Sicada_06_032).

Water sampling was carried out 59 times in the lake and 62 times in the stream for major solutes (see below), and between 6 and 14 times for trace elements in both the lake and the stream, over a period of almost 4 years (March 2002 to January 2006). At both sampling sites on each sampling occasion, field measurements of pH, EC, dissolved oxygen and water temperature were carried out, and a control measurement of pH and EC was made in the laboratory within 24 h. Water samples for other chemical analyses were collected using a peristaltic pump system (ASF Thomas SR 10/100), filtered through 0.45 µm disposable filters (Millipore) for determination of the dissolved phase, and analysed in

commercial accredited laboratories in Sweden (ALS Analytica AB; Dept of System Ecology, Stockholm University; Åspö chemistry laboratory, SKB) and abroad (Paavo Ristola OY, Finland). The analytical methods are summarised below and the analytical precision is given in Table 1.

The alkalinity was determined with hydrochloric acid, where carbon dioxide was vaporised and then calculated as HCO_3^- . Samples for the determination of Br^- , Cl^- and SO_4^{2-} were collected in polypropylene bottles, filtered and determined by ion chromatography. Filtered and acidified (1 ml HNO_3 /100 ml water) samples collected in polypropylene bottles were used for the determination of Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cu, Dy, Eu, Er, Fe, Gd, Ho, K, La, Lu, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pr, Rb, Sb, Si, Sm, Sr, Tb, Th, Tm, U, V, Y, Yb, Zn and Zr by inductively coupled plasma mass spectrometry (ICP-MS). The concentrations of total organic carbon (TOC) and dissolved organic carbon (DOC) were measured on unfiltered and filtered samples, respectively, by a carbon analyzer (Shimadzu TOC-5000). The particulate carbon (POC) was collected on glass fibre filters which under combustion were converted to carbon dioxide following determination by elementary-analyzer (LECO CHNS-932). Dissolved oxygen (O_2) was determined by the Winkler titration method and chlorophyll *a* was determined spectrophotometrically after extraction with acetone.

The phosphorous and nitrogen species were determined as follows: soluble reactive phosphorus (SRP) was determined by the method defined by (Murphy and Riley, 1962). On filtered samples in an acid solution, phosphate together with molybdenum and antimony formed antimony phosphorous molybdate acid, which was then reduced to a blue complex (the molybdenum blue reaction) and determined spectrophotometrically. The results, here reported as SRP, may also contain phosphate displaced from acid labile inorganic colloids/particles, and phosphate released by the hydrolysis of acid labile phosphate esters (Baldwin, 1998; Haygarth et al., 1997; Turtola, 1996; Zhang and Oldham, 2001). Total phosphorous (TP) was determined using an acidic persulphate digestion followed by the molybdenum blue reaction and analysed by spectrophotometry. The particulate phosphorous (POP) was collected on glass fibre filters followed by an acidic persulphate digestion and the molybdenum blue reaction. Ammonium was determined using hypochlorite and phenol to produce indophenol, which was determined spectrophotometrically. Any NO_3^- in the samples was reduced to NO_2^- , which was further converted to the required azo dye. The recorded value is here reported as NO_3^- , as this species is assumed to be the much more common of the two in the studied waters. Total nitrogen (TN) was determined using an alkaline persulphate digestion to form NO_3^- , which was then determined as above. The particulate nitrogen (PON) was collected on glass fibre filters which under combustion were converted to molecular nitrogen (N_2) following determination by elementary-analyzer (LECO CHNS-932). Dissolved organic nitrogen (DON) was calculated as follows: $\text{DON} = \text{TN} - (\text{NH}_4^+ + \text{NO}_3^- + \text{PON})$.

Flow measurements

Water discharge values from the outlet of Kungsträsket stream (PFM005764, same location as water sampling point

PSM000068) was obtained from an automatic discharge gauging station (installed by SKB in November 2003 and reinstalled in October 2004). Discharge values exist from April 2004 and were retrieved from the SICADA database on March 20, 2006 (F51P Sicada_06_055). The hydrograph of Kungsträsket stream was found to be similar to that at a regional hydrological station (Tärnsjön) performed by the Swedish Meteorological and Hydrological Institute (SMHI). Therefore, the hydrograph of the studied stream is regionally representative.

Stream flux calculations

Solute fluxes in the stream were calculated by multiplying the daily discharge by estimated daily solute concentration obtained by linear interpolation of the measured monthly to semi-monthly solute concentrations. These fluxes were further summarised to whole-period fluxes and divided by 20 to get an average monthly flux, which was further multiplied with 12 to get an average yearly flux for the period when discharge was determined (i.e. last 20 months). The yearly flux value was then divided by the catchment area and the unit is thus $\text{kmol/km}^2/\text{year}$.

Speciation modelling of U and rare earth elements (REE)

The software Visual MINTEQ version 2.5 was used for a hydrochemical speciation calculation of selected metals (U and REEs) using generic values for inorganic and organic complexation constants (Gustafsson, 2006; Rönneback et al., in press). All available U and REE data were used (six stream-water samples for each and seven lake-water samples for U and nine for the REEs). It was assumed that oxidising conditions occurred, and thus, U was present entirely as U(VI).

Results and discussion

Organic carbon

The DOC concentrations, which were very similar to the TOC concentrations, were overall lower in the lake than in the stream (Table 1, Fig. 2), and in the stream poorly correlated with flow. As a result of the latter phenomena, much larger quantities of DOC was transported during high than low flows, resulting in an average yearly flux of more than 187 $\text{kmol/km}^2/\text{year}$ (Table 2). The measured POC concentrations were, in line with the small differences between DOC and TOC, low (Table 1).

In boreal catchments, DOC originates mainly from organic soils or layers, and wetlands (histosols) are suggested to be the most important source (Kortelainen and Saukkonen, 1992; Heikkinen, 1994; Kortelainen and Saukkonen, 1998; Laudon et al., 2004). The explanation for the overall high DOC concentration in the studied waters is thus leakage from wetlands that cover 10% of the catchment area. The controls and pathways of dissolved organic carbon are, however, complex, as indicated by different mechanisms and sources suggested for different catchments. For example, DOC dilution during snowmelt has been observed in wetland-dominated catchments explained by sub-

Table 1 Analytical precision and selected data of the chemical variables

		Precision ^a (%)	Bolundsfjärden lake (<i>n</i> = 59)			Kungsträsket stream (<i>n</i> = 62)			Swedish lakes ^e	Swedish streams ^f	Svecofennian streams ^g
			Min	Median	Max	Min	Median	Max	Average	Average	Median
pH	—	—	6.9	8.3	9.3	6.7	7.4	8.1	6.8	6.8	6.8
EC	(mS/m)	—	16	40	114	22	36	52	7.7	12	65
HCO ₃ [−]	(mM)	4	1.2	2.1	3.4	1.5	2.7	3.7	0.32	0.59	
SO ₄ ^{2−}	(mM)	10	0.09	0.18	0.41	0.05	0.12	0.63	0.06	0.12	
Br [−]	(mM)	9	0.0002	0.002	0.017	0.001	0.001	0.003			
Ca	(mM)	4	0.58	1.09	1.75	0.87	1.4	1.8	0.19	0.36	0.14
Cl [−]	(mM)	6	0.38	1.43	5.22	0.14	0.49	1.4	0.27	0.20	0.11
K	(mM)	6	0.02	0.08	0.17	0.01	0.05	0.12	0.02	0.04	0.03
Mg	(mM)	4	0.07	0.23	0.74	0.10	0.18	0.33	0.06	0.09	0.08
Na	(mM)	4	0.16	1.2	5.8	0.19	0.56	1.4	0.20	0.24	0.14
Si	(mM)	4	0.001	0.03	0.20	0.10	0.17	0.29	0.04	0.11	0.14
TOC	(mM)	10	0.71	1.3	2.1	1.2	1.7	2.1	0.92	1.0	
DOC	(mM)	8	0.52	1.3	2.0	0.72	1.7	2.0			
POC	(mM)	4	0.01	0.03	0.21	0.01	0.02	0.10			
TN	(μM)	4	35	71	93	47	69	96	28	64	
NH ₄ ⁺	(μM)	0.8 or 5 ^b	0.15	0.72	13	0.01	1.2	13	6.6	3.0	
NO ₃ [−]	(μM)	0.2 or 2 ^c	0.01	0.13	11	0.03	2.0	30	3.6	36	
PON	(μM)	5	0.80	3.6	21	1.26	2.5	9.3			
DON	(μM)		28	65	80	42	61	89			
TP	(μM)	6	0.19	0.36	0.67	0.26	0.38	2.1	0.58	1.3	
SRP	(μM)	0.7 or 3 ^d	0.01	0.03	0.10	0.01	0.04	0.83	0.36		
POP	(μM)	5	0.06	0.17	0.58	0.08	0.17	0.58			
O ₂	(mM)	5	0.03	0.32	0.42	0.03	0.18	0.26			
Chlorophyll <i>a</i>	(μg/l)	5	0.10	1.4	6.6						
Al	(nM)	12	370	673	9043	441	808	2580			8858
As	(nM)	20	2.1	7.07	40	1.68	3.99	4.81		3.9	7.2
Ba	(nM)	7–10	110	139	181	134	172	207	48		555
Cd	(nM)	9	0.01	0.04	0.42	0.01	0.04	0.06		0.09	0.23
Co	(nM)	8	0.83	1.2	1.9	0.83	1.3	2.2		1.7	5.1
Cr	(nM)	7–10	1.7	2.6	4.5	2.5	3.4	4.4		5.8	14
Cu	(nM)	8	6.5	12	19	7.6	14	23		14	15
Fe	(μM)	6	0.45	1.5	5.2	1.5	3.5	10.5			22
La	(nM)	10	0.38	0.82	2.0	0.85	1.56	1.63	0.59		
ΣREE	(nM)		1.1	2.1	6.1	2.9	4.3	5.2			
Mn	(μM)	8	0.02	0.14	1.2	0.07	0.53	1.2			0.94
Mo	(nM)	7–10	3.1	6.3	11	2.6	4.3	9.9	0.50		1.7
Ni	(nM)	8	5.3	7.2	12	7.0	11	13		12	16
Pb	(nM)	7–10	0.33	0.69	3.1	0.21	0.30	0.36		1.2	0.87
Rb	(nM)	10	25	33	48	10	26	48	13		26
Sb	(nM)	10	0.53	0.70	1.1	0.34	0.61	0.67	0.29		0.33
Sr	(μM)	4	0.35	1.0	1.7	0.54	0.99	1.5			0.40
Th	(nM)	10	0.04	0.04	0.23	0.04	0.17	0.24	0.06		0.34
U	(nM)	12	6.8	9.1	13	10	13	18	0.20		0.44
V	(nM)	5	4.1	5.1	12	4.0	4.9	12		5.5	16
Y	(nM)	10	0.86	1.7	5.0	2.2	3.4	3.9	1.3		
Zn	(nM)	12	7.0	16	197	8.41	30	48		63	70
Zr	(nM)	10	0.54	3.2	6.6	2.6	4.1	9.3	0.33		

^a Measurement uncertainty: 95% confidence interval (Nilsson and Borgiel, 2005).^b 0.8%: 0.06–1.4 μM, 5%: >1.4 μM.^c 0.2%: 0.01–1.4 μM, 2%: >1.4 μM.^d 0.7%: 0.02–0.65 μM, 3%: >0.65 μM.^e Major element data for 2782 lakes in Sweden (The Swedish National Survey, 2005) and trace element data (242 lakes) from SEPA (1999).^f Seven hundred and twenty-five watercourses of various size in Sweden (The Swedish National Survey, 2000), trace element median values (76 watercourses) from SEPA (1999).^g One hundred and sixty-three watercourses of various size in Svecofennian megablock 1.1.4 (Salminen et al., 2004).

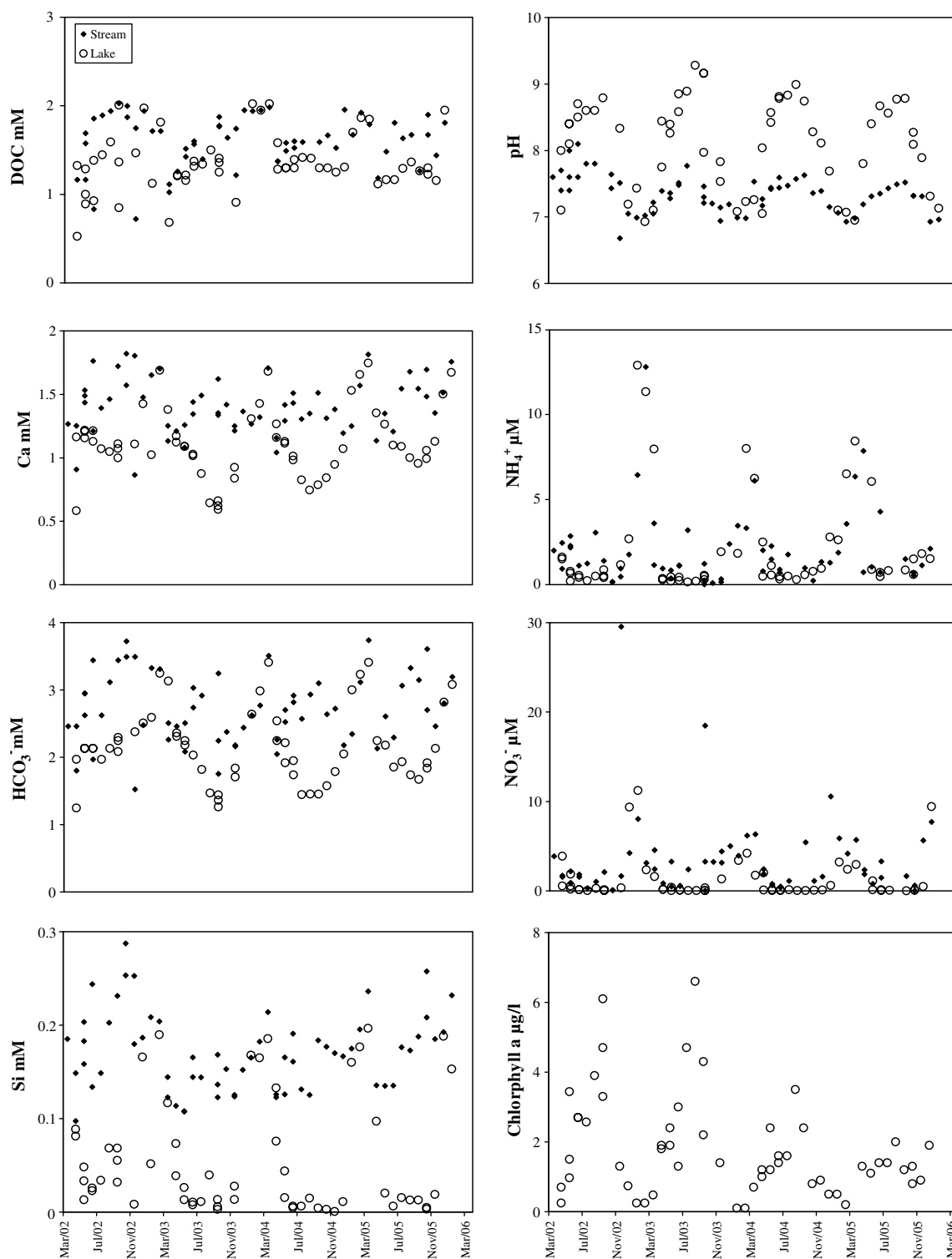


Figure 2 Seasonal concentration variations of selected variables in the lake (open circles) and in the stream (black diamonds).

surface flow paths over frozen wetlands (Laudon et al., 2004), and in a large unregulated Swedish river (Kalix River) an increase in DOC concentration during melt-water discharge was explained by release of dissolved organic matter from the upper soil profile and peatlands during such periods (Ingri et al., 2005).

Nutrients (P, N, Ca, HCO_3^- , Si), pH and O_2

During the winter the concentrations for each of Ca and HCO_3^- was similar in the stream and the lake, but in summer (except 2002) the concentrations decreased considerably in

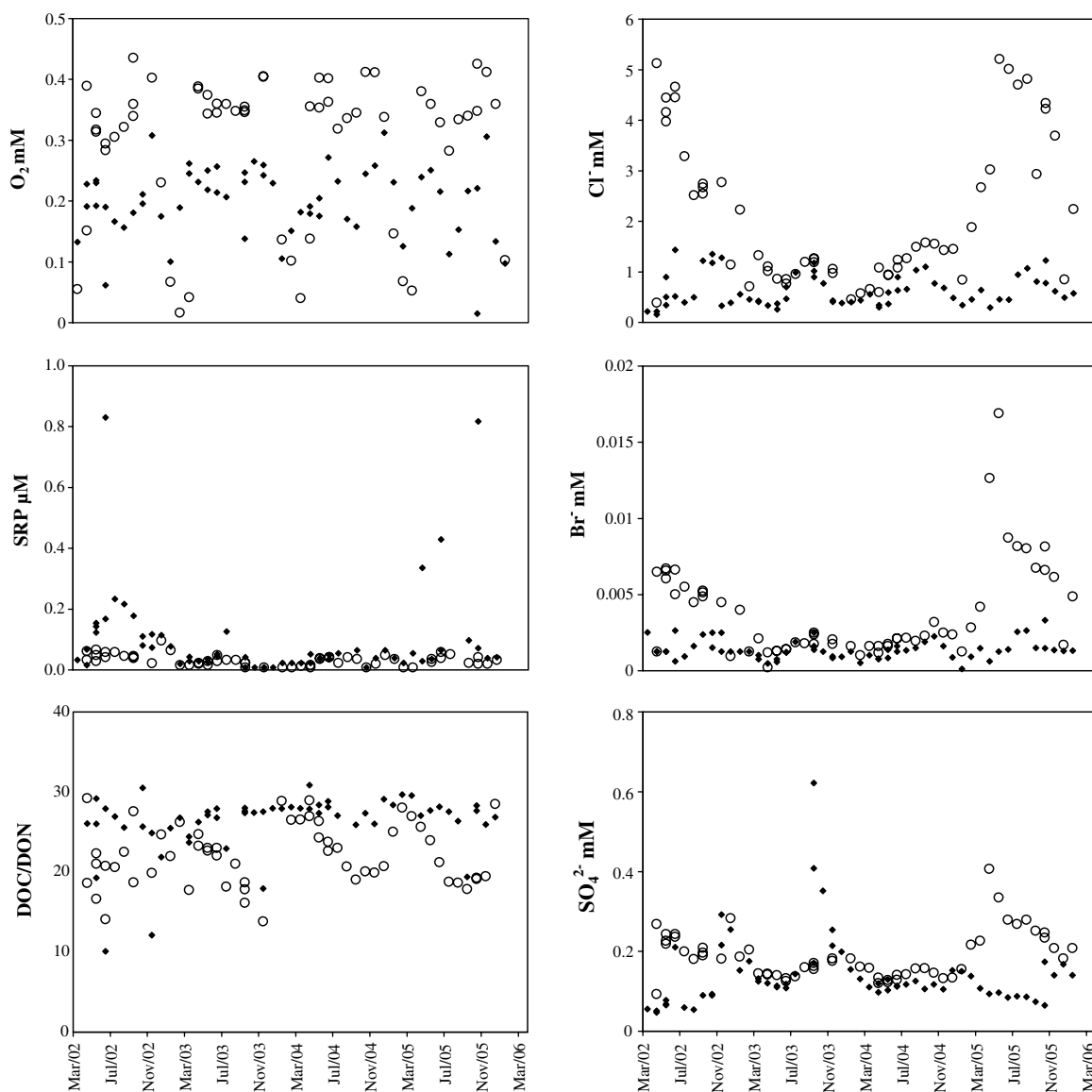


Figure 2 (continued)

the lake (Fig. 2). For Si this phenomenon was even more pronounced (Fig. 2). The concentrations of both NH_4^+ and NO_3^- increased considerably during the winter in both the lake and the stream, while the concentrations were much lower during the rest of the year, and for NO_3^- in the lake it was extremely low (Fig. 2). pH had an inverse pattern, i.e. increased values in the lake in summer (Fig. 2). By using the stream (inflow to the lake) as a reference, these patterns clearly showed that in the lake in summer there was an in situ removal from the aquatic phase of Ca, inorganic C, NH_4^+ , NO_3^- , Si and protons. This, in turn, is a result of biological activity supported by the high concentrations in summer of chlorophyll *a* and O_2 caused by photosynthesis (Fig. 2). The particulate fractions were strongly correlated with the chlorophyll concentration: PON (Spearman correlation coefficient for $n = 54$; $r_s = 0.84$), POP ($r_s = 0.78$), POC ($r_s = 0.77$). The yearly stream fluxes are given in Table 2. A particularly high number was calculated for DON ($>6.8 \text{ kmol/km}^2/\text{year}$).

At all times, i.e. also during the concentration minima during the summer, the Ca and HCO_3^- concentrations were relatively high (Table 1; see min values). This is due to chemical weathering of the calcareous till and the subsequent extensive leaching of Ca and HCO_3^- . It is well known that Ca in many surface water systems is directly controlled by chemical weathering and a Ca/ HCO_3^- ratio of 0.5 is expected to result from the dissolution of calcite according to the reaction (Langmuir, 1997): $\text{H}_2\text{O} + \text{CO}_2 + \text{CaCO}_3 \rightarrow 2\text{HCO}_3^- + \text{Ca}^{2+}$. The ratio of Ca/ HCO_3^- in the lake and the stream had median values of 0.52 (range 0.4–0.6) and 0.51 (range 0.4–0.8), respectively, which support a calcite source. While in many surface waters there is a correlation between HCO_3^- and pH, in the lake here studied there was an inverse correlation between these two variables. This is caused by uptake of both HCO_3^- and protons by primary producers in summer resulting concomitantly in an increase in pH.

Table 2 Annual fluxes in Kungsträsket stream

	kmol/km ² /year
Br ⁻	0.11
Ca	153
Cl ⁻	54
HCO ₃ ⁻	289
K	6.0
Mg	20
Na	55
Si	19
SO ₄ ²⁻	14
Sr	0.10
DOC	187
POC	2.7
TN	7.8
NH ₄ ⁺	0.20
NO ₃ ⁻	0.50
DON	6.8
PON	0.29
TP	0.05
SRP	0.01
POP	0.02

NH₄⁺ refers to NH₄⁺-N, NO₃⁻ refers to NO₃⁻-N + NO₂⁻-N and SRP refers to PO₄-P.

The reason for the exceptionally low dissolved Si concentration in the lake during the growing season is the development of diatoms in early spring, which is not occurring in the stream (Fig. 2). The diatoms are a group of phytoplankton algae that have silicified cell walls (Wetzel, 2001) and, thus, Si is efficiently taken up and utilised by the growth of such species (Garnier et al., 1995; Wall et al., 1998). The diatom production is greatest in the spring when the water is rich in nutrients, but during the growing season these species are gradually outcompeted and replaced by green algae and cyanobacteria not dependent on Si availability. Still, dissolved Si in the studied lake was very low until late autumn (November–December), which can be explained by: (1) removal by sedimentation of diatoms, a process which is more rapid than weathering of aluminosilicate minerals supplying Si (Wetzel, 2001), and (2) continuous and temporally extended diatom growth, which in oligotrophic lakes such as the one studied is not uncommon (Wetzel, 2001). The rapid increase in Si concentrations in November–December, to values similar to those in the stream, is a result of diminished uptake by diatoms and/or inputs of stream water enriched in Si causing the concentrations to rapidly equilibrate with those existing in the stream (Neal et al., 2005). The Si concentrations in the stream and in the lake during winter months are regulated by weathering rates and equilibrium with aluminosilicate minerals, which continuously supply the surface water with Si.

The total P concentration in the lake was rather low (median = 0.36 µM) when compared with that in lakes throughout Sweden (average = 0.58 µM), while the SRP level was very low in both the lake (median = 0.03 µM) and in the stream (median = 0.04 µM) as compared to the Swedish reference data (Table 1). The SRP concentrations in the lake

were not dependent on season (Fig. 2). The inorganic N (NO₃⁻ and NH₄⁺), in a manner similar to P, was low in both the lake and stream when compared to Swedish average values (Table 1). In contrast, the total N concentration in the lake was high (median = 71 µM). This is due to an abundance of organic N associated with the dissolved humic substances.

In the stream, the ratio of DOC to DON was very stable over time and was mostly between 25 and 30 (Fig. 2). This reflects an allochthonous input of humic substances (i.e. from terrestrial systems) carrying N, and minor in stream biological productivity. In the lake, in contrast, the DOC/DON ratio showed a seasonal variation over the last three study-years with values in winter similar to those in the stream and decreased values in the other seasons reaching minima in summer and/or autumn (Fig. 2). A possible additional source of DON in the spring–summer–autumn period in the lake is autochthonous production, although allochthonous inputs are still the major sources of the organic matter (Arheimer et al., 1996; Chapman et al., 2001). Arheimer et al. (1996) and Chapman et al. (2001) attributed summer increases in DON concentrations to biological activity within the aquatic environment. Autumn increases in DON concentrations are related also to increased inputs from terrestrial sources, e.g. decomposition on recent litter fall (Triska et al., 1984; Hagedorn et al., 2001).

Alkali and alkaline earth metals (Na, Mg, K, Sr) and selected anions (Cl⁻, SO₄²⁻, Br⁻)

A U-shaped temporal profile occurred in the lake, but not in the stream, for Na, Mg, K, Cl⁻ and Br⁻ (Fig. 2) and to some extent for Sr and SO₄²⁻, i.e. the concentrations were increased during April 2002 to December 2002 and during March 2005 to December 2005 (Cl⁻, Br⁻ and SO₄²⁻ shown in Fig. 2). When the Cl⁻ concentration increased in the lake, the ratios of Mg/Cl, SO₄/Cl, K/Cl and Sr/Cl decreased, and when Cl⁻ reached 3–5 mM the ratios of Mg/Cl and SO₄/Cl became similar to those in sea water while K and Sr did not reach the sea water ratio (Fig. 3). The ratios of Na/Cl⁻ (median 0.85) and Br⁻/Cl⁻ (0.0017) were similar to those in sea water (Fig. 3). These patterns show that: (1) the reason for the elevated concentrations of these solutes in the lake at both ends of the sampling period is inflow of Baltic brackish-water, (2) K and Sr is, in contrast to Na, Cl⁻, Mg, SO₄²⁻ and Br⁻, never strongly dominated by intruding brackish-water. Consequently, an important control of these major solutes in the lake is random inflow of brackish water. This inflow, in turn, is caused by a combination of wind direction, distribution of regional air pressure and extent of water in the terrestrial water bodies, while there is no tidal influence. Since the brackish-water intrusions did not reach the stream, the stream-fluxes given in Table 2 are the result of input through weathering and atmospheric deposition only.

In the stream, the concentrations of Na, Mg, Cl⁻ and Br⁻ and to some extent Sr were inversely related to discharge (Cl⁻ and Mg shown in Fig. 4). This is a common phenomena (Rice and Bricker, 1995; Holloway and Dahlgren, 2001) related to variable source areas at varying hydrological condi-

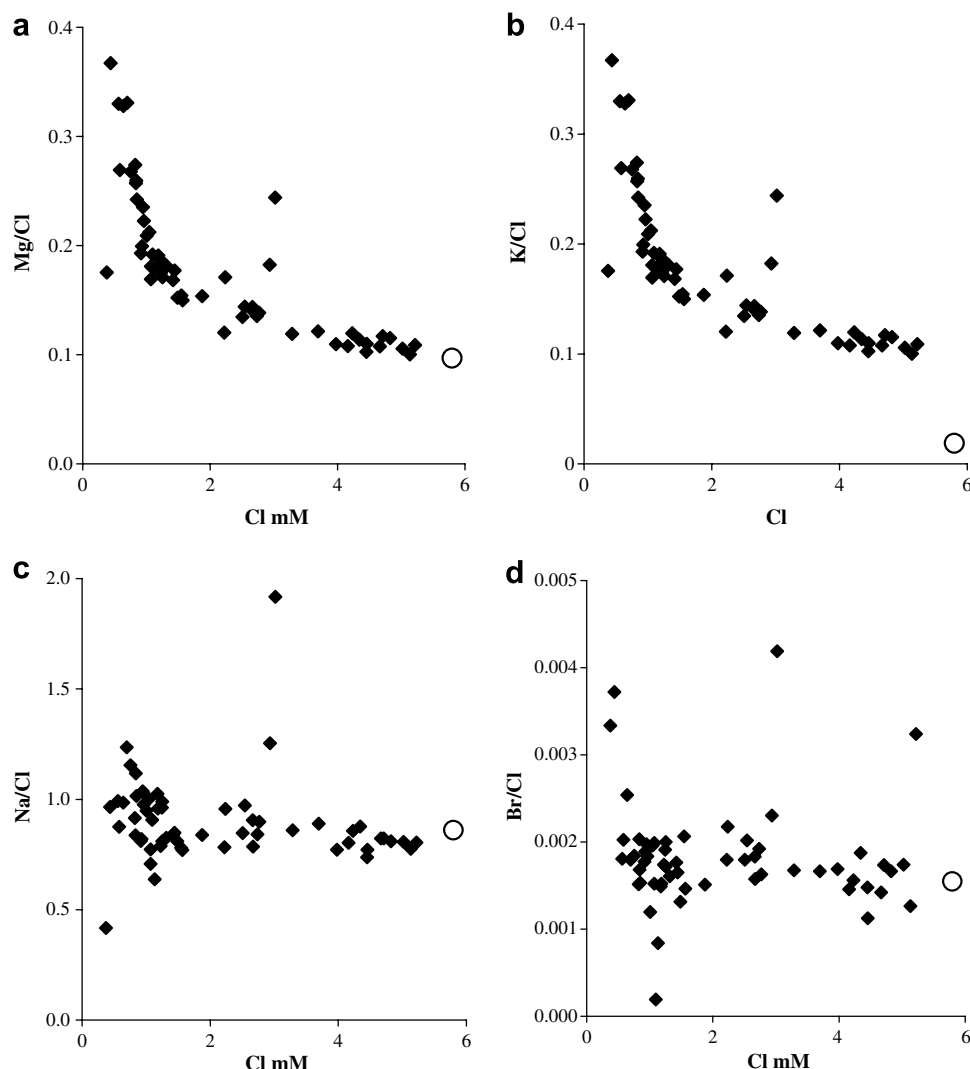


Figure 3 Selected hydrochemical plots for the Bolundsfjärden Lake. The corresponding ratio for Sea water is indicated with an open symbol (Pilson, 1998).

tions. During dry periods water table drawdown results in discharge from deeper layers where the water is enriched in major ions due to weathering of calcite and aluminosilicates (plagioclase, biotite, etc.) and/or existence of old brackish-water (Laaksoharju, 2005). Sulphate, in contrast, was uncorrelated with flow (Fig. 2). On three sampling events in September–October 2003 SO_4^{2-} was particularly high in the stream (Fig. 2) most likely reflecting oxidation of sulphides as other major solutes were not increased and as fine-grained potentially sulphide-bearing sediments cover up to a few percentage of the drainage area (Sohlenius et al., 2004).

When the brackish-water inflow to the lake was low (or non-existent), i.e. in between the two inflow events at both ends of the sampling period, the patterns and concentrations in the lake of Na, Mg, K, Cl^- , SO_4^{2-} and Br^- were similar to those in the stream (Fig. 2). This shows, that at periods of limited brackish-water impact, these solutes are largely controlled by input from catchment sources (weathering products and trapped brackish-water in bedrock fractures)

controlled indirectly by the hydrology (i.e. water levels in the soil) (see Fig. 5).

Trace elements

The concentrations of trace elements (not determined in all samples) were similar in the lake and the stream (Table 1). The only significant difference (Mann–Whitney test, $\alpha = 0.01$) occurred for Fe (higher in the stream) and Pb (higher in the lake). In comparison to reference waters, the trace element concentrations were overall low or on an average level, except for U, La, Mo and Zr which were clearly elevated (Table 1). The behaviour of the former two, being of particular interest in terms of risks associated with nuclear-fuel waste, were studied in some more detail (the reasons for elevated Mo and Zr concentrations were not further considered in this study).

There are at least three possible explanations for the elevated U concentrations. First, the area has recently risen

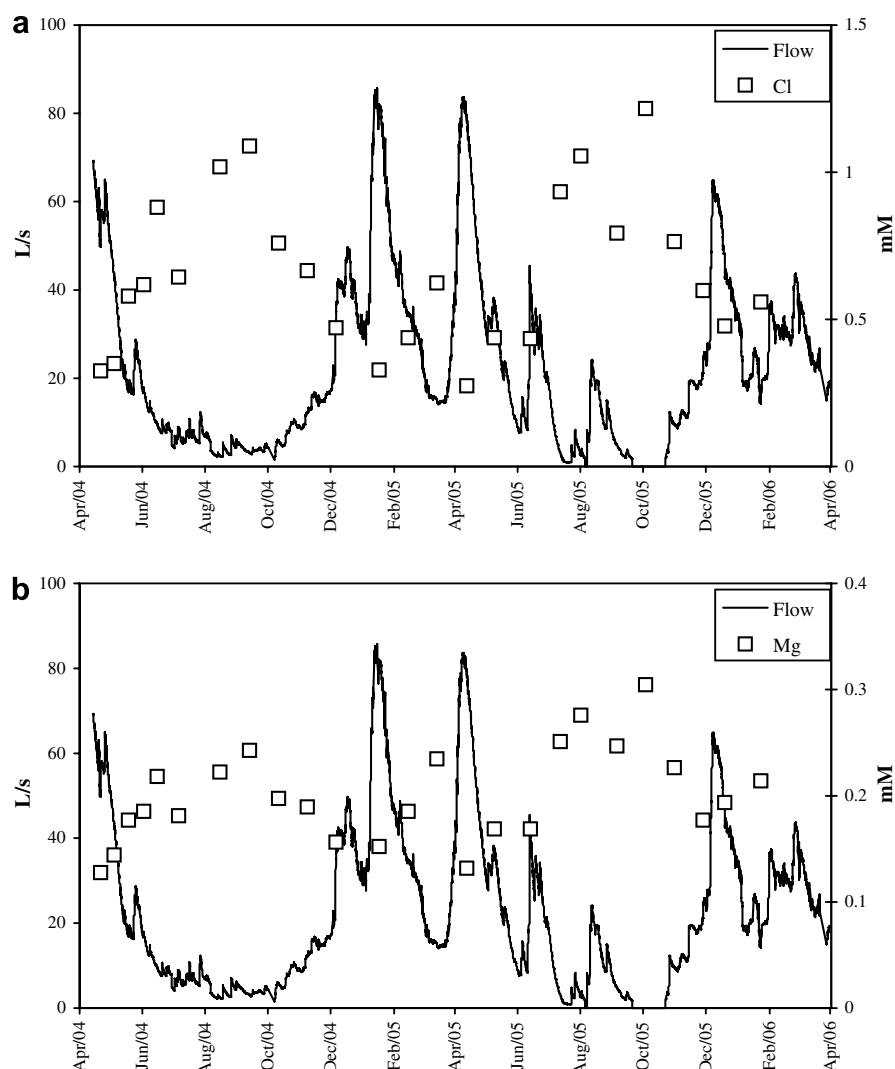


Figure 4 Concentrations of selected chemical elements plotted on the hydrograph for the Kungsträsket stream.

above the sea level and thus contains small and scattered deposits of sulphidic postglacial sediments that may contain reduced U(IV) which under oxidised conditions are converted to soluble and mobile U(VI). Second, glacial till that in the area has a higher concentration of U (1.8 ppm) than the average for the Baltic shield (1.0 ppm) (Salminen et al., 2004). Third, the underlying bedrock which is composed of granites and granodiorites which are most likely enriched in U.

The speciation calculation predicted that in all analysed waters the dominating U species (>90%) was the calcium uranyl carbonate complex ($\text{CaUO}_2(\text{CO}_3)_3$ (aq.)), with minor contribution from another carbonate complex or DOC. These results are in line with earlier studies showing that calcium uranyl carbonate complexes are important in the aqueous chemistry of U(VI) at circumneutral pH values (Bernhard et al., 1996, 2001; Kalmykov and Choppin, 2000; Fox et al., 2006), and that in areas where calcium carbonate is abundant in soils the U(VI) sorption decreases as a result of formation of soluble calcium uranyl carbonate (Zheng et al., 2003). Uranium can also be abundantly associated with colloidal Fe (Andersson et al., 2001) and Al (Arai et al., 2006), not measured in this study. However, the very

low Fe and Al concentrations in contrast to the very high U concentrations in the waters (Table 1) make a large contribution of such species unlikely.

The ΣREE abundance was similar in the stream and lake (Table 1), and all REEs in all samples were predicted to be carried to >99% as organic complexes which has been indicated also for other waters elsewhere (Tang and Johansson, 2003; Sonke and Salters, 2006). The NASC-normalised fractionation patterns (values were taken from Haskin et al. (1968) except for Dy which were from Gromet et al. (1984)) of all samples, in both the lake and stream, were characterised by a relative increase across the lanthanide series (Fig. 4). This pattern is in agreement with the speciation calculation as the stability of REE-DOC complexes increase from the light to the heavy REEs (Sonke and Salters, 2006). In contrast, overburden groundwaters of the area have ΣREE concentrations which are about an order of magnitude higher (median 46.7 nM) and characterised by a flat to HREE-depleted pattern (Rönnback et al., in press). There is therefore no evidence, first, of a change in the behaviour of REEs as they enter the lake from the inflow stream and, second, that simple dilution of overburden groundwaters is

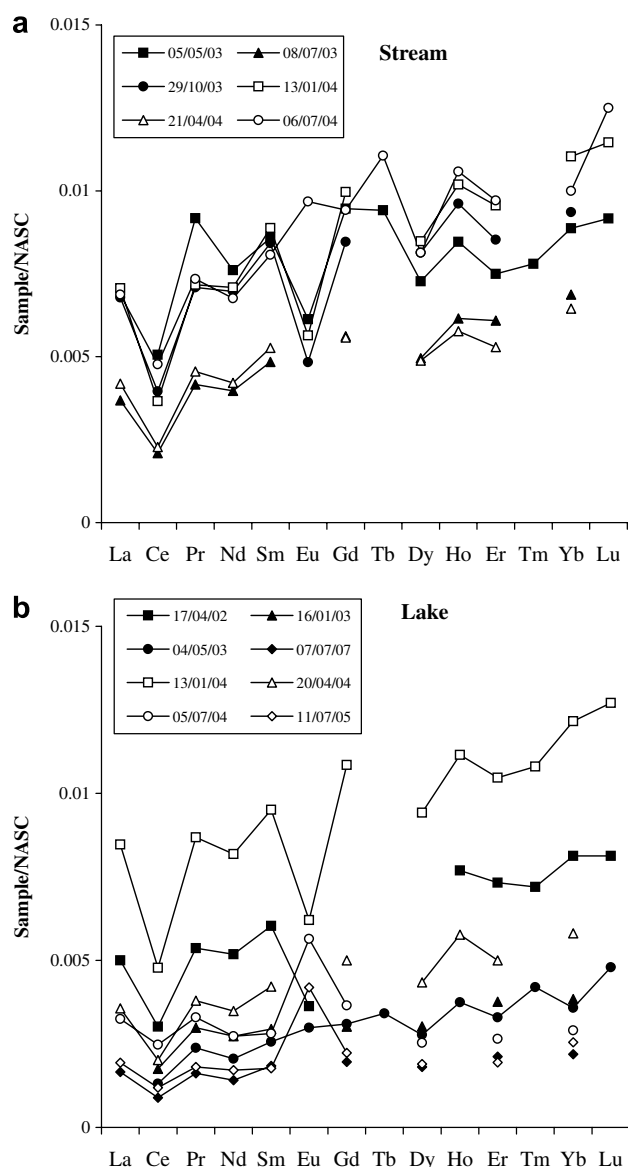


Figure 5 NASC-normalised REE fractionation patterns in the Kungsträsket stream and the Bolundsfjärden Lake. The symbols correspond to day/month/year.

the main control of REE abundance and speciation in the surface waters. The REEs in the stream and lake are therefore either derived from near-surface soil/humus weathering or consist of overburden groundwaters modified on route to the surface. Assuming similar behaviour of one or several trivalent actinides (e.g. Am^{3+} and Cm^{3+}), it is reasonable to suggest complex and/or limited vertical pathways, and small changes as water is transported over the surface environment (from stream to lake).

Conclusions

The main conclusions of the study are:

- As a result of the calcareous overburden caused by redistributed Paleozoic deposits, Ca and HCO_3^- concentrations were relatively high in both the stream and lake throughout the period.

- Limnic primary production resulted in decreased concentrations of Ca, HCO_3^- , NH_4^+ , NO_3^- and Si, and increased pH and concentrations of chlorophyll *a*, O_2 , DON, POC, PON and POP in the lake in summer, but in other seasons (in winter in particular) when the production was minimal or non-existent the concentrations in the lake and the inflow stream were similar.
- Intrusion of brackish-water resulted in moderately to strongly increased concentrations of Cl^- , Na, Mg, Br^- , SO_4^{2-} , K and Sr in the lake: the ratio versus Cl^- where for Na and Br^- always similar to those in sea water, for Mg and SO_4^{2-} similar to those in sea water at elevated Cl^- concentrations ($>3 \text{ mM}$), while K and Sr always occurred in relative excess as compared to sea water.
- The U concentrations were high in both the stream and the lake, and were predicted to be carried to $>90\%$ in the form of calcium uranyl carbonate, in a model in which however colloidal Fe and Al oxyhydroxides were not considered.
- The REEs had similar concentrations and fractionation patterns in the stream and lake, unlike those found in the overburden groundwaters, and in contrast to U was predicted to be carried as organic complexes.
- In terms of the area being chosen as a site for bedrock disposal of spent nuclear fuel, of particular importance is further investigations into the sources and mechanisms of the high U concentrations in the surface waters and confirmation of the importance of the calcium uranyl carbonate complex in the surface transport of this metal. Also, the abundance of humic acids, predicted to carry the REEs which consist of analogues for several actinides, deserve special attention in a safety assessment perspective focusing on radionuclide contamination of the surface environment.

Acknowledgements

This study was financially supported by Äspö Research School. We would like to thank the Swedish Nuclear Fuel and Waste Management Company (SKB) for kindly providing us with the data. We are also grateful to the following persons for the help and information we received: U. Brising, J.-P. Gustafsson, P.-H. Johansson, V. Linde, A.-C. Nilsson and M. Tröjbom.

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