Chemical Geology 364 (2014) 93–102

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

XAS study of iron speciation in soils and waters from a boreal catchment

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ARTICLE INFO

Article history:
Received 3 September 2013
Received in revised form 26 November 2013
Accepted 26 November 2013
Available online 5 December 2013

Editor: J. Fein

Keywords:
Fe speciation
XAS
Stream water
Soil solutions
Ground water
Krycklan catchment

ABSTRACT

Iron (Fe) is a key element, strongly influencing the biogeochemistry of soils, sediments and waters, but the knowledge about the variety of Fe species present in these systems is still limited. In this work we have used X-ray absorption spectroscopy (XAS) to study the speciation of Fe in soils and waters from a boreal catchment in northern Sweden. The aim was to better understand the controls of Fe speciation across different, but adjacent landscape elements including soil, soil solution, groundwater and stream water draining catchments with contrasting land characteristics. Our results showed that all samples contained mixtures of Fe(II) and Fe(III). The soils consisted of Fe phyllosilicates, Fe (hydr)oxides and Fe complexed by natural organic matter (NOM). All aqueous samples contained Fe(II)– and Fe(III)–NOM complexes, often in combination with Fe(III) (hydr)oxides that were associated with NOM. The variation in contribution from Fe–NOM and Fe (hydr)oxides was controlled by pH and total concentrations of NOM. The XAS spectra suggested formation of mononuclear Fe–NOM complexes consisting of chelate ring structures, but it could not be determined whether they originated solely from Fe(III)– or from a mixture of Fe(II)/Fe(III)–NOM complexes. Our collective results showed that the Fe speciation was highly variable across the different landscape elements and streams. This variation was manifested both in the distribution between mononuclear Fe–NOM complexes and Fe (hydr)oxides associated with NOM and between Fe(II) and Fe(III). These results highlight the complexity of Fe speciation in natural environmental systems and thus the challenges in interpreting Fe reactivity.

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1. Introduction

Iron (Fe) plays a major role in several geochemical processes, e.g. adsorption, desorption and redox reactions, in soils, sediments and surface waters. The environmental conditions in these systems determine which of several possible forms of Fe (Fe species) that predominate, and it is the properties of these species that control the geochemical behavior of Fe. In this respect, the presence of natural organic matter (NOM) is important as Fe–NOM interactions largely govern the Fe speciation in organic rich soils and aquatic environments (Rose et al., 1998). For instance, complexation with NOM suppresses the hydrolysis of Fe, which will have a strong influence on its solubility. These interactions will also affect the binding of other trace metals to NOM through competitive binding to high affinity sites (Weber et al., 2006). Furthermore, the interactions with NOM may influence the redox state of Fe (Borch et al., 2010). Except for soils where native Fe concentrations typically allow for spectroscopic/structural characterization, the recent knowledge about Fe–NOM interactions has primarily been obtained from studies of model systems (Pullin and Cabaniss, 2003; van Schaik et al., 2008; Karlsson and Persson, 2010, 2012). However, less is known about Fe species that exist in different natural environments, especially those present in the solution phase (e.g. soil, sediment solutions, stream and lake waters) where low native Fe concentrations often prevent compositional and structural characterization (Sjöstedt et al., 2013).

Recently, we have presented a gentle and non-invasive method for pre-concentrating Fe species in natural waters prior to X-ray absorption spectroscopy (XAS) measurements (Sundman et al., 2013). This method was based on the electrostatic attraction between negatively charged Fe–NOM species and positively charged ion-exchange resins. In agreement with previous studies, the method was shown to preserve the local structures of the metal–ligand complexes (Bargar et al., 1999; Kaplun et al., 2008). Samples from natural stream water analyzed using this approach displayed a great variability in the Fe speciation (Sundman et al., 2013). Two main pools consisting of Fe–NOM complexes and Fe (hydr)oxides were identified, and both pools were indicated to contain at least two species or more. These two pools were also identified in rivers by Allard et al. (2004), who used a combination of ultrafiltration and electron paramagnetic resonance spectroscopy. Furthermore, stream waters as well as Fe–fulvic acid systems have

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Abbreviations: CN, coordination number; DOC, dissolved organic carbon; EXAFS, extended X-ray absorption fine structure; LCF, linear combination fitting; MS, multiple scattering; NOM, natural organic matter; TOC, total organic carbon; WT, wavelet transform; XANES, X-ray absorption near edge structure; XAS, X-ray absorption spectroscopy.

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0009-2541/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemgeo.2013.11.023

been indicated to contain minor concentrations of Fe(II)–NOM complexes (Pullin and Cabaniss, 2003; Sundman et al., 2013). These examples alone indicate the complexity of Fe speciation in different natural environments and highlight questions on how to describe and interpret Fe reactivity in natural environments and what environmental parameters control this complexity.

Mechanistic studies of Fe speciation under different environmental conditions and tracing the development and transformation are ways to approach these questions. Recent studies by Ilina et al. (2013) and Neubauer et al. (2013) using isotopic and flow-field flow fraction techniques, respectively, have demonstrated the power of this approach. This is now feasible also with direct spectroscopic probes since we can access the aquatic Fe speciation using the method discussed above. In this study, we have characterized Fe species at the thoroughly studied Krycklan Catchment (Laudon et al., 2013). This site is of particular interest as it has been monitored since the 1980s and there are records of numerous environmental parameters including records of trace metal concentrations (e.g. Björkvald et al., 2008). Previous studies have shown that the chemical patterns of the stream waters are controlled by the catchment soils that are drained (Laudon et al., 2011). The aims of this study were to build on these previous results focusing specifically on iron, and investigate: 1. the variations in Fe speciation across different, but adjacent landscape elements (i.e. soil, soil solution, groundwater and stream water); and 2. the variations in Fe speciation in stream water as a function of catchment type drained. For this latter purpose water was collected from five different streams draining forested soils, wetland dominated soils and a mixed catchment following Berggren et al. (2009). All samples were characterized by means of Fe K-edge XAS, either by analyzing the native samples or after pre-concentration with our recently described method (Sundman et al., 2013).

2. Materials and methods

2.1. Sites and samples

All samples were collected at the Krycklan catchment, Sweden (64°, 16′N, 19°, 46′E). This is a boreal catchment with gneissic bedrock covered with till (Ivarsson and Johnsson, 1988); for a detailed map of the experimental site see Buffam et al. (2007). A brief summary of the Krycklan streams is presented in Table 1. The concentration of dissolved organic carbon (DOC) in these streams depends on hydrology and the proportion of forest to wetland in the drained catchment (Laudon et al., 2011). During low flow conditions DOC concentrations in streams are significantly higher in the wetlands compared to the forested catchments. During the spring flood, which is the largest hydrological event of the year, the concentration declines in the wetland streams due to dilution, whereas the DOC increases in the forested streams. These differences and changes are explained by the hydrological flow pathways and the source area of the DOC and have impact on both carbon quality and interactions between DOC and metals (Bergknut et al., 2010). According to recent measurements with oxygen loggers and of redox potentials in streams within the Krycklan catchment (unpublished data) the stream waters collected should be well aerated.

The stream waters were collected in thoroughly acid-washed polyethylene bottles, rinsed three times in the sampled stream, and filled under water to avoid air bubbles. All samples were collected in the autumn and early winter at relatively low flow conditions (0.3 to 0.5 mm day^{-1}). One set of samples consisted of stream water, ground water, soil and soil solution samples from a forested catchment designated C2; for more information about the sampling site see Table 1 and Laudon et al. (2013). The soil solutions and ground water were collected as described in Ågren et al. (2008). Briefly, the soil solutions were collected by applying vacuum to suction lysimeters. The initial volume was discarded and subsequently samples were collected over a 24-hour period. The samples were collected in acid-washed glass bottles; air was replaced by nitrogen gas and thereafter evacuated prior to sampling. The samples were kept cool and dark after sampling and then immediately transferred to and further prepared in the laboratory. The soil samples were collected in double plastic bags, cooled after sampling, frozen upon return to laboratory and stored in a freezer (−18 °C) until shipping to the synchrotron for analysis. The other set of samples consisted of stream waters collected at five different sites, C1, C2, C3, C4 and C10 (Table 1). These waters were kept refrigerated in the dark until sample preparation and analysis.

2.2. Sample preparation

The aqueous samples were pre-concentrated according to a procedure previously described (Sundman et al., 2013). Briefly, the commercial adsorbent Dowex 1 × 8, chloride form 200–400 mesh (Sigma Aldrich) was used and cleaned repeatedly with Milli-Q water prior to sample preparation. The stream waters were handled under a stream of nitrogen whereas the soil solutions and the ground water were handled in a glove box, filled with nitrogen. Aliquots for pH, total organic carbon (TOC) and Fe analyses were taken prior to addition of adsorbents. A weighted and cleaned amount of adsorbent was added to each sample solution and manually rotated on a regular basis for 7 days. To avoid light induced degradation, all samples and aliquots were covered with aluminum foil. The samples were centrifuged at 5000 rpm for 5 min and the wet paste was collected in small test tubes, filled with nitrogen gas, sealed with plastic film and then covered with aluminum foil before being refrigerated and stored for XAS analysis. Aliquots for analyses (TOC and Fe) were also taken after the

Table 1

Overview of selected characteristics of the Krycklan Catchment streams (from Buffam et al., 2007). Included are also information about the XAS sample preparation and results from the analysis of pH, $\mathrm{Fe_{tot}}$ and TOC measurements for the water/resin samples.

Sample	Name	Landcovertype[c]	pH	V (l)	$\mathrm{Fe_{tot}}$ (μM)[d]	Adsorbed $\mathrm{Fe_{tot}}$ (%)	TOC (mg/l)[d]	Adsorbed TOC (%)
C2, stream water[a]	Västrabäcken	Forested	4.5	0.4	16.5	82.3	18.7	42.7
C2, stream water[a]	Västrabäcken	Forested	4.5	1.2	16.5	27.7	18.7	34.8
S4, soil solution, 50–60 cm[a]	Västrabäcken	Forested	4.4	0.5	54.4	73.5	25.3	34.7
S4, soil solution, 20–30 cm[a]	Västrabäcken	Forested	4.3	0.5	39.4	42.6	42.3	50.6
Ground water[a]	Västrabäcken	Forested	4.4	0.8	17.6	75.0	22.3	76.2
C1, stream water[b]	Risbäcken	Forested	4.9	0.5	19.1	56.2	15.5	58.3
C2, stream water[b]	Västrabäcken	Forested	5.4	0.5	9.8	87.8	12.0	59.1
C3, stream water[b]	Lillmyrbäcken	Wetland	4.3	0.5	9.8	36.5	39.9	29.7
C4, stream water[b]	Kallkälsmyren	Wetland	4.6	0.5	16.2	39.6	28.9	30.0
C10, stream water[b]	Stormyrbäcken	Mixed	5.8	0.5	19.1	44.9	13.4	44.9

[a] Stream water, soil solutions and ground water from the same site.
[b] Stream water from different sites.
[c] The definition was based on the wetland coverage, according to <2% wetland is defined as forested, 2–30% wetland is defined as mixed and >30% wetland is defined as wetland.
[d] Start values analyzed before adsorption on the resin.

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