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Influences of dissolved organic carbon on stream water chemistry in two forested catchments in central Sweden

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Abstract Stream water chemistry in two headwater streams draining two small, adjacent catchments in Bispgården, central Sweden was studied during the 2003 and 2004 growing seasons. The two catchments closely resemble each other in regard to size, shape and drainage density, with the major difference found in the area of wetland lining the streambeds. The emphasis of the study was to investigate the stream water chemistry of these closely resembling catchments, regarding the quality and quantity of dissolved organic carbon (DOC) and its influence on the concentrations of di- and trivalent cations. The streams showed significant differences in the content and size distribution of DOC and in the distribution of cations between the different size fractions. For both streams the high flow events induced by precipitation influenced the chemistry of the streams through increase of organic matter and its associated cations. Fanbergsbäcken, with relatively low pH and high DOC concentration, had a greater amount of high molecular mass (HMM) DOC to which approximately 75% of Al and Fe and about 50% of Ca and Mg were associated. Gråbergsbäcken, with a higher pH and lower DOC level, had approximately 65% of Al, 40% of Fe and 30% of Ca and Mg associated to its HMM DOC fraction. Sixteen different low molecular mass organic acids were found in the stream water, of which oxalic and lactic acid were present in the highest concentrations.

Keywords Catchment · Dissolved organic carbon · Low molecular mass organic acid · Metals · Size fraction · Stream water

Introduction

In stream ecosystems, organic matter measured as dissolved organic carbon (DOC) is of great importance in mobilization and transport of trace metals and contaminants, in regulating acid–base chemistry and as a primary food source in the aquatic food web (Hope et al. 1994; Kalbitz et al. 2000; Oliver et al. 1983; Pettersson and Bishop 1996). DOC is commonly defined as organic molecules that pass through a 0.45 μm-filter, and therefore includes a wide variety of compounds with different sizes and properties (Kalbitz et al. 2000). Due to its heterogeneous complexity, however, characterisation of DOC is difficult without dividing it into smaller groups

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according to certain properties, such as size. The low molecular mass (LMM) fraction of DOC (<1 kDa) contains compounds such as LMM organic acids (LMMOAs) and fulvic acids, both of which possess a strong ability to complex metals such as Al and Fe (van Hees and Lundström 2000). The high molecular mass (HMM) fraction of DOC contains organic substances >1 kDa in size and smaller than 0.45 µm, predominantly made up of humic substances such as humic acids which also adds to the metal binding capacity of DOC (Tipping 1998). There are no absolute limits defined for the sizes of fulvic and humic acids, but it is generally assumed that as the molecular weight increases, the charge density decreases, and that humic acids might be formed by subunits from the fulvic fraction (Reemtsma and These 2003; Shin et al. 1999; Sutton and Sposito 2005).

Stream water wetlands, i.e. riparian zones, constitute an important source of DOC to stream water in forested catchments (Bishop et al. 1994; Bishop et al. 2004; Hinton et al. 1998; Laudon et al. 2004). During high flow events the water table rises in the soil, flow paths change and old water stored in unsaturated soil becomes mobilized (Vestin et al. 2008a). Even superficial flows over the soil may occur. This causes rapid variations in stream water chemistry as a consequence of increased DOC concentration, changing the composition of organic matter and thereby also the amount of cations and nutrients associated to DOC.

The current study was conducted on two-first-order streams in adjacent forested catchments during two growing seasons (2003 and 2004). The catchments were similar in shape, size and drainage density—all physical characteristics that influence runoff (Arnell 2002). Due to their location, they were also exposed to similar weather conditions and precipitation. Previous studies conducted by Vestin et al. (2008b) in one of the two catchments indicated a high association of cations with HMM DOC in soil solution, and a similar result was observed in stream water on a single isolated occasion.

The main objective of the current study was to investigate the role of DOC as driver of stream water chemistry induced by stream water flow, focusing on the quantity and quality of DOC, its seasonal fluctuations and its influence on cation concentrations in the stream water of both catchments. The quality measurements used were titration for estimating the carboxylic content, and size fractionation by ultrafiltration for establishing whether the cations were present in the LMM fraction (i.e. in free form or associated to LMM DOC) or in the HMM fraction (most likely associated to HMM DOC). The presence of LMM organic acids (LMMOA) as a constituent of DOC in the stream waters was also determined, an area that essentially lacks previous investigation. LMMOA are potent complexing agents for Fe and Al and will contribute to the amount of these cations recovered in the LMM fraction.

Materials and methods

Site description

The study took place in two small, adjacent forested catchments, 50 and 40 ha, respectively, in Bispgården (63°07N, 16°70E), central Sweden (Fig. 1). Each catchment is drained by a first order forest stream. The forest consists mainly of 50 to 80 year-old Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris)* and the catchments are located at an altitude of 258 m above sea level, which is above the highest coastline in this area, and therefore lacks postglacial surficial sediments common to postglacial deltas. The climate and the chemical deposition for the two catchments are estimated to be closely similar. The parent material consists of gneiss and granite, and the catchments show great similarities in ground vegetation and tree stand. The catchments are also similar in shape, which is crucial when measuring parameters closely related to catchment runoff (Arnell 2002). The annual precipitation is approximately 700 mm and the average temperature +2°C. The daily runoff based on measurements and simulations has been presented earlier in Vestin et al. (2008a).

Stream characteristics

Both streams, known as Fanbergsbäcken and Gråbergsbäcken (Fig. 1), originate from small mires, with estimated areas of 0.2 ha and 1 ha, respectively. Gråbergsbäcken, however, also receives water from a spring, making it less sensitive to drought. Like the majority of the forest streams in central and northern

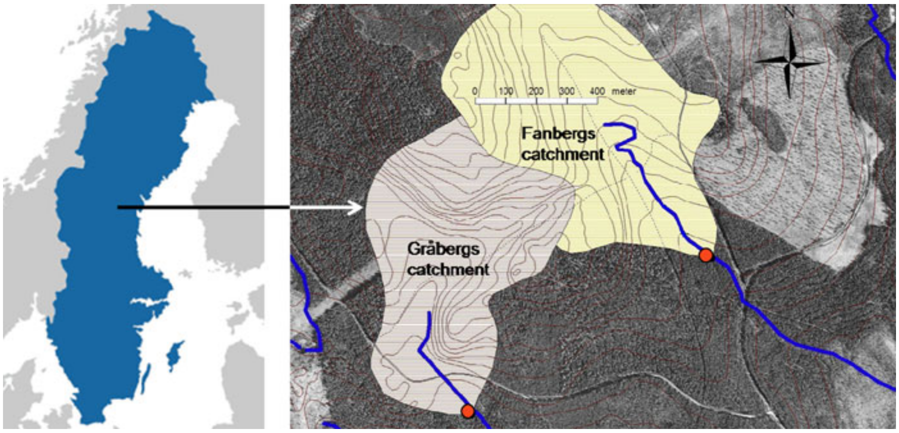

Fig. 1 The investigated streams (Fanbergsbäcken to the *right* and Gråbergsbäcken to the *left* in the picture) located in two small, bordering catchments in Bispgården (63°07N, 16°70E) in central Sweden

Sweden, these streams have been subjected to ditching, which is common in many peatlands and wet mineral soils to improve forest productivity (Ivarsson and Jansson 1994). The scars from this treatment are more visible in Gråbergsbäcken, where the streambed cuts deeper into the soil and the stream water lacks contact with the shallow organic soil layers for the last 80% of its stretch. An increase in flow would therefore raise the surface of Gråbergsbäcken, but essentially no flooding of the banks would occur. The deeper streambed might also lead to a higher influence of groundwater from deeper flow paths in the soil. In Fanbergsbäcken the traces of the ditching are less obvious, and the stream is shallower and has a more pronounced riparian zone that lines at least 60% of the stream and is evenly distributed throughout its stretch, which would cause the riverbed to expand up over the banks in several areas along the stream at high flows.

Sampling

The sampling season lasted from April to November in 2003 and 2004 as the streams were frozen in winter. The sampling points were located at the outlet of each catchment. Stream water samples from both sampling points were collected manually every second week and with higher frequency during high flows. A level logger (Trutrack, Christchurch, New Zealand) continuously measured the flow in Fanbergsbäcken. The water was collected in polyethylene bottles and kept cool until pre-treatment within 24 h after sampling.

Chemical analyses

All samples were stored refrigerated until analysis unless otherwise mentioned. The pH was determined within 1 day using a Beckman Φ32 pH-meter. For all other analyses the stream water was filtrated by 0.45 μm membrane filter (Millex-HV, Millipore). Samples for cation analysis (Ca, Mg, Fe, Al, K, Na, Si) were acidified with ultrapure HNO_3 before analysis with inductively coupled plasma mass spectrometry (ICP-MS) (VG PQ ExCell, Thermoelemental, Winsford, England). DOC was determined within 2 days of sampling and quantification was achieved by catalytic oxidation and IR detection with a Shimadzu TOC analyzer, TOC-5050A (Shimadzu, Kyoto, Japan). Anion determination of F, Cl and SO_4 was performed within 2 days of sampling by ion chromatography with Dionex DX-120 (Dionex, Sunnyvale, CA, USA). Flow injection analysis (FIA) with a FIAstar 5000 (Foss, Höganäs, Sweden) was used for the determination of quickly reactive aluminium (Al_{qr} (Clarke et al. 1992)) within 2 days of sampling. Samples for analysis of NH_4 and PO_4 were stored frozen until analysis with FIA.

Some stream water samples were separated into a smaller size fraction (nominal molecular weight cutoff 1 kDa), here referred to as the LMM fraction of the substance, by means of a stirred cell method (Amicon model 8050), in which the water samples are passed through a YM-1 membrane of regenerated cellulose (Millipore Corporation, Billerica, MA 01821) under a N_2 pressure of 3.5 bar. For further details on this method see van Hees et al. (2001). DOC and cations were determined for these samples and the amount of elements associated with the high molecular mass (HMM) fraction ($M_w > 1$ kDa) was calculated by subtracting the concentration recovered in the LMM-fraction ($M_w < 1$ kDa) from the total concentration.

Samples for determination of total acidity were stored frozen until analysis by titration. After thawing, the sample was first passed through a column with a strong cation exchange resin (Dowex 50 × 8), and then titrated with 0.01 M NaOH to pH 7. A constant flow of N_2 was supplied to the sample to remove any atmospheric CO_2 during the titration, which was performed with an autoburette system (702 SM Titrino, Metrohm Ltd., Herisau, Switzerland) and a glass electrode (Mettler-Toledo). For further details on this method, see Hruska et al. (1996).

Samples for analysis of LMMOAs were stored frozen and then determined by liquid chromatography–tandem mass spectrometry (LC–MS/MS; Bylund et al. 2007). The LC–MS/MS system was comprised of a Shimadzu LC-10AD pump, an Agilent 1100 autoinjector, a Supelcogel C610-H column (300 × 7.8 mm) and an API3000 mass spectrometer (MDS Sciex, Concord, Canada). The mobile phase consisted of 10% (v/v) methanol and 0.01% (v/v) formic acid in MilliQ-water.

Data analysis

The focus in this article is on the 2003 season, for which a larger dataset was collected. This season also had greater variability in precipitation, which gave an opportunity to monitor larger variability in flow, and thus greater responses in the water chemistry. The data from 2004 is generally considered as base flow and used to validate the findings from 2003.

To achieve the COOH-concentration, the equivalents of strong acid concentration by means of the sum of F, Cl, NO_3, PO_4 and SO_4 were subtracted from the total acidity. The anion deficiency (AD) was calculated as the difference between the charge equivalents of the measured anions and cations. Site density was calculated as the amount of carboxylic groups per mg DOC.

All mathematical and statistical data analyses were completed using Microsoft Excel 2003. Correlation patterns were determined via Pearson correlation coefficients and their significance evaluated via *t*-tests. Differences were evaluated via paired t-tests, whenever appropriate. Differences between the streams in the proportional distribution of the size fractions, however, were evaluated via non-parametric sign test. The acceptance limit for significance was $P < 0.05$.

Results and discussion

The 2003 growing season was characterized as being normal to dry with a major storm event in the middle of August, resulting in a 10-fold increase in stream flow for a couple of hours. This resulted in a large response in the stream water chemistry with elevated DOC concentrations and a substantial decrease in pH (Fig. 2), which dominated the seasonal pattern and could be traced by rapid changes in concentration for most of the different parameters measured. The 2004 season was very dry, lacking heavy rain events and thus any large fluctuations of the water chemistry (Vestin et al. 2008a).

DOC

The DOC concentrations in the two streams were positively correlated during both sampling seasons (Table 1), which indicate that the catchments are equally affected by precipitation, causing a similar pattern in runoff from the streams. The pH was generally one unit lower in Fanbergsbäcken compared to Gråbergsbäcken, which was directly related to its significantly higher DOC content and hence also organic acidity (Fig. 2; Table 2). In 2003, the total concentration of DOC was positively correlated with its HMM fraction (DOC > 1 kDa) in both streams (Table 3), even though the DOC in Fanbergsbäcken consisted of significantly larger relative amounts of HMM DOC than Gråbergsbäcken, where approximately equal amounts of carbon were found in the two size fractions (Tables 2, 4). The concentrations of HMM DOC were nonetheless positively correlated between the streams (Table 1).

In 2003, pH and DOC were negatively correlated in both streams with a major decline in pH and a corresponding increase in DOC occurring during the storm event in August (Fig. 2; Table 3), while in 2004 there was a significant correlation in Fanbergsbäcken ($r = -0.62$) but not in Gråbergsbäcken ($r = -0.12$).

The carboxylic concentration, estimated by titration, was correlated between the streams for both

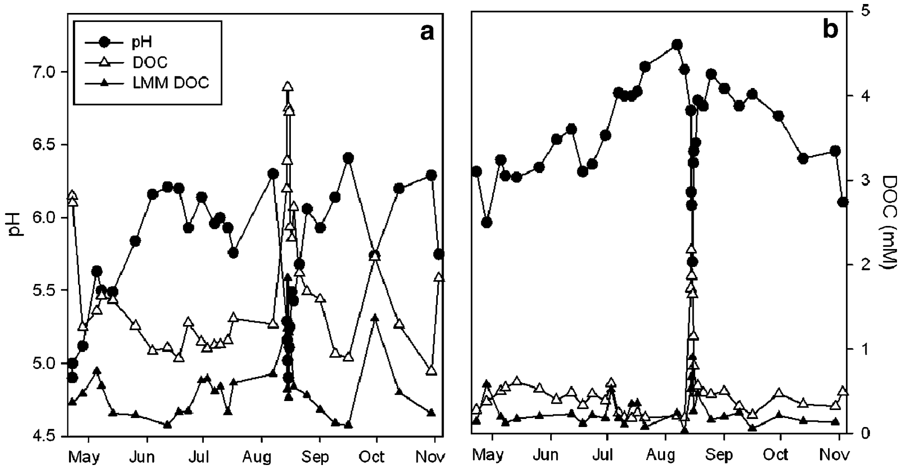

Fig. 2 Temporal variation in pH, DOC and LMM DOC ($M_w < 1$ kDa) (mM) in Fanbergsbäcken ($n = 35$, 36, 29) (**a**) and in Gråbergsbäcken ($n = 36$, 37, 31) (**b**) during 2003

Table 1 Pearson correlation values between Fanbergsbäcken and Gråbergsbäcken during 2003 and 2004, significant correlations ($P < 0.05$) marked with *

	2003	2004
DOC	0.81* ($n = 34$)	0.76* ($n = 23$)
HMM DOC	0.75* ($n = 28$)	
COOH	0.66* ($n = 34$)	0.52* ($n = 15$)
Al	0.73* ($n = 25$)	0.06 ($n = 21$)
Fe	0.71* ($n = 25$)	0.34 ($n = 21$)
Ca	0.84* ($n = 25$)	0.93* ($n = 21$)
Mg	0.78* ($n = 25$)	0.91* ($n = 21$)

sampling seasons (Table 1) and to DOC in both streams (Table 3; 2004: Fan: $r = 0.77$, Grå: $r = 0.53$), but showed a higher concentration (μeq/l) in Fanbergsbäcken (Fig. 3; Table 2) in accordance with the higher content of DOC in this stream. The difference in site density for the streams emphasizes the differences in DOC composition. Fanbergsbäcken, with an average of 10.0 (SD 1.40) μeq/mg DOC ($n = 36$), is well within the range of the universal model proposed by Oliver et al. (1983) and of that reported for Swedish sites by Bergelin et al. (2000) and Hruska et al. (2003). In Gråbergsbäcken the

Table 2 Median concentrations (1st–3rd quartile) for Fanbergsbäcken and Gråbergsbäcken during the sampling seasons 2003–2004

Site	2003		2004	
	Fan	Grå	Fan	Grå
pH	5.76 (5.36–6.14)	6.54 (6.32–6.82)	5.62 (5.48–5.81)	6.16 (6.06–6.37)
DOC (mM)	1.4 (1.1–2.4)	0.5 (0.3–0.6)	1.4 (1.1–2.0)	0.4 (0.3–0.5)
HMM DOC (mM)	0.9 (0.7–1.3)	0.2 (0.1–0.3)		
COOH (μeq/l)	171.5 (137.4–300.1)	72.3 (47.8–107.4)	178.6 (143.9–203.7)	80.26 (61.7–91.7)
Fe (μM)	5.9 (3.4–10.7)	0.9 (0.7–1.6)	4.8 (3. 8–5.3)	1.0 (0.7–1.3)
HMM Fe (μM)	3.9 (2.5–6.2)	0.3 (0.0–0.7)		
Al (μM)	17.6 (12.9–29.5)	5.0 (3.4–7.4)	16.1 (13.3–18.2)	5.7 (3.7–6.4)
HMM Al (μM)	12.3 (10.4–16.3)	2.3 (1.5–4.8)		
Alqr (μM)	1.9 (0.0–6.3)	0.0 (0.0–1.9)	1.1 (0.7–1.8)	0.0 (0.0–0.0)
Ca (μM)	52.5 (40.7–70.2)	64.7 (61.3–69.5)	40.4 (37.1–48.3)	58.5 (55.9–65.7)
HMM Ca (μM)	29.1 (19.4–34.6)	21.0 (15.1–29.1)		
Mg (μM)	25.4 (19.6–33.6)	23.2 (22.2–25.3)	19.9 (18.2–23.3)	20.2 (19.4–23.5)
HMM Mg (μM)	10.8 (8.0–15.7)	5.4 (4.0–7.9)		
K (μM)	8.5 (5.6–11.6)	9.9 (8.6–15.4)	7.1 (5.3–8.8)	8.9 (8.1–9.7)

High molecular mass (HMM) fractions calculated by subtracting the concentration in the LMM fraction ($M_w < 1$ kDa) from the total concentration

Table 3 Pearson correlation coefficients for 2003

	pH	DOC	HMM DOC	COOH	Fe	HMM Fe	Al	HMM Al	AlQR	Ca	HMM Ca	Mg	HMM Mg
pH		**−0.85* (35)**	**−0.81* (28)**	**−0.83* (35)**	**−0.92* (27)**	**−0.88* (16)**	**−0.95* (27)**	**−0.80* (16)**	**−0.76* (26)**	**−0.92* (27)**	**−0.79* (16)**	**−0.90* (27)**	**−0.71* (16)**
DOC	−0.51* (36)		**0.92* (29)**	**0.95* (36)**	**0.92* (28)**	**0.92* (17)**	**0.93* (28)**	**0.79* (17)**	**0.65* (27)**	**0.92* (28)**	**0.74* (17)**	**0.91* (28)**	**0.66* (17)**
HMM DOC	−0.47*(30)	0.96* (31)		**0.87* (29)**	**0.85* (22)**	**0.90* (17)**	**0.91* (22)**	**0.90* (17)**	**0.66* (24)**	**0.84* (22)**	**0.85* (17)**	**0.84* (22)**	**0.80* (17)**
COOH	−0.59* (39)	0.87* (36)	0.85* (31)		**0.94* (28)**	**0.90* (17)**	**0.95* (28)**	**0.80* (17)**	**0.62* (27)**	**0.94* (28)**	**0.78* (17)**	**0.93* (28)**	**0.69* (17)**
Fe	−0.51* (27)	0.91* (28)	0.88* (23)	0.82* (27)		**0.98* (17)**	**0.98* (28)**	**0.83* (17)**	**0.81* (24)**	**0.98* (28)**	**0.76* (17)**	**0.98* (28)**	**0.65* (17)**
HMM Fe	−0.36 (16)	0.91* (17)	0.91* (17)	0.79* (25)	0.97* (17)		**0.97* (17)**	**0.90* (17)**	**0.74* (13)**	**0.95* (17)**	**0.81* (17)**	**0.96* (17)**	**0.71* (17)**
Al	−0.67* (27)	0.95* (28)	0.91* (23)	0.89* (27)	0.93* (28)	0.92* (17)		**0.87* (17)**	**0.83* (24)**	**0.97* (28)**	**0.81* (17)**	**0.97* (28)**	**0.72* (17)**
HMM Al	−0.56* (16)	0.96* (17)	0.98* (17)	0.90* (24)	0.92* (17)	0.90* (17)	0.99* (17)		**0.71* (13)**	**0.81* (17)**	**0.94* (17)**	**0.82* (17)**	**0.91* (17)**
AlQR	−0.64* (25)	0.64* (26)	0.63* (24)	0.55* (25)	0.68* (21)	0.84* (13)	0.78* (21)	0.92* (13)		**0.86* (20)**	**0.78* (13)**	**0.85* (20)**	**0.69* (13)**
Ca	−0.43* (27)	0.91* (28)	0.87* (23)	0.81* (27)	0.94* (28)	0.93* (17)	0.93* (28)	0.90* (17)	0.71* (21)		**0.78* (17)**	**0.99* (28)**	**0.65* (17)**
HMM Ca	−0.49 (16)	0.93* (17)	0.95* (17)	0.88* (25)	0.91* (17)	0.87* (17)	0.92* (17)	0.92* (17)	0.76* (13)	0.90* (17)		**0.77* (17)**	**0.96* (17)**
Mg	−0.25 (27)	0.81* (28)	0.80* (23)	0.70* (27)	0.87* (28)	0.84* (17)	0.81* (28)	0.79* (17)	0.60* (21)	0.96* (28)	0.84* (17)		**0.65* (17)**
HMM Mg	−0.59* (16)	0.86* (17)	0.92* (17)	0.86* (25)	0.83* (17)	0.82*(17)	0.87* (17)	0.90* (17)	0.71* (13)	0.85* (17)	0.95* (17)	0.78* (17)	

Fanbergsbäcken in bold font and Gråbergsbäcken in regular font with sampling occasions (n) in parentheses. All significant correlations ($P \leq 0.05$) marked with *

Table 4 The median value (1st–3rd quartile) of the fraction of the different substances recovered in the HMM-fraction ($M_w > 1$ kDa) in both streams during 2003

	Fan3	Grå3	P (sign test)
DOC ($n = 29, 31$)	68% (55–81%)	58% (50–69%)	0.043
Ca ($n = 17, 17$)	54% (47–67%)	35% (23–45%)	0.013
Mg ($n = 17, 17$)	48% (36–60%)	24% (19–37%)	0.057
Al ($n = 17, 17$)	73% (61–86%)	67% (50–82%)	1
Fe ($n = 17, 17$)	79% (73–87%)	40% (0–71%)	0.023

Sign test performed on seasonal series to evaluate differences between the streams

temporal variation of site density was greater with a higher average of 14.1 (SD 6.84) μeq/mg DOC ($n = 36$).

The discrepancy present between site densities of the streams might be attributable to the large differences in DOC concentration and fractionation. In Gråbergsbäcken, the relative fraction of LMM DOC was larger which indicates that more fulvic compounds with higher charge density (COOH/C-ratio) were present (Stevenson 1994). It should be noted, however, that in this stream the low DOC concentration and a higher concentrations of the strong acid anions F and NO_3 will yield a higher uncertainty for the calculated site density values due to error propagation compared to Fanbergsbäcken (Hruska et al. 2001).

Oxalic and lactic acid were the dominant LMMOAs in both streams with respective peak concentrations of 3.43 and 4.65 μM in Fanbergsbäcken, and 2.13 and 3.07 μM in Gråbergsbäcken, with peak concentrations of oxalic acid coinciding with peak DOC concentrations. Low concentrations of malonic, succinic, malic, tartaric, cis-aconitic and citric acid were found at almost every sampling occasion while citraconic and ketoglutaric acid were found at approximately half of the sampling occasions (Table 5). Glutaric, fumaric and isocitric acid were found occasionally, while pyruvic, trans-aconitic and isocitric acid were rarely found over their limit of detection. Of note was that shikimic acid, one of the more abundant LMM organic acids in the soil close to the stream (Vestin et al. 2008b), was not recovered in any of the stream water samples. The order of magnitude in which the acids were recovered in the streams was very similar (Table 5), and the

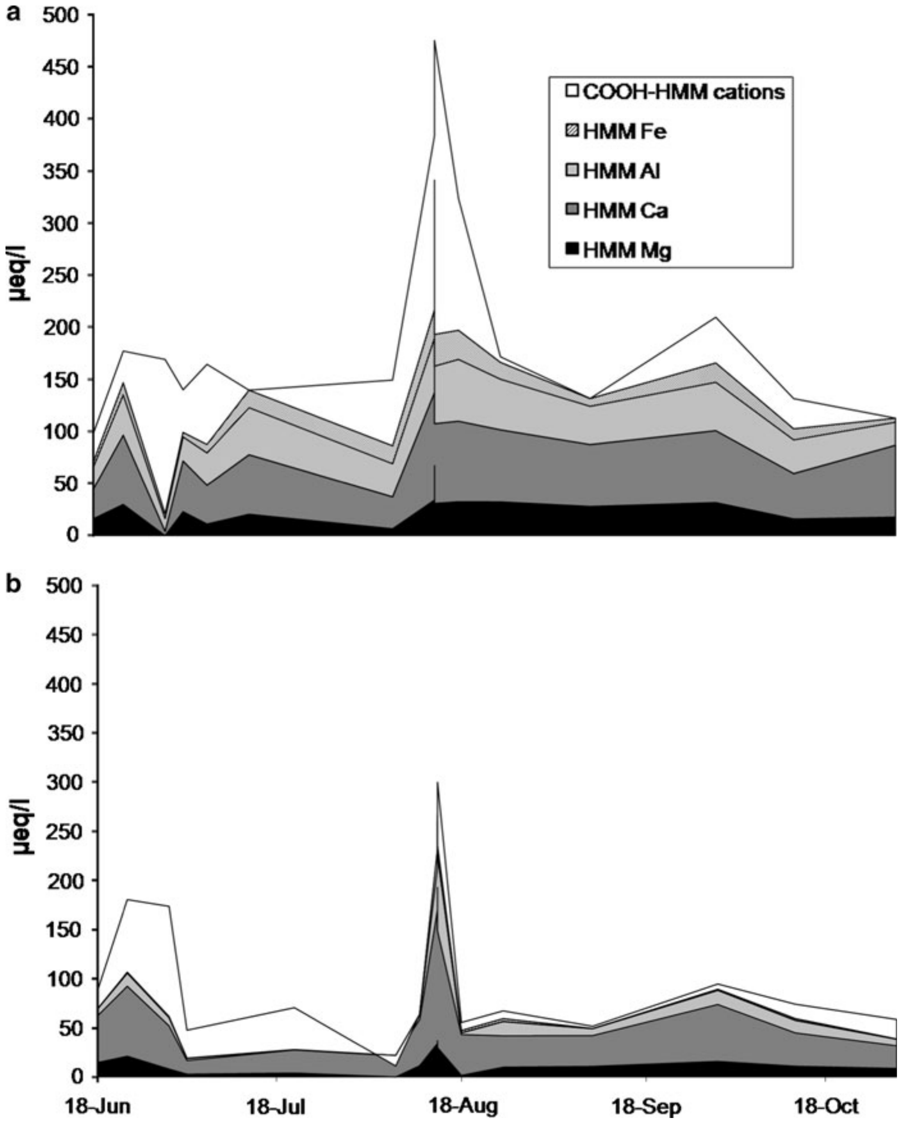

Fig. 3 Temporal variation of cations (µeq/l) associated to the HMM fraction ($M_w > 1$ kDa) of DOC (*cumulative*), and the total amount of COOH (µeq/l) (*top line*) in Fanbergsbäcken (**a**) and Gråbergsbäcken (**b**), respectively, during 2003

total concentration of LMMOAs did not differ significantly between the streams, even though the DOC concentration was higher in Fanbergsbäcken. This might be an effect of the high turnover rates for LMMOAs (van Hees et al. 2002), which may keep the concentrations at a base level at all times, or alternatively that LMMOAs are not controlled by the same mechanisms as other substance groups contributing to the DOC concentration.

Very little information regarding the occurrence of LMMOAs in stream water is available in current literature. Of the acids determined in this investigation, lactic acid has been reported in stream surface water at a concentration of 141 µg/l (1.6 µM; (Hlavacova et al. 2005), and citric acid in an inlet to a Swedish, unproductive, subarctic lake of 179 µg C/l (2.5 µM; (Jonsson et al. 2007)) which was one order of magnitude higher than the highest concentration recovered in this investigation. The fraction of carbon in LMMOAs has been shown to constitute a maximum of 5 and 10% of DOC in soil solutions (van Hees and Lundström 2000; Strobel 2001). In this investigation there were occasions where up to 6% of the DOC in Gråbergsbäcken constituted of LMMOA-carbon (attributed to extremely low DOC concentration during dry periods with low flow), but at most sampling occasions this figure was less than 2%. In Fanbergsbäcken the fraction was less 1% for the entire season.

Table 5 The average concentration (nM), standard deviation (SD) and times (n) recovered above the limit of detection of 13 LMMOAs in Fanbergsbäcken and Gråbergsbäcken during 2003

Acid	Fan ($n_{\mathrm{tot}} = 19$)	SD	n recovered	Grå ($n_{\mathrm{tot}} = 20$)	SD	n recovered
cis-Aconitic	9.04	4.31	19	5.78	4.18	19
Citraconic	2.84	1.03	10	2.50	1.27	8
Citric	13.0	4.19	19	12.9	4.65	20
Fumaric	7.44	22.4	2	0.00	0.00	0
Glutaric	2.02	8.18	2	4.03	11.1	2
α-Ketoglutaric	6.68	6.04	9	4.75	4.79	7
Lactic	743	489	15	1085	950	18
Malic	32.2	16.4	19	28.4	15.2	20
Maleic	2.59	2.34	5	0.89	1.94	2
Malonic	88.2	45.3	19	56.2	50.5	19
Oxalic	1202	770	19	676	510	19
Succinic	34.5	16.7	19	37.5	19.9	20
Tartraic	12.3	8.71	19	9.08	8.73	15
Tot LMMOAs	2160			1920		

The standard deviation is to be seen as an indication of the temporal distribution

Earlier studies of stream water chemistry during spring flood and autumn storms in northern Sweden have shown that DOC is the most important driving mechanism of the pH decline in forested catchments (Laudon and Bishop 2002). The organic acidity is thus of major importance for the pH of the stream water. At high flow, superficial flow paths that activate new sources and an increased washout of DOC have been proposed as the reason for the large increase in DOC (Bishop and Pettersson 1996; Vestin et al. 2008b). The same patterns were observed in both streams in this investigation, which indicates that the same mechanisms are applicable here, and that the process is independent of the different concentrations of DOC and the difference in size distribution in the two streams (Fig. 2).

The seasonal variation of DOC concentration was greater in Gråbergsbäcken with a relative standard deviation (RSD) of 85% compared to 52% for Fanbergsbäcken. This is mainly due to a proportionally stronger increase of DOC during the high flow event in August. The riparian zone in Fanbergsbäcken might have acted as a buffer during this event, inhibiting excessively fast and large changes from occurring, while in Gråbergsbäcken, which lacks a well-pronounced riparian zone, the chemistry becomes more sensitive to rapid changes in flow. In Gråbergsbäcken the return to the background level was also more rapid than in Fanbergsbäcken (Fig. 2).

Fe and Al

Total Fe and Al were significantly correlated with DOC in both streams during 2003 and 2004 (Table 3), except for Fe, which was not correlated to DOC in Gråbergsbäcken during 2004 likely due to the low concentrations and lack of high flow events. The correlations emphasize the importance of DOC for the transport of cations and metals in stream water. Both total Fe and total Al were found in significantly higher concentrations in Fanbergsbäcken than in Gråbergsbäcken (Figs. 4, 5; Table 2), and the concentrations of Al was substantially higher than of Fe in both streams. Fanbergsbäcken had a significantly higher amount of Fe associated with the HMM fraction, 79% versus 40% for Gråbergsbäcken (Table 4). The lower association of Fe to HMM DOC in Gråbergsbäcken was possibly due to higher fraction LMM DOC and the low total concentration of Fe (Table 2). Björkvald et al. (2008) and Kortelainen et al. (2006) have shown that the hydrogeochemistry of Fe is highly dependent on the catchments coverage of wetlands, and in this investigation the higher abundance of wetlands lining the stream channel in Fanbergsbäcken might be the explanation for the significantly higher concentrations of Fe in this stream.

Over the 2003 season, a majority of the Al was found associated to the HMM fraction of DOC (Fig. 5;

Fig. 4 Seasonal variation of Fe and LMM Fe ($M_w < 1$ kDa) (μM) in Fanbergsbäcken ($n = 28$, 24) (**a**) and Gråbergsbäcken ($n = 28$, 24) (**b**) during 2003

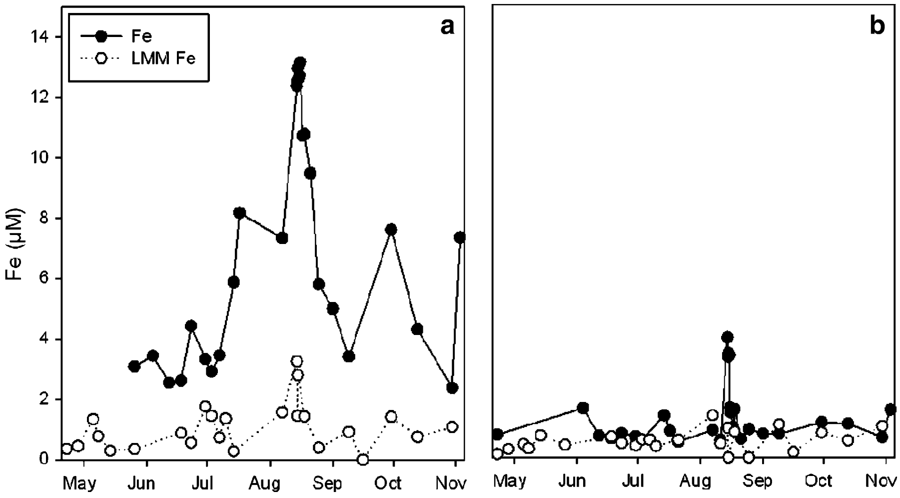

Fig. 5 Seasonal variation of total Al and LMM Al ($M_w < 1$ kDa) (μM) in Fanbergsbäcken ($n = 28$, 24) (**a**) and Gråbergsbäcken ($n = 28$, 24) (**b**) during 2003

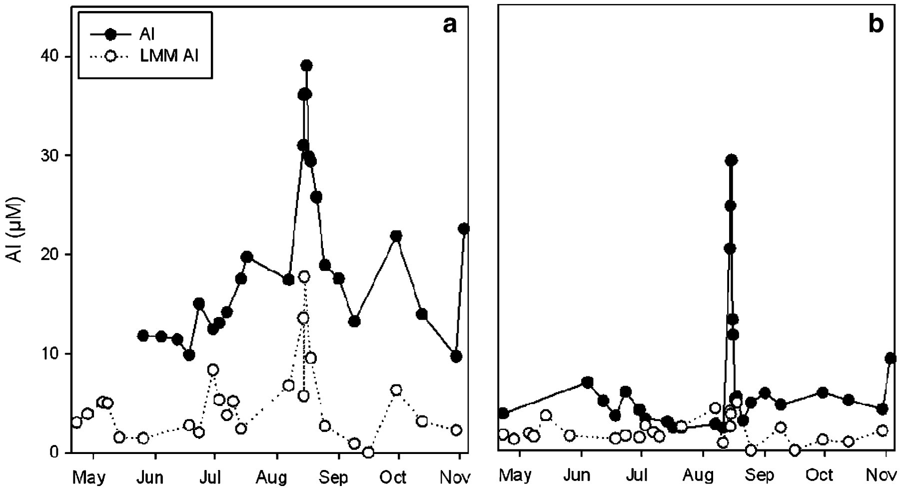

Table 4), in accordance with previous studies of the behaviour of Al in soil solution (Riise et al. 2000; van Hees et al. 2001; Vestin et al. 2008b). No significant difference in the association of Al to the HMM DOC could be seen between the streams (Table 4). The HMM fraction of Al was strongly correlated to both DOC and total Al (Table 3) in both streams.

The concentration of Al_{qr} in both streams was negatively correlated to pH (Fan: $r = -0.81$, Grå: $r = -0.64$). The Al_{qr} concentrations (Table 2) were, however, low or undetectable in both streams during most of the season except for high flow–low pH events such as during early spring and the storm event in August where modest increases could be seen. Hence most of the Al < 1 kDa was complexed by LMM DOC and corresponded to ~30% of the total Al (Fig. 5).

During 2003, the concentrations of Fe and Al were positively correlated between the streams, but in 2004 no such correlation was registered (Table 1). This is probably a direct effect of the low concentrations of these substances in combination with the absence of high flow events during the 2004 season.

Base cations

The divalent base cations, Ca and Mg, were both positively correlated between the two streams during both sampling seasons (Table 1). Both Ca and Mg were positively correlated with DOC and its HMM fraction in both streams during 2003, which indicates that these elements have a considerable association with organic matter in stream water, similar to the

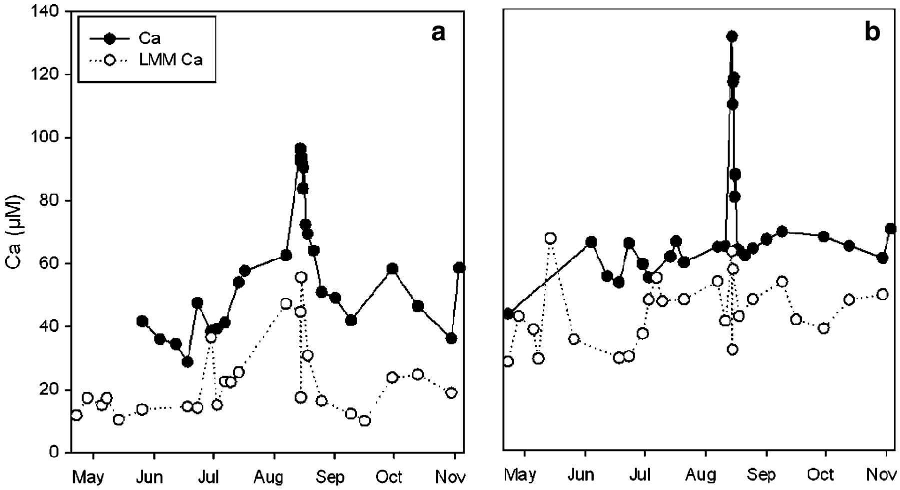

Fig. 6 Seasonal variation of total Ca and LMM Ca ($M_w < 1$ kDa) (µM) in Fanbergsbäcken ($n = 28$, 24) (**a**) and Gråbergsbäcken ($n = 28$, 25) (**b**) during 2003

observations for Fe and Al (Table 3). Ca was present in higher concentrations in Gråbergsbäcken during both seasons (Fig. 6), while Mg showed higher concentration in Fanbergsbäcken (data not shown). The higher concentrations of Ca in Gråbergsbäcken might be attributable to the higher influence of groundwater due to the deeper stream channel in this stream. The distribution of the cations between the LMM fraction and HMM fraction also differed greatly, with a higher recovery of Ca in the HMM fraction in Fanbergsbäcken (54%), compared to Gråbergsbäcken (35%; Table 4). In both streams, Mg was less associated to the HMM fraction than Ca.

During the high flow event in August, peak values of around 80% of Ca and Mg associated to HMM DOC were reached. Such high association of Ca to HMM DOC has previously been reported by Benedetti et al. (2003), from river water in Rio Negro, Brazil. It was also in accordance with an investigation of soil solution sampled by centrifugation close to Fanbergsbäcken in 2004, where around 70% of the Ca and Mg in the top soil layers were recovered in the HMM fraction (Vestin et al. 2008b). This confirms a superficial flow in the soil during high flow/high precipitation events where the stream water adopts the chemistry of the soil it was last in contact with (similar to findings by Bishop et al. (2004)).

Total Ca and Mg were strongly and positively correlated to each other in both streams during both seasons (Table 3; 2004: Fan: $r = 0.95$, Grå: $r = 0.98$). These substances therefore seem to behave comparably in stream water and demonstrate a similar relationship towards DOC.

The monovalent base cations, Na and K, showed very small variations over the season (Vestin et al. 2008a), and were not strongly affected by changes in flow or DOC concentrations. Na and K were most likely present as free ions and experienced only weak or no association to DOC.

Ion balance

The ion content was slightly different between the streams with higher Al, Fe and Mg in Fanbergsbäcken, while Ca, F, NO_3, Si and HCO_3 were higher in Gråbergsbäcken. Figure 7 shows the charge balances for the streams at the sampling occasion with the highest concentration of DOC during the season, which occurred during the storm event in August, compared to an average charge balance (CB) from the whole season with the high flow values in August (eight sampling occasions during 5 days) excluded. As a seasonal average, Ca was the dominating cation charge contributor in both streams while the anionic charge was predominately made up by the anion deficiency (AD) in Fanbergsbäcken and HCO_3 in Gråbergsbäcken. The AD consists of carboxylic- and hydroxylic groups, both free and associated to cations.

During the high flow event the charge in Fanbergsbäcken and Gråbergsbäcken increased by 80 and 60%, respectively, compared to the seasonal averages, with Ca and AD as the dominating charge contributors for both streams. The increase in AD was caused by the increase in carboxylic content as a consequence of increased DOC concentration, which was also the

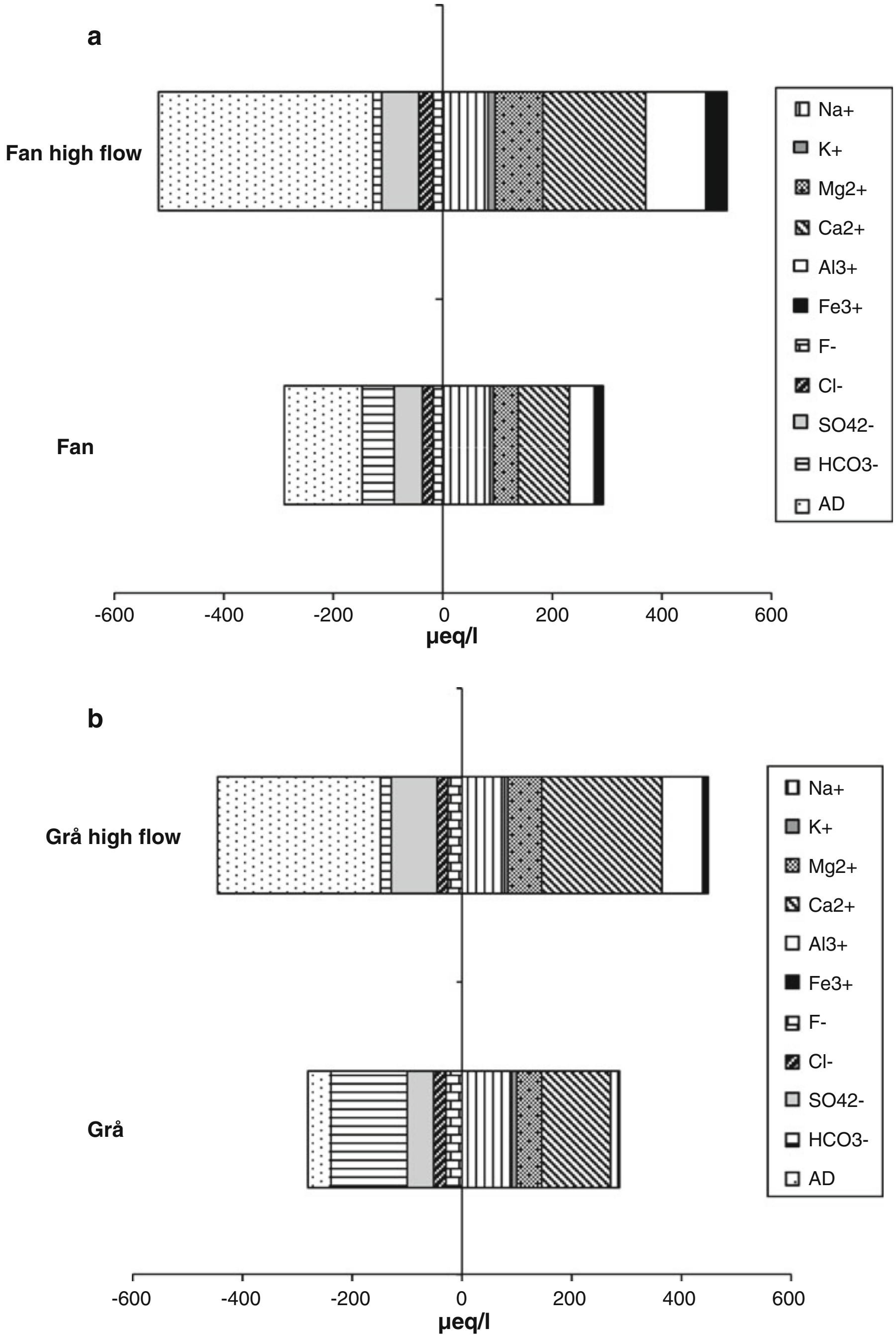

Fig. 7 Charge balance (CB) for Fanbergsbäcken (**a**) and Gråbergsbäcken (**b**) (µeq/l). At the top is the CB for the sampling occasion with the highest DOC-concentration 2003 and at the bottom the average over season 2003 (high flow sampling occasions excluded). H, NH_4, NO_3, PO_4 were all present in very low concentrations, and was therefore removed to clarify the diagram, AD denotes anion deficit

main contributor to the increase of Ca, Mg, Fe and Al in both streams due to association. Both streams also showed an increase of SO_4. A decrease of HCO_3 corresponding to an increase in AD and decrease in pH could be seen, which was most likely caused by a shift from HCO_3 rich groundwater to more acidic event water as the main water contributor.

There was no dramatic change in site density at the high flow, which verifies that the carboxylic content follows the DOC concentration; this was confirmed by significant correlations at all sampling locations.

In contrast to the findings of Laudon and Bishop (2002) and Laudon et al. (2000), no dilution of base cations could be seen in either of the investigated streams during high flow. On the contrary, a strong increase was seen in the concentrations especially for ions that showed close relationships with DOC (Ca, Mg, Fe, Al). This difference compared to the aforementioned studies might be attributable to a large number of factors including geographical location and stream size.

Conclusions

The total DOC concentrations were significantly positively correlated between the streams, even though the quantity of the DOC differed substantially. This indicates that precipitation is the common driver for the DOC-concentration for both streams causing similar seasonal pattern. HMM-DOC was a large part of the total DOC in both streams contributing to high recoveries of metals and base cations in this fraction. The quality showed large differences, with higher organic acidity and higher a amount of HMM-DOC in Fanbergsbäcken, resulting in a higher association of cations to HMM-DOC in this stream. Al showed a similar pattern in association to HMM DOC in both streams, while Fe was found in a relative higher amount associated to HMM DOC in Fanbergsbäcken. Ca was found associated to HMM DOC to 54% in Fanbergsbäcken and 35% in Gråbergsbäcken, which was higher than expected.

The most common LMMOAs found in the streams were oxalic- and lactic acid. LMMOAs did not differ significantly in concentrations between the streams, even though DOC did so. This might be a consequence of a high turnover rate for these substances, which would keep the concentration in stream water at a base level. It might have a greater impact in Gråbergsbäcken, where it as a consequence of the lower DOC-level would make up a higher relative amount, possibly contributing to a higher relative cation concentration in the LMM-fraction.

Even though large differences between the concentrations of DOC and associated cations recovered in the streams were present, the seasonal patterns showed significant correlations indicating that precipitation induced changes in flow trigger similar responses in the stream water chemistry of both catchments.

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