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S. Regensburg, D. Schild, T. Schäfer, F. Huber and M.E. Malmström: Removal of uranium(VI) from the aqueous phase by iron(II) minerals in presence of bicarbonate 1617
D.M.C. Huminicki and J.D. Rimstidt: Iron oxyhydroxide coating of pyrite for acid mine drainage control 1626
P.S. Whitfield and L.D. Mitchell: *In situ* laboratory X-ray powder diffraction study of wollastonite carbonation using a high-pressure stage 1635
A. Augustsson, B. Bergbäck and M. Åström: Trace metals in recharge and discharge ground waters at two sites at the Baltic coast of Sweden 1640
X. Diaz, W.P. Johnson, D. Fernandez and D.L. Naftz: Size and elemental distributions of nano- to micro-particulates in the geochemically-stratified Great Salt Lake 1653
J. Hu, P. Peng and A.R. Chivas: Molecular biomarker evidence of origins and transport of organic matter in sediments of the Pearl River estuary and adjacent South China Sea 1666
N. Cory, I. Buffam, H. Laudon, L. Björkvald, C.-M. Mörth, S. Köhler and K. Bishop: Particulate aluminium in boreal streams: Towards a better understanding of its sources and influence on dissolved aluminium speciation 1677
F. Buzek, T. Paces and I. Jackova: Production of dissolved organic carbon in forest soils along the north–south European transect 1686
S. Wang, Y. Jia, S. Wang, X. Wang, H. Wang, Z. Zhao and B. Liu: Total mercury and monomethylmercury in water, sediments, and hydrophytes from the rivers, estuary, and bay along the Bohai Sea coast, northeastern China 1702
R. Pérez-López, J. Cama, J. Miguel Nieto, C. Ayora and M.W. Saaltink: Attenuation of pyrite oxidation with a fly ash pre-barrier: Reactive transport modelling of column experiments 1712
Y.Q. Gao, L. Liu and W. Hu: Petrology and isotopic geochemistry of dawsonite-bearing sandstones in Hailaer basin, northeastern China 1724
Y. Liao, L. Zhou, S. Bai, J. Liang and S. Wang: Occurrence of biogenic schwertmannite in sludge bioleaching environments and its adverse effect on solubilization of sludge-borne metals 1739
M. Masson, J. Schäfer, G. Blanc, A. Dabrin, S. Castelle and G. Lavaux: Behavior of arsenic and antimony in the surface freshwater reaches of a highly turbid estuary, the Gironde Estuary, France 1747

Continued on outside back cover

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Particulate aluminium in boreal streams: Towards a better understanding of its sources and influence on dissolved aluminium speciation

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ABSTRACT

The adverse impacts of the inorganic labile monomeric Al (Al_i) fraction on aquatic organisms have meant that Al (Al_{tot}) determination and even speciation has become a routine part of environmental monitoring and assessment. However, if samples are not filtered prior to analysis then particulate Al ($Al_{tot(p)}$) could influence the determination of Al_{tot}, and therefore the determination of the more toxicologically important (Al_i), both when it is measured analytically or modelled from Al_{tot}. This paper shows that the Al/DOC ratio in unfiltered samples can identify the $Al_{tot(p)}$ fraction, and thus improve the speciation of Al_i. These findings are based on data from a study in a 67 km^2 catchment in northern Sweden during the snowmelt-driven spring flood of two consecutive years. Filtered and unfiltered samples were studied to determine the spatial and temporal patterns in $Al_{tot(p)}$. The concentrations of $Al_{tot(p)}$ were greatest in larger downstream sites where significant silt deposits are located. The sites with no silt in their drainage area showed a mean difference between filtered ($Al_{tot(f)}$) and unfiltered ($Al_{tot(uf)}$) samples of 6%, while sites with silt deposits had a mean difference of 65%. The difference between filtered and unfiltered samples was greatest at peak flow. Spikes in $Al_{tot(p)}$ did not behave consistently during fractionation with a cation exchange column, resulting in increases in either measured $Al_{i(f)}$ or non-labile monomeric Al ($Al_{o(f)}$). $Al_{tot(p)}$ spikes were associated with sharp increases in the Al:DOC ratio. The baseflow Al:DOC ratio could be used to model filtered Al_{tot} from DOC with a Spearman rho of 0.75.

1. Introduction

Aluminium toxicity is strongly dependent on the form the Al takes. The effects of Al on freshwater biota, and in particular the effects of the labile inorganic form, Al_i (Boyer et al., 1996; Poleo et al., 1997) has meant that the analysis of Al_{tot} has been complimented by a variety of approaches to determine the ecologically relevant Al_i. The presence of particulate Al ($Al_{tot(p)}$) compromises the ability to accurately determine Al_i, both directly through measurement, and indirectly through modelling from $Al_{tot(uf)}$ concentration and related constituents such as DOC and pH. Filtration can usually solve the problem of interference by $Al_{tot(p)}$, but due to the added expense of filtration, it would be desirable to identify $Al_{tot(p)}$ without this labour intensive procedure.

There are a variety of analytical fractionation methods to determine inorganic species of Al. The most commonly applied methods are based on Al determination before and after the solution is passed through a cation exchange column to separate the labile and non-labile fractions. Aluminium determination is typically undertaken by atomic spectroscopy (inductively coupled plasma (ICP), graphite furnace) or spectrophotometrically following extraction (commonly with pyrocatecholviolet or hydroxyquinolin). Other fractionation methods have been proposed e.g. reaction time based (flow injection analysis (FIA) method), ion chromatography and ion mobility in an electric field. The most commonly used method for Al fractionation (Wickstrom et al., 2000), however, is still the use of a cation exchange column based upon the method of Driscoll (1984) coupled with quantification by emission spectroscopy. Particulate Al is not differentiated from the dissolved fraction when determining Al_{tot} using these common methods (Sherrell and Ross, 1999). Due to the rapid changes in Al speciation, it is often difficult to routinely measure Al_i. Modelling techniques e.g. WHAM (Tipping et al., 1995) make it possible to predict Al_i

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Nomenclature

Samples which have not been filtered are denoted with the subscript (uf) and filtered samples (0.4/0.45 μm filter) with the subscript (f)

Al_{tot}	total aluminium
$Al_{tot(p)}$	particulate aluminium (that which is removed by filtration with a 0.45 μm filter), $Al_{tot(p)} = Al_{tot(uf)} - Al_{tot(f)}$
Al_i	labile monomeric aluminium (operational definition: bound in the cation exchange column)
Al_o	non-labile monomeric aluminium (operational definition: cation exchange column eluate)
DOC	dissolved organic carbon

from Al_{tot} and other constituents (e.g. F, pH, DOC). In these calculations, Al_{tot} is not supposed to include $Al_{tot(p)}$. Thus, particulate Al will confound the modelling of Al_i. Furthermore, $Al_{tot(p)}$ can interfere with laboratory determination of Al_i. Filtering can remove $Al_{tot(p)}$, but it would be desirable to avoid this step by finding a reliable way to identify the presence of $Al_{tot(p)}$ and correct for it.

The majority of studies examining $Al_{tot(p)}$ focus on chemical re-precipitates in extreme conditions such as acid mine drainage (Kimball et al., 1995; Peiffer et al., 1997). Filtration studies however have shown that a significant fraction of Al under natural conditions in a variety of different surface water environments can be present in particulate form (Goenaga et al., 1989; Lin and Coller, 1998; Dupre et al., 1999; Koshikawa et al., 2007; Teien et al., 2007).

During high flow episodes, greater suspended sediment loads can occur leading to $Al_{tot(uf)}$ concentrations dominated by particulates (Shafer et al., 1997; Teien et al., 2007). Recent work in northern Sweden has documented elevated $Al_{tot(uf)}$ in association with peak flow during spring flood (Cory et al., 2006). In this boreal region, the spring flood is the most critical hydrological period when up to half the annual discharge occurs over a period of 3 to 4 weeks (Bishop and Pettersson, 1996; Laudon et al., 2000). High flow episodes during spring snowmelt are often associated with acid conditions and increases in toxic Al fractions that are a key limitation on aquatic biota. The concentration of Al_i is a critical component of ecological status in these waters, and the possibility of particulate Al being present complicates the assessment of such waters.

Particulate and colloidal Al are not in themselves regarded as toxic (Bjerknes et al., 2003). It is not clear, though, how their presence affects the determination of $Al_{tot(uf)}$ and subsequent fractionation/speciation either through direct determination or modelling. Recent work by Teien et al. (2007) has shown that $Al_{tot(p)}$ can lead to significant over estimation of $Al_{i(uf)}$. It would thus be desirable to be able to identify when $Al_{tot(p)}$ is influencing $Al_{tot(uf)}$ determination. Recognizing the impact of $Al_{tot(p)}$ on the determination of Al species would enable the improvement of the quantification of toxicological effects of Al during operational environmental monitoring when samples are not routinely filtered.

This study was undertaken in order to investigate the influence of $Al_{tot(p)}$ on the determination of $Al_{tot(f)}$ and $Al_{tot(uf)}$ from 15 stream sites in a 67 km^2 boreal catchment during the spring flood over two consecutive years. In addition, 2 of the 15 sites were further analyzed for Al speciation using a cation exchange column directly coupled to an ICP. These data were analyzed to identify the particulate influence on the determination of both $Al_{tot(uf)}$ and the subsequent Al fractions. Of particular interest was the influence landscape characteristics have on the occurrence of particulate Al interferences. Furthermore, since the ratio of $Al_{tot(uf)}$ to DOC has been shown to remain stable during spring episodes, (Cory et al., 2006), knowing how $Al_{tot(p)}$ affects this ratio in unfiltered samples ($Al_{tot(uf)}$/DOC) may enable its use as a proxy indicator of $Al_{tot(p)}$ interference.

2. Site description

The study area comprises the upper 67 km^2 of the Krycklan river catchment in northern Sweden (64°14′N, 19°46′E). The Krycklan catchment ranges from 130 to 369 m in elevation. Throughout the catchment, gneissic bedrock is overlain by glacial till varying in thickness up to tens of meters (Ivarsson and Johnsson, 1988). Well-developed Fe-podzol soils are common, with organic-rich soils near the channel of smaller streams (Bishop et al., 1994). In the lower reaches of the catchment, larger streams have deeply incised channels carving through an area of fine, well sorted sediments, primarily fine sand and silt which were deposited in the distal part of a postglacial river delta (Tamm and Malmström, 1926).

Annual mean air temperature is 1 °C; with 600 mm annual mean precipitation, of which one-third falls as snow. Snow cover persists for 171 days on average (1980–1999) (Ottosson-Löfvenius et al., 2003). The catchment is forested primarily with mature Scots pine *(Pinus sylvestris)* and Norway spruce (*Picea abies*), with some deciduous shrubs and trees including birch (*Betula* spp.), alder (*Alnus incana*) and willow (*Salix* spp.) commonly found in the riparian forest along larger streams (Andersson and Nilsson, 2002). The forested landscape is interspersed with patches of sphagnum-dominated peat wetlands, covering 8% of the total catchment area, and with a large percentage coverage in some of the smaller subcatchments (Table 1).

The 15 intensively studied subcatchments reported here span a wide range of size, soil type and land cover (Table 1). While most of the catchments are independent of one another, six of the larger streams receive some flow from other study sites upstream (Fig. 1). Further details on the Krycklan catchment and stream sites can be found in Cory et al. (2006) and Buffam et al. (2007). Stream water chemistry has been monitored regularly for the past 24 years in one 50 ha subcatchment (Bishop et al., 1990; Laudon et al., 2004). Subsurface pathways dominate stream flow delivery in forested sites, with overland flow rare due to high infiltration capacity of the till soils (Nyberg et al., 2001).

3. Materials and methods

The water sampling strategy was based on grab samples taken approximately every second day during the 5-week period encompassing spring flood (April–May), with less intensive sampling at low flow conditions prior to, and after the snow melt period. The streams were sampled on 22 occasions in 2004 and 19 occasions in 2005. Water samples were collected in acid-washed 250 mL high-density polyethylene bottles, following multiple rinses. Samples were kept chilled until transport to the laboratory.

Al analysis was undertaken both before filtration ($Al_{tot(uf)}$) and afterwards ($Al_{tot(f)}$). The particulate fraction ($Al_{tot(p)}$) is defined as the difference between $Al_{tot(uf)}$ and $Al_{tot(f)}$ and can be present in many forms such as mononuclear or polynuclear species and

Table 1
Site characteristics, soil types and landcover. Courtesy of the Swedish geological survey and the national land survey of Sweden.

Site	Area (km^2)	Stream order	Sedimentology (%)						Landcover (%)					
			Peat	Silt	Alluvial	Till	Thin soil	Other[a]	Lake	Forest	Clearcut	Open land	Arable	Wetlands
C1	0.6	1st				94	6			90	8			2
C2	0.15	1st				86	14			98				2
C3	0.03	1st	54			46				63				38
C4	0.14	1st	60			9	32			45				55
C5	0.9	1st	41			48	6		5	59				36
C6	1.3	1st	28			57	10	3	3	72				25
C7	0.48	2nd	18			68	15			82				18
C8	2.4	2nd	16			63	2	2		88				12
C9	3.1	2nd	15	6		69	6	3	1	84	0.1			15
C10	2.9	2nd	29			58	11	1		72	1			27
C12	5.1	3rd	18	3		66	8	5		81	3		0.2	16
C13	7.2	3rd	12	16		6	10	2	1	88	0.2	0.2	0.3	11
C14	11.6	3rd	8	31	2	50	7	2	0.1	86	4	1	3	6
C15	18.2	4th	13	2	8	65	8	0.8	2	77	5	2	0.2	14
C16	67	4th	9	27	3	52	7	2	1	84	4	1	2	8

[a] Combined data for areas of rock, gravel and sand.

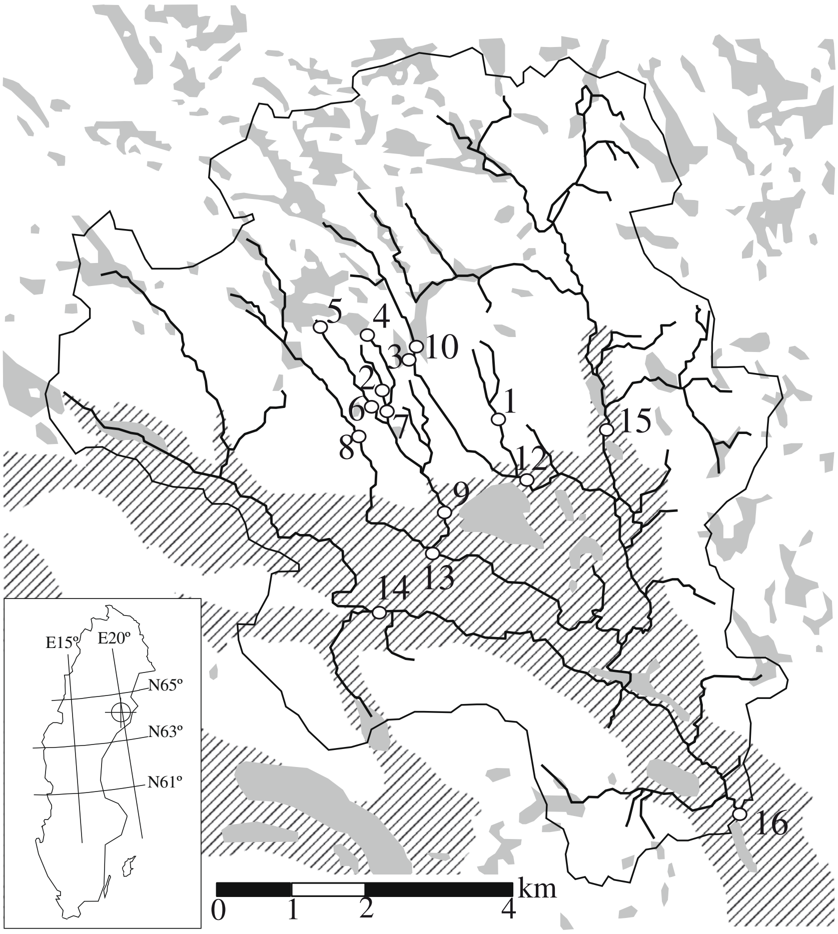

Fig. 1. Location of the sampling sites throughout the Krycklan catchment, and catchment location in Sweden (small panel). Shown are areas of peat wetlands (grey) and silt deposits (striped), the rest of the catchment (81%) is predominantly glacial till. © National Land survey of Sweden 1998, from road map dnr 507-98-4720 and © Swedish Geological survey.

hydroaluminiumsilicates. One aliquot of each sample was measured as bulk water and one after filtration using either a syringe-driven 0.45 μm MCE membrane filter or a 0.4 μm Millipore polycarbonate filter. No upper size limit for particulate Al has been defined. Although previous research has shown that this pore size allows substantial colloidal Al to pass (Kennedy et al., 1974; Lin and Coller, 1998; Dupre et al., 1999), the filter pore size was selected for two reasons. Firstly 0.45 μm is a commonly used boundary for the division of dissolved and particulate fractions in operational monitoring. Secondly, filter clogging is a practical concern with the high concentrations of organic matter observed in many forested boreal headwaters, such as those in this study. Samples were then preserved by acidifying with 1% v/v suprapur HNO_3 (65% MERCK).

In both 2004 and 2005, $Al_{tot(uf)}$ and $Al_{tot(f)}$ concentrations were determined for all samples using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Varian Vista Ax), equipped with a sea spray nebulizer and micro concentric spray chamber. All samples were shaken prior to analysis to ensure any particulate matter was still in suspension. The sea spray nebulizer allows particles up to 75 μm to pass through to the plasma. To check the accuracy a certified standard, Spectra pure Standards; SPS-SW1 (50 ppb with 2% standard uncertainty), was analyzed on a regular basis. The difference between analyzed and certified values was typically less than 2% and never greater than 5%. Using the statistical recommendations of Magnusson et al. (2004) the standard uncertainty in the analysis was calculated as 2.6% taking into account the laboratory bias, standard uncertainty in the certified standard and the standard uncertainty for the measurements.

In order to examine the contribution of aluminosilicate minerals to $Al_{tot(p)}$, selected samples were analyzed for Si using the same filtration, preservation and analytical techniques as listed above for Al_{tot}. Particulate Si ($Si_{tot(p)}$) was estimated as the difference between unfiltered and filtered Si_{tot}.

On a subset of samples from the 2004 spring flood, Al fractionation was undertaken. The samples were collected from sites C2 and C16, representing catchments with (C2) and without (C16) silt deposits in their drainage basin. The samples for fractionation were taken during all phases of the 2004 spring flood episode.

Aluminium fractionation was undertaken on both the filtered and unfiltered samples. The fractionation was based on the use of a cation exchange column (Driscoll, 1984) directly coupled to the ICP-OES. The labile monomeric fraction of the Al_{tot}, termed Al_i, is retained in the column, while the non-labile monomeric fractions, including those bound to DOC, collectively termed Al_o, passes through. The Al_i, including all cationic forms (Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, AlF^{2+}, AlF_2^+, $Al(SO_4)^+$), was calculated as the difference between the Al_{tot} and Al_o, see Eq. (1).

$$Al_i = [Al_{tot} - Al_o] \tag{1}$$

The cation exchange column was 140 mm long, with a diameter of 5 mm, and a flow rate of 4 mL min^{-1} mL^{-1} amberlite (IR-120 Plus, 99% Na form, 1% H form, Sigma–Aldrich). The instrument setup during Al determination followed Rodriguez-Rosa et al. (1986).

Analytical uncertainty of the Al fractionation was determined using repeated measurement of known control samples from 2002–2004. The 95% confidence level lies at 6.4% for the determination of Al_{tot} and 8.4% for determination of Al_o. Using error propagation, as shown in Eq. (2), the error associated with Al_i can be calculated. For example a sample with Al_{tot} of 200 μg L^{-1} and Al_o 180 μg L^{-1} has an Al_i of 20 μg L^{-1} ± 19.8.

$$\delta Al_i = [(\delta Al_{tot})^2 + (\delta Al_o)^2]^{\frac{1}{2}} \tag{2}$$

Hourly stream discharge was calculated for all sites using measurements of stream height and established height-discharge rating curves. For illustrative purposes discharge data are presented for site C7, which has been monitored since 1980 using a 90° V-notch weir in a heated dam house. Measurements of discharge at the other 14 sites confirmed that changes in flow were generally synchronous, with for instance maximum spring discharge at all sites occurring during a single 72-h period. During analysis the discharge was divided into four broad categories: base flow, rising limb, peak flow and falling limb.

On one sampling occasion during the spring flood in 2004 (April 28), the concentration of minerogenic suspended solids (SSmin) was determined for each stream. Approximately 1 L of sample water was filtered using a pre-weighed 47 mm Whatman GF/F 0.7 μm nominal pore size glass fiber filter, dried for 18 h at 55 °C, and ashed for 2 h at 525 °C. The remaining material constituted the SSmin.

The mineralogical characterization of selected soil (site 2) and sediment samples (site 2, 14 and 16) was carried out by X-ray diffraction (XRD) analyses at a step size of 2θ = 0.05° between 3° and 85° (Philips PW 1800; Co. anode). Semiquantitative weight fractions of various minerals are determined using a series of characteristic intensities for each mineral and are valid for minerals with weight fractions above 5%.

Samples for dissolved organic C (DOC) were either filtered (syringe-driven 0.45 μm MCE filter, Millipore) (during 2004) or left unfiltered (during 2005), then frozen until analysis with a Shimadzu TOC-V_{CPH} analyzer. A comparison among sites covering the extremes of observed flows showed that there was no measurable difference in the OC concentration due to filtering. This result is in agreement with other studies of northern Swedish surface waters (Ivarsson and Jansson, 1995; Laudon and Bishop, 1999; Gadmar et al., 2002) which have found particulate organic C concentration to be negligible relative to the dissolved fraction. Thus, the term DOC is used for all samples in this study. The ratio of $Al_{tot(uf)}$ to DOC was then calculated to examine differences from typical values for each stream, as proposed by Cory et al. (2006).

The variation in $Al_{tot(f)}$ and $Al_{tot(p)}$ was correlated with catchment characteristics from Table 1 using Redundancy Analysis (RDA) in the program CANOCO for Windows v.4.54. All samples ($N = 585$ from 39 sampling occasions at 15 sites) were used in the analysis. Catchment variables were not transformed with the exception of catchment area, which was log-transformed. Initial examination of the response data with Detrended Correspondence Analysis indicated that RDA was the appropriate multivariate analysis to use since the data were linearly distributed (gradient length < 3). The significance level of each catchment variable was first tested individually using the Monte Carlo routine ($N = 499$ permutations) provided in the CANOCO program. Significant variables ($p < 0.05$) were then included as potential predictors for $Al_{tot(f)}$ and $Al_{tot(p)}$. All significant variables which had loading scores of >0.2 on either of the two primary RDA axes were included in the final RDA analysis.

4. Results

In 2004 the spring flood (Fig. 2) started from a base flow of ~0.1 mm day^{-1}. There was an initial small rise in discharge around April 16th, due to milder weather, followed by the main peak in flow from April 28th to May 9th which reached maximum flow rates of ~6.8 mm day^{-1}. Flow then declined back to base flow levels by June 13th. In 2005 the spring flood (Fig. 2) commenced on April 15th and discharge increased from baseflow (~0.1 mm day^{-1}) to a peak in discharge of ~9.7 mm day^{-1} on May 3rd before declining back to base flow by June 10th.

The samples showed a general increase in $Al_{tot(uf)}$ during elevated flow followed by a decline during the falling limb, but concentrations did not return to pre-flood base flow levels within the time frame of the sampling. See Cory et al. (2006) for a more detailed discussion of the temporal and spatial variation in $Al_{tot(uf)}$ during these spring floods. Differences between $Al_{tot(f)}$ and $Al_{tot(uf)}$ ranged from ~0% to over 700% (Table 2). With the samples grouped into flow periods, 95% had higher concentrations of $Al_{tot(uf)}$ than $Al_{tot(f)}$. More than half of the sample groups showed statistically significant differences at $p = 0.01$ and a third at $p = 0.001$ (single tailed paired *t*-test).

A redundancy analysis (RDA, Canoco for Windows v. 4.5) of $Al_{tot(f)}$ and $Al_{tot(p)}$ (Fig. 3) showed that most of the variance in the relationship between catchment variables and $Al_{tot(f)}$ and $Al_{tot(p)}$ could be explained by the variance in $Al_{tot(p)}$, which is positively

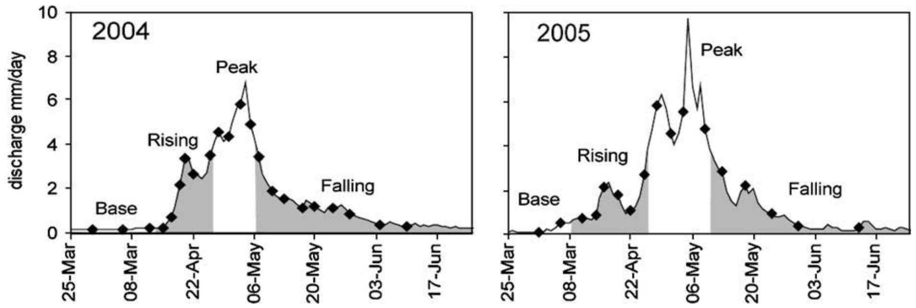

Fig. 2. Discharge and sampling dates for the 2004 and 2005 spring floods. The time scale is cut to focus on the spring flood. Greyed areas are used to differentiate the flow periods.

Table 2

Concentrations of $Al_{tot(uf)}$ and $Al_{tot(f)}$ from samples at 15 stream sites during 2004 and 2005, divided into four discharge regimes centred around the spring flood. Concentrations, in µg L^{-1}, shown as mean values with standard deviation and number of samples. Differences between filtered and unfiltered samples are shown as a percentage difference from the filtered value, an asterisk denotes a statistically significant difference. The difference between $Al_{tot(f)}$ and $Al_{tot(uf)}$ was normally distributed in all of the site-flow groups except for two, marked with a superscript a. For these two groups, the differences were log-transformed prior to statistical analysis.

Site	Base flow 0.1–1.9 mm day^{-1}			Rising limb 0.5–3.5 mm day^{-1}			Peak flow 4.5–5.8 mm day^{-1}			Falling limb 4.9–0.3 mm day^{-1}		
	$Al_{tot(f)}$	$Al_{tot(uf)}$	Diff. (%)	$Al_{tot(f)}$	$Al_{tot(uf)}$	Diff. (%)	$Al_{tot(f)}$	$Al_{tot(uf)}$	Diff. (%)	$Al_{tot(f)}$	$Al_{tot(uf)}$	Diff. (%)
C1	269 ± 29 (5)	299 ± 45 (5)	11	411 ± 52 (12)	497 ± 136 (12)	21	501 ± 15 (8)	549 ± 45 (8)	10^{*}	432 ± 47 (14)	504 ± 110 (14)	$17^{*\ a}$
C2	291 ± 19 (5)	308 ± 18 (5)	6	439 ± 114 (12)	461 ± 90 (12)	5	482 ± 23 (8)	500 ± 31 (8)	4	385 ± 26 (14)	405 ± 30 (14)	5^{**}
C3		213 ± (1)		196 ± 44 (11)	197 ± 46 (11)	1	150 ± 10 (8)	161 ± 17 (8)	7	177 ± 24 (14)	189 ± 20 (14)	7^{*}
C4	92 ± 6 (5)	97 ± 7 (5)	5^{*}	56 ± 20 (12)	60 ± 23 (12)	6	31 ± 5 (8)	41 ± 12 (8)	30	57 ± 16 (14)	65 ± 22 (14)	14^{**}
C5	135 ± 3 (5)	140 ± 3 (5)	4^{*}	123 ± 18 (11)	131 ± 17 (11)	6	91 ± 10 (8)	96 ± 11 (8)	5	106 ± 2 (14)	117 ± 9 (14)	11^{**}
C6	116 ± 14 (5)	131 ± 12 (5)	13^{**}	186 ± 31 (12)	210 ± 38 (12)	13^{**}	148 ± 21 (8)	168 ± 24 (8)	13^{*}	133 ± 6 (14)	150 ± 8 (14)	13^{**}
C7	155 ± 14 (5)	168 ± 14 (5)	9	242 ± 44 (12)	243 ± 48 (12)	0	241 ± 22 (8)	259 ± 32 (8)	7	220 ± 20 (14)	239 ± 20 (14)	8^{**}
C8	194 ± 43 (5)	212 ± 36 (5)	9^{**}	336 ± 34 (12)	359 ± 43 (12)	7^{**}	318 ± 21 (8)	337 ± 25 (8)	6^{*}	277 ± 29 (13)	293 ± 35 (14)	6^{**}
C9	95 ± 12 (4)	122 ± 12 (4)	29^{**}	231 ± 35 (12)	313 ± 61 (12)	35^{**}	290 ± 45 (8)	456 ± 193 (8)	58	210 ± 34 (14)	313 ± 97 (14)	49^{**}
C10	89 ± 13 (5)	109 ± 19 (5)	22^{**}	174 ± 23 (12)	194 ± 34 (12)	12^{*}	142 ± 11 (8)	157 ± 16 (8)	11	141 ± 14 (14)	151 ± 19 (14)	7^{**}
C12	118 ± 21 (5)	227 ± 170 (5)	93	304 ± 90 (12)	499 ± 95 (12)	64^{**}	402 ± 209 (8)	1050 ± 652 (8)	161^{*}	214 ± 53 (14)	566 ± 145 (14)	165^{**}
C13	146 ± 21 (5)	196 ± 33 (5)	34	230 ± 30 (12)	376 ± 144 (12)	64^{**}	395 ± 160 (8)	1134 ± 953 (8)	187	223 ± 27 (14)	375 ± 218 (14)	68^{*}
C14	147 ± 59 (5)	226 ± 109 (5)	54^{**}	204 ± 46 (12)	315 ± 87 (12)	55^{**}	263 ± 108 (8)	530 ± 318 (7)	101	141 ± 22 (14)	536 ± 131 (14)	153^{**}
C15	76 ± 23 (5)	99 ± 15 (5)	30	152 ± 16 (12)	294 ± 171 (12)	93^{*}	170 ± 26 (8)	221 ± 42 (8)	30^{**}	127 ± 13 (14)	161 ± 19 (14)	27^{**}
C16	73 ± 29 (4)	110 ± 30 (5)	51	183 ± 45 (12)	807 ± 742 (12)	340^{*}	667 ± 531 (8)	2715 ± 1706 (8)	307^{*}	141 ± 52 (14)	1255 ± 2364 (14)	$792^{*\ a}$

[*] $p < 0.01$, single tailed paired *t*-test.

[**] $p < 0.001$, single tailed paired *t*-test.

[a] Kolmogorov–Smirnov test.

associated with catchments with a large area and high fraction of silt surficial sediments, typified by open or arable land use. The remaining variance in the $Al_{tot(f)}$ was strongly positively associated with forest landcover underlain by till surficial sediments, and strongly negatively associated with catchments with a high proportion of peat wetlands. Clearcut proportion was weakly positively associated with both $Al_{tot(f)}$ and $Al_{tot(p)}$, while lake proportion was associated with low $Al_{tot(f)}$. Once these catchment variables were accounted for, no others added substantial explanatory power. Factors loading on axis 1 ($Al_{tot(p)}$) were presence of silt deposits (0.35), catchment area (0.34), arable land use (0.29), and open land use (0.27), with other factors loading < 0.20. For axis 2 ($Al_{tot(f)}$) the factor scores were high for forest cover (0.61), till sediments (0.59), wetlands (−0.59), peat coverage (−0.58), lakes (−0.29), and clearcuts (0.27), with all other factors loading <0.20.

In both 2004 and 2005 the sites with silt in their drainage area showed significantly larger differences between $Al_{tot(f)}$ and $Al_{tot(uf)}$ than sites with other soil types. These differences were apparent at all discharge regimes, and were most pronounced during peak flow (Fig. 4). Overall, areas with no silt in their discharge areas had a median difference between $Al_{tot(f)}$ and $Al_{tot(uf)}$ of 6.1% (2.4% and 11.1% for 25th and 75th percentiles, respectively), whereas areas with silt deposits had a median difference in $Al_{tot(f)}$ and $Al_{tot(uf)}$ of 65% (30% and 155% for 25th and 75th percentiles, respectively).

Within these groupings there were significant inter-site variation (Table 2), with the catchment outlet (Site C16) showing the largest differences between $Al_{tot(f)}$ and $Al_{tot(uf)}$.

Aluminium fractionation was undertaken on filtered and unfiltered samples from two sites during the 2004 spring flood. Site C2, a headwater site which has no silt in its drainage area showed good agreement between filtered and unfiltered samples for all Al fractions (Fig. 5, left side). Site C16, which has both a larger drainage area and substantial silt deposits (Fig. 1), showed three occasions with significant differences in $Al_{tot(f)}$ and $Al_{tot(uf)}$ coinciding with peak flow (Fig. 5, right side). The response in the individual Al fractions to these increases in differences was not consistent. Two of the occasions with elevated $Al_{tot(uf)}$ resulted in increases in $Al_{o(uf)}$ with little change in $Al_{i(uf)}$, while the remaining occasion showing an increase in $Al_{i(uf)}$ with little change in $Al_{o(uf)}$ (Fig. 5).

Differences between the two sites were also observed in the $Al_{tot(uf)}$:DOC ratio, a measure which has been previously suggested to estimate particulate influence (Cory et al., 2006). The upstream forested site (site C2) has a higher ratio, which remained stable throughout the spring flood and showed no significant differences (*t*-test, $p > 0.01$) between filtered and unfiltered samples (Fig. 5). The downstream site (C16) showed significant differences for filtered and unfiltered samples for both 2004 and 2005 (paired *t*-test, $p = <0.001$). The filtered samples had a relatively constant ratio

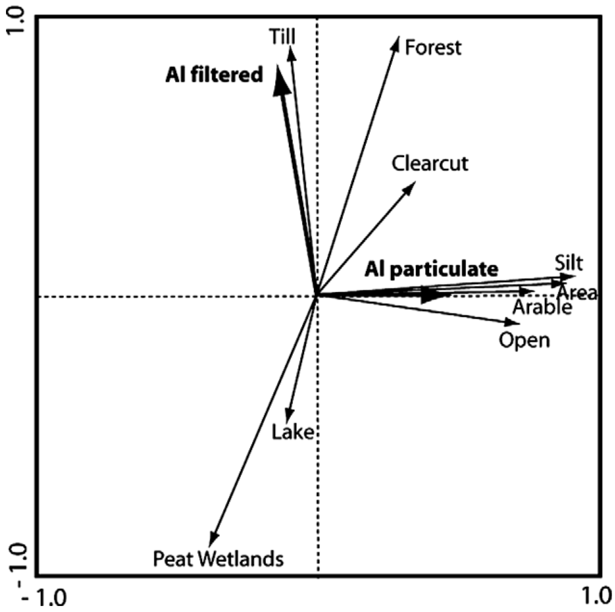

Fig. 3. RDA of $Al_{tot(f)}$ and $Al_{tot(p)}$ ($N = 585$ samples) with catchment variables from Table 1 as explanatory variables. Catchment variables were only included if they had loadings of >0.2 on one of the two main PC axes.

throughout the spring flood (Fig. 5). The unfiltered samples from site C16 showed a similar pattern to the filtered samples except during elevated discharge when the $Al_{tot(uf)}$:DOC ratio rose sharply in combination with the increases in $Al_{tot(uf)}$. Peak values for the unfiltered $Al_{tot(uf)}$:DOC ratio were ~3 times the filtered levels.

The concentration of $Al_{tot(p)}$ was well correlated to the total mineral suspended sediment fraction at peak flow (Fig. 6 – left panel). The ratio of Al to Si in the particulate fraction was consistent over time at approximately 1:2 (Fig. 6 – right panel) for site C16, which had the highest concentrations of particulates. Mineralogical and optical analysis of eight silty sediment samples collected at sites 2, 14 and 16 reveal a rather homogeneous mineralogical composition. Semiquantitative XRD analysis indicates decreasing weight fractions of quartz (42 ± 3%), calcic-sodic plagioclase (25 ± 1%), K-feldspar (19 ± 2%), hornblende (9 ± 1%), muscovite or biotite (2–7%) and amphiboles and traces of garnet and hematite. These results are very close to the average mineralogical composition available for a series of soils at site 2.

5. Discussion

On several occasions, $Al_{tot(uf)}$ was several hundred percent higher than $Al_{tot(f)}$. The observed differences between $Al_{tot(f)}$ and $Al_{tot(uf)}$ can be attributed to the presence of $Al_{tot(p)}$. The presence of significant $Al_{tot(p)}$ is consistent with other filtration studies of dissolved and solid phase Al e.g. (Goenaga et al., 1989; Xu and Harsh, 1993; Teien et al., 2007; Björkvald et al., 2008). Colloidal Al, assuming a neutral charge, will pass through the filters used in this study, however, Goenaga et al. (1989) showed that, where filter sizes down to 0.015 µm were used, only 48–86% of the influence of colloids on Al_{tot} is removed with a standard 0.4 µm filter. Since the presence of large $Al_{tot(uf)}$ discrepancies were limited to high flows in areas with erodible sediments; in the results presented here colloids are not believed to pose a serious problem. $Al_{tot(uf)}$ peaked several hundred percent higher than filtered levels on several occasions, illustrating the extent to which $Al_{tot(p)}$ can impact the determination of $Al_{tot(uf)}$.

It is proposed that the increases in $Al_{tot(p)}$ in the larger downstream catchments are due to a combination of two main factors: (1) discharge; (2) streambed/bank conditions (i.e. stream bank erosion). There must be a supply of fine particulate matter and also sufficient flow in order to re-suspend these particles. Differences of more than 100% between $Al_{tot(f)}$ and $Al_{tot(uf)}$ are not seen in the sites without silt in their drainage area, even during elevated flow conditions. In the larger downstream sites with silt deposits there are significant differences between $Al_{tot(f)}$ and $Al_{tot(uf)}$ at all elevated flow conditions. Both catchment area and the presence of silt deposits are strongly correlated to the levels of $Al_{tot(p)}$; however, they are also co-correlated (Fig. 3). This means that it is difficult to say if it is the presence of a silt deposit per se or the resulting effect of a larger catchment size that is the significant driver behind $Al_{tot(p)}$. However, by examining, for example sites C8 (above silt area) and C9 (within silt area) which are of similar size (2.4 and 3.1 km^2, respectively) a sharp contrast can be seen in the differences between filtered and unfiltered samples. The percentage difference between $Al_{tot(f)}$ and $Al_{tot(uf)}$ for site C8 peaked at 9%, whereas site C9, which is within the silt area, had a percentage difference at peak flow of 58%. This suggests that the presence of silty surficial sediments, rather than catchment area, is the dominant catchment characteristic related to high $Al_{tot(p)}$ concentrations.

The fine fraction (<0.09 mm) of till in the area is composed primarily of quartz, with smaller amounts of plagioclase, potassium feldspar, biotite and amphiboles (Miskovsky, 1987). The soils at site two have a mean SiO_2 content of 71% with Al_2O_3 contributing 11% by weight and are close to the values reported by Tamm and

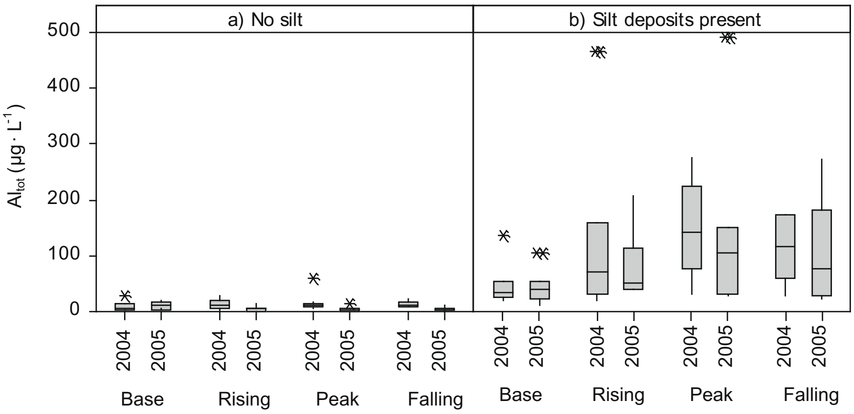

Fig. 4. Percentage difference between $Al_{tot(f)}$ and $Al_{tot(uf)}$. (a) Data from sites with no silt in their drainage basin ($n = 9$) and (b) data from sites with silt deposits within their drainage area ($n = 6$). The samples have been grouped by discharge stages and year with the left hand boxes for 2004 and the right hand boxes for 2005. Two outlying points from (a) are not shown; one positive and one negative. Four outlying points from (b) are not shown, all positive, with a peak value of >5000%.

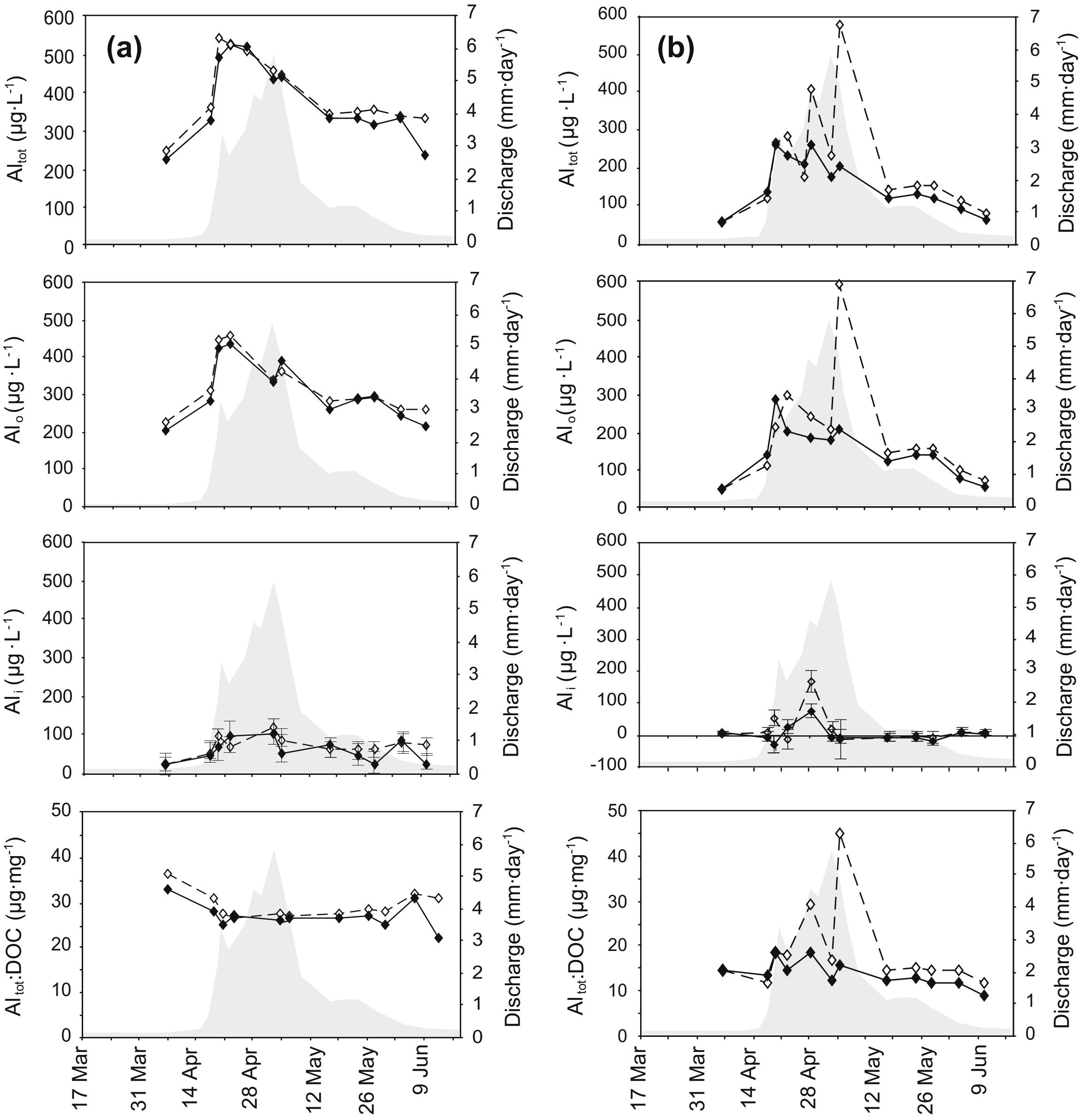

Fig. 5. Al fractionation (top three panels) and $Al_{tot(uf)}$:DOC ratios (lower panel) for (a) forested headwater site C2 (left side) and (b) silt influenced site C16 (right side) during the 2004 spring flood episode. Time courses for filtered (filled symbols) and unfiltered (open symbols) are shown.

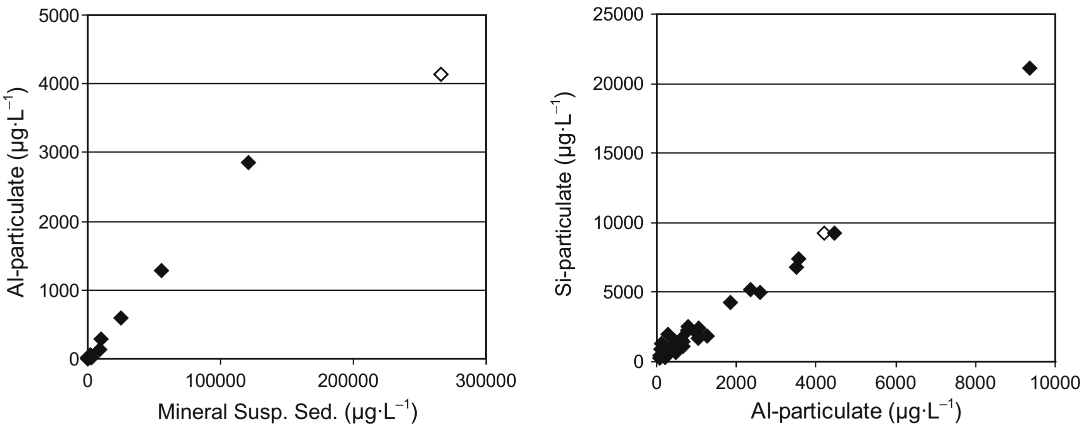

Fig. 6. Left panel – Relationship between $Al_{tot(p)}$ and total mineral suspended sediment showing all the stream sites ($N = 15$), $r^2 = 0.96$, during a single peak flow sampling occasion (April 28, 2004). Site C16 is highlighted with an unfilled marker. Right panel – Relationship between $Si_{tot(p)}$ and $Al_{tot(p)}$ for site C16 during all sampling occasions in spring 2004 and 2005 ($N = 53$), $r^2 = 0.99$. The peak flow sample from the left panel (April 28, 2004) is again highlighted with an unfilled marker.

Malmström (1926). This corresponds to an average molar Al:Si ratio in the till of approximately 1:5. The ratio of $Al_{tot(p)}$:$Si_{tot(p)}$ at C16, the site with the highest $Al_{tot(p)}$ concentrations, was much higher (1:2) than the average ratio in the till. The content of secondary aluminosilicate minerals is below 1% by weight in both the soils and sediments. This suggests that if primary aluminosilicate minerals contribute to the observed stream $Al_{tot(p)}$, the stream suspended sediment must contain, relative to till, proportionally higher fractions of high Al:Si minerals. Given that the larger grains of the primary minerals quartz, feldspar and plagioclase are too large to be transported in suspension it is very probable that suspended particles of muscovite (Al:Si = 1) and or biotite (Al:Si, 1:3) contribute to the observed lower Al to Si ratio.

Inclusion of $Al_{tot(p)}$ in the determination of $Al_{tot(uf)}$ will affect both laboratory and computer modelling based fractionation/speciation. For laboratory fractionation, even if $Al_{tot(p)}$ passes conservatively through the cation exchange column, the analytical uncertainty associated with $Al_{i(uf)}$ will increase with increasing $Al_{tot(p)}$. As Al_i is determined indirectly, an increase in Al_{tot} and Al_o will increase the uncertainty based upon Eq. (2). This analytical uncertainty is shown by the error bars for Al_i in Fig. 5. It can be seen that the differences in $Al_{i(uf)}$ seen at peak flow are still prominent even when analytical uncertainty is taken into account. For computer-based speciation, the Al species are calculated directly from the concentration of Al_{tot} and therefore any error in Al_{tot} due to particulate interference will give a proportional error in the subsequent speciation. Thus the ability to identify ecologically significant Al_i in unfiltered samples is contingent upon being able to identify $Al_{tot(p)}$ in other ways.

The subset of samples which were subjected to a full Al fractionation revealed unpredictable behaviour in $Al_{tot(p)}$ in the exchange column. Increases in $Al_{tot(uf)}$ associated with $Al_{tot(p)}$ led to inconsistent fractionation with increases associated with either $Al_{i(uf)}$ or $Al_{o(uf)}$. If the $Al_{tot(p)}$ is neutrally charged then it should, in theory, pass conservatively through the column and be assigned to the organic fraction. However, the cation exchange column itself may act as a physical filter retaining either particulate and colloidal Al or large polymeric molecules. This physical filtering process within the exchange column is also consistent with both the findings of Xu and Harsh (1993) who found differences in colloids of up to one third after samples were passed through a cation exchange column and Teien et al. (2007) who observed significant differences in Al_i concentration after filtration due to retention of particulate/colloidal Al in the exchange column.

Having established that $Al_{tot(p)}$ has the potential to influence both determination of $Al_{tot(uf)}$ and also subsequent $Al_{tot(uf)}$ fractionation/speciation, a simple modelling approach to overcome this issue was developed so that the $Al_{tot(p)}$ can be identified in unfiltered samples. It is well established that in humic rich surface waters there is typically a proportional relationship between dissolved $Al_{tot(uf)}$ and DOC at a given site, (Hruska et al., 2001; Cory et al., 2006). The high concentrations of DOC in this catchment (mean = 17.5 ± 7.5 mg^{-1} L max = 49.9 mg^{-1} L) provide abundant binding sites for Al. The $Al_{tot(uf)}$:DOC ratio during baseflow can be assumed to be relatively unaffected by particulate Al, and it has been shown that in sites with little particulate influence this ratio remains relatively stable throughout the spring flood (Cory et al., 2006). Therefore large deviations from this baseflow ratio can be attributed to interference from $Al_{tot(p)}$. Having established the samples with particulate interference, the baseflow $Al_{tot(uf)}$:DOC ratio can then be used to calculate an estimated $Al_{tot(f)}$ concentration from the DOC concentration (Eq. (3)).

$$\text{Calculated } Al_{tot(f)} = DOC^{*}(Al_{tot(uf)} : DOC)_{baseflow} \tag{3}$$

Particulate interference was defined as an increase of 100% or more in the $Al_{tot(uf)}$:DOC ratio from baseflow reference conditions. All samples with particulate interference were then modelled using Eq. (3). Modelled $Al_{tot(f)}$ calculated using the $Al_{tot(uf)}$:DOC baseflow ratio for samples with particulate interference (51 samples) increase the overall correlation of $Al_{tot(uf)}$ to $Al_{tot(f)}$ from 0.32 to 0.76, the average percentage difference decreased from 15% to 12.4%.

The two sites which show significantly poorer modelled results are site C3 (3 ha mire dominated site) and site C16. At C3 the mire remained frozen during almost the whole baseflow period with initial flow occurring over ice, this meant that the establishment of a baseflow $Al_{tot(uf)}$:DOC ratio was based on a single sample. This can be seen in the large differences between the ratios (Table 3) for sites three and four (the other site with significant wetland cover). Site 16 has two samples which showed particulate interference in both the filtered and unfiltered samples, presumably due to the impact of both colloidal and particulate matter. These two peak flow samples had $Al_{tot(f)}$ and $Al_{tot(uf)} > 1000$ µg^{-1} L, the samples were not consecutive and the remaining samples from the site were ~250 µg^{-1} L. In these cases the modelled values are more likely to represent the actual situation for this site (modelled values are ~250 µg^{-1} L).

Table 3

Results of modelling $Al_{tot(f)}$ using the baseflow $Al_{tot(uf)}$:DOC ratio. Correlations and percentage differences are for the results compared to observed $Al_{tot(f)}$.

Site	Baseflow $Al_{tot(uf)}$:DOC ratio	Observed $Al_{tot(uf)}$		All samples modelled		Only particulate impacted samples modelled[a]	
		r^2	% diff.	r^2	% diff.	r^2	% diff.
1	29.22	0.67	19.83	0.96	12.91	0.83	14.69
2	34.58	0.96	10.12	0.92	29.89	0.96	10.12
3	16.00	0.96	7.59	0.56	134.37	0.96	7.59
4	3.00	0.96	13.77	0.84	30.05	0.96	13.77
5	6.15	0.83	11.27	0.18	23.10	0.83	11.27
6	10.24	0.97	15.56	0.49	26.47	0.97	15.56
7	12.11	0.87	9.48	0.63	11.23	0.87	9.48
8	16.52	0.99	7.94	0.99	13.26	0.99	7.94
9	13.94	0.74	59.18	0.97	8.46	0.73	40.83
10	10.54	0.95	14.17	0.99	17.62	0.95	14.17
12	14.18	0.10	183.70	0.61	12.98	0.53	40.09
13	16.27	0.37	152.21	0.92	12.97	0.75	32.53
14	15.17	0.07	141.99	0.87	11.30	0.76	37.73
15	13.13	0.56	67.77	0.87	15.82	0.78	36.96
16	19.65	0.36	802.20	0.38	40.75	0.10	69.58
All sites		0.32	14.97	0.75	21.40	0.76	12.41

[a] Samples where $Al_{tot(uf)}$:DOC is more than 100% greater than the baseflow ratio.

In DOC rich waters with a strong Al to DOC relationships the baseflow $\mathrm{Al_{tot(uf)}}$:DOC ratio provides a simple tool for identifying samples with particulate influence and, for the majority of sites, calculating a $\mathrm{Al_{tot(p)}}$. This helps in interpreting the toxicological significance of $\mathrm{Al_{tot}}$ and $\mathrm{Al_{i}}$ concentrations by limiting the effects of particulate Al interference.

6. Conclusions

This study has shown that at sites with high flow and fine bottom sediment, $\mathrm{Al_{tot(p)}}$ influenced the concentrations of $\mathrm{Al_{tot(uf)}}$. The $\mathrm{Al_{tot(p)}}$ did not behave consistently when passed through a cation exchange column. The resulting increases in $\mathrm{Al_{tot(uf)}}$ increased the uncertainty in the determination of $\mathrm{Al_{i(uf)}}$, both analytically, or through modelling. These factors together mean that $\mathrm{Al_{tot(p)}}$ has the potential to seriously influence determination of Al concentrations and fractionation in operational environmental monitoring, where samples are not always routinely filtered. A clearer understanding of the spatial distribution of $\mathrm{Al_{tot(p)}}$ coupled with quantitative measures such as $\mathrm{Al_{tot(uf)}}$:DOC ratios will aid in identifying samples which require filtration or ancillary information in the data analysis.

Samples which have a significant contribution from $\mathrm{Al_{tot(p)}}$ showed changes in $\mathrm{Al_{tot(uf)}}$:DOC ratios which otherwise remained reasonably stable in the unaffected or filtered samples. This change from the baseflow $\mathrm{Al_{tot(uf)}}$:DOC ratio could be used to identify particulate influenced samples. The baseflow $\mathrm{Al_{tot(uf)}}$:DOC ratio was then used to estimate $\mathrm{Al_{tot(f)}}$ and therefore subsequently $\mathrm{Al_{tot(p)}}$. Linear correlations of observed $\mathrm{Al_{tot(p)}}$ from filtration and modelled $\mathrm{Al_{tot(p)}}$ using the baseflow $\mathrm{Al_{tot(uf)}}$:DOC ratio at the sites with significant particulate interference had an $r^2 > 0.98$. This modelling could be used as a substitute for measurements of $\mathrm{Al_{tot(p)}}$ in particulate influenced samples in subsequent speciation analysis.

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