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The impact of fluoride on Al abundance and speciation in boreal streams

Tobias Berger [a,*], Frédéric A. Mathurin [a], Jon Petter Gustafsson [b,c], Pasi Peltola [a], Mats E. Åström [a]

[a] Department of Biology and Environmental Science, Linnaeus University, SE-391 82 Kalmar, Sweden
[b] Department of Soil and Environment, Swedish University of Agricultural Sciences, Box 7014, SE-750 07 Uppsala, Sweden
[c] Division of Land and Water Resources Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

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ABSTRACT

The impact of fluoride on the abundance and speciation of aluminium (Al) was investigated in three boreal streams characterised by overall high concentrations of fluoride and dissolved organic matter. Stream-water sampling was carried out several times a year for at least 4 years, and a chemical equilibrium model (Visual MINTEQ) was applied in order to model the proportion of colloidal and organically/inorganically complexed Al in the waters. The Al concentrations in filtered (0.45 μm) water samples were inversely correlated with pH, and reached values up to approximately 1 mg/L during low pH conditions (pH < 6.0). In a stream with high fluoride concentrations, as compared to a similar stream with only moderately elevated fluoride concentrations, the Al concentrations were consistently elevated. For the stream with high concentrations of fluoride and Al, the model predicted both high concentrations and proportions of Al-fluoride complexation. This prediction indicates that high fluoride levels contribute to raise both the Al abundance and the ratio of inorganic to organic Al complexation in stream water. In contrast, for another stream with high fluoride concentrations and consistently high (near neutral) pH, there was no evidence of fluoride affecting Al concentration or complexation. These results show that it is important to focus future studies on the role of high levels of dissolved fluoride on both the speciation and the toxicity of Al in stream water.

1. Introduction

The effect of dissolved fluoride on Al toxicity is complex and ambiguous. Although fluoride complexes of Al are sometimes proposed to mitigate Al toxicity to some extent in comparison to other inorganic Al complexes, they still represent a bioavailable and thus possibly toxic fraction in comparison to organically bound Al (Gensemer and Playle, 1999; Bi, 2001; Haag et al., 2001; Frankowski and Ziola-Frankowska, 2010; Deng et al., 2011). Modelling work has suggested that fluoride can potentially be important in controlling the presence and speciation of monomeric Al in surface waters (Sjöstedt et al., 2010). Laboratory experiments also point in this direction; that is, it has been demonstrated that increased fluoride pollution increases the mobilisation and leaching of Al in acid soils (Moore and Ritchie, 1988; Harrington et al., 2003) and that increasing fluoride concentrations below pH 7.5 cause an increase of dissolved Al in water (Wang et al., 2010). Overall, however, the effects of high fluoride levels on Al abundance, speciation and toxicity under natural catchment conditions are not well characterised.

In northern Europe (Norway, Sweden and Finland), stream waters are characterised by overall low pH (Salminen et al., 2005) and an episodic strong decline in pH during the spring flood and other high-flow events (Cory et al., 2006; Buffam et al., 2008; Warby et al., 2008; Laudon et al., 2011). These low pH values mainly result from the widespread occurrence of organic soils and the vulnerable acid-neutralising capacity of the soils and regolith (Laudon et al., 2001). In these streams, therefore, the Al concentrations are typically elevated (Salminen et al., 2005) because of the well-known fact that Al solubility and mobilisation are enhanced under acidic conditions (Gensemer and Playle, 1999). In some areas of northern Europe, streams also have elevated fluoride concentrations in comparison to European streams in general (Salminen et al., 2005). One such area is "the Laxemar area" (located in SE Sweden), where high fluoride concentrations, up to several mg/L, are caused by the leaching of fluorine-rich bedrock (granites) and regolith (till) (Berger et al., 2012). Accordingly, in addition to the effects from pH, fluoride may also affect both Al abundance and speciation in streams in this and other similar areas.

The overall aim of the study was to assess the impact of high concentrations of natural dissolved fluoride on Al concentrations and speciation in stream water. The study was located in the Laxemar area, and included one stream with high fluoride concentrations as a result of the leaching of fluorine-rich geological materials (Berger et al., 2012)

Abbreviations: $Al_{0.45}$, analytical data of aluminium after filtration by a 0.45 μm pore size membrane filter (i.e., excluding particulate Al); Al_c, modelled inorganic colloidal aluminium, i.e., the proportion of $Al_{0.45}$ occurring as $Al(OH)_3(s)$; Al_i, modelled inorganic monomeric aluminium, i.e., the sum of aquo, hydroxy and other inorganically complexed forms; Al_{i-F}, modelled fluoride-complexed aluminium; Al_o, modelled organically complexed aluminium; Al_d, modelled dissolved aluminium, i.e., $Al_i + Al_o$ (all dissolved Al species are listed in Tables A2–A3, Appendix A).

* Corresponding author.
E-mail address: tobias.berger@lnu.se (T. Berger).

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and two other previously unstudied streams nearby. Water sampling was carried out during various hydrological conditions, and the Al concentrations were determined from 0.45 µm filtered samples. Visual MINTEQ version 3.0 (Gustafsson, 2012) was used to define the Al speciation according to an approach developed by Sjöstedt et al. (2010) and recently applied by Köhler et al. (2014).

2. Material and methods

2.1. Setting

The catchment areas of the Kärrsvik (KV) stream (outlet coordinates: 57°26′38″N; 16°37′26″E), the Ekerum (EK) stream (57°25′8″N; 16°38′33″E) and the Laxemar (LX) stream (57°25′4″N; 16°38′38″E) are included in this study (Fig. 1). These catchments are generally similar in terms of landscape morphology, with low relief dominated by coniferous and mixed forests (Table 1). These streams are characterised as mesotrophic brown-water systems. Small coastal streams, such as these, play an important role as spawning grounds and feeding areas for many fish species in the Baltic Sea. Six species of fish are found here, according to a survey conducted in LX and EK in 2006: the Ide (*Leuciscus idus*), Common Roach (*Rutilus rutilus*), Burbot (*Lota lota*), Northern Pike (*Esox lucius*), Eurasian Ruffe (*Gymnocephalus cernuus*) and Tench (*Tinca tinca*) (Andersson, 2006; Nordén et al., 2008).

All three catchments are below the highest Holocene coastline and do not reach higher than 63 m.a.s.l. (Table 1). LX has the largest catchment (40.1 km^2), followed by KV (27.2 km^2) and EK (2.8 km^2) (Table 1). The annual mean temperature is 6.4 °C and the annual precipitation generally reaches a total of 600–700 mm (Werner et al., 2006). These streams have strong seasonal variations in water flow, due to snowmelt during the spring flood and periods of rainfall mainly during the summer and from late autumn to mid-winter. KV and LX are perennial and hold permanent water flows, whereas EK represents an intermittent stream and is usually dry at several locations along its length during the summer. The average specific water discharge is 6.1, 7.3 and 5.5 L/s/km^2 for KV, LX and EK, respectively. The annual runoff for the region is estimated to be approximately 150–180 mm (Lindborg, 2005; Werner et al., 2008).

The bedrock of the area is dominated by 1.8 Ga granites and quartz monzodiorites of the Trans-Scandinavian Igneous Belt (TIB) (Wahlgren et al., 2004, 2008). In the northern part of the area, an outcrop of the younger (1.45 Ga) fluorine-enriched Götemar granite pluton occurs (Kresten and Chyssler, 1976; Friese et al., 2012). The region is intersected in several directions by a number of fracture zones. During the Quaternary period, several glaciations influenced the area. The ice sculpted the bedrock surface and removed weathered surface layers. The present surface is thus influenced by mechanical erosion and low-temperature chemical weathering during the Weichselian glaciation and the current inter-glacial period. Exposed bedrock and thin till layers dominate the area; however, the regolith is considerably thicker and often contains glacial clay in the valleys (Sohlenius and Hedenström, 2008). As the coastline regressed due to land uplift, the glacial deposits were partly eroded, resulting in local deposits of sorted materials (Rudmark et al., 2005). Podzols, Leptosols and Regosols are the most common soil types. Wetlands and areas that are used as arable land are to a varying extent underlain by different types of Histosols, that is, soils with a high content of organic matter (Sohlenius and Hedenström, 2008). Other reservoirs of organic matter are the spodic and O horizons of Podzols and postglacial clays (i.e., gyttja clay).

Table 1
Selected features of the catchments.

	Kärrsvik (KV)	Ekerum (EK)	Laxemar (LX)
Area (km^2)[1]	27.2	2.8	40.1
M a.s.l (min–max)[1]	2–50	1–31	1–63
Land use[1]			
Coniferous- and mixed forest[2]	88	84	86
Decidous forest	1	0	1
Water surface	0	0	1
Wetland[3]	4	0	2
Agriculture land	4	12	5
Remaining open land	3	4	5

[1] From Brunberg et al. (2004).
[2] Including cut forest.
[3] Including wetlands in both forest and open land.

2.2. Sampling and analysis

Stream waters were sampled near the outlet every second to fourth month for approximately 4.5 years at KV (August 2005–December

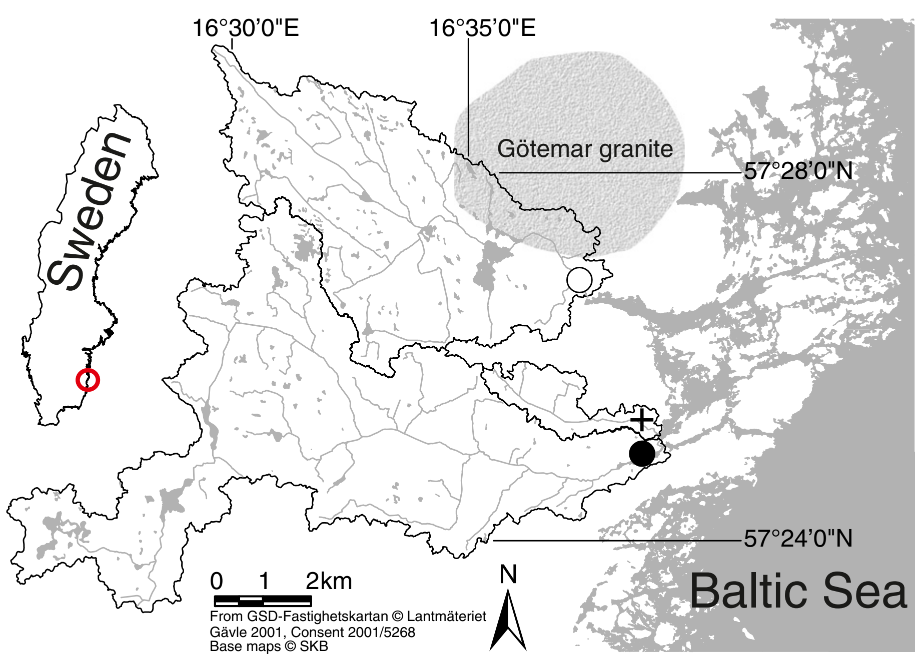

Fig. 1. Overview of the study area. Symbols indicate sampling points near the stream outlets of Kärrsvik (KV; open circle), Ekerum (EK; cross) and Laxemar (LX; filled circle).