ALUMINIUM PRECIPITATES FROM GROUNDWATER OF AN AQUIFER AFFECTED BY ACID ATMOSPHERIC DEPOSITION IN THE SENNE, NORTHERN GERMANY

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Abstract. White precipitates collected from stream bottoms and well tubes in the Senne area consist of amorphous aluminium hydroxide, coprecipitated with minor amounts of sulfate, phosphate and silica. The precipitates have presumably formed by the interaction of slightly alkaline water from calcareous subsoil sediments, with acidic water draining off sandy soils affected by high inputs of acidic atmospheric deposition. From many hydrochemical studies, precipitation of aqueous aluminium is known to occur in subsurface horizons of acid soils affected by acid rain. On the basis of presumed equilibrium with soil solutions, jurbanite, $AlOHSO_4 \cdot 5H_2O$, is often assumed to be the secondary mineral involved. However, direct evidence for jurbanite from solid phase analysis is lacking. This first analysis of such a secondary phase does not support the jurbanite hypothesis, and shows that amorphous Al hydroxide can be formed instead.

1. Introduction

In many parts of Germany and surrounding countries, acidic atmospheric deposition has caused serious acidification of sandy forest soils that initially had a low acid neutralization capacity. In many such soils, exchangeable base levels and soil pH have dropped significantly over the past decades (Rastin and Ulrich, 1985; Van Breemen *et al.*, 1988; Bredemeier *et al.*, 1990), and at present buffering of strong acids is dominantly by dissolution of secondary Al phases from surface soil horizons. The secondary Al is mainly bound to organic matter and it has accumulated in the soil over millenia by natural weathering and soil forming processes (Mulder *et al.*, 1989). In the mineral horizons of such strongly acidified soils, the mobilized Al is mainly present as Al^{3+} and other inorganically complexed dissolved Al forms. Only a small part is organically complexed dissolved Al (Mulder *et al.*, 1987). Generally, Al^{3+} is the dominant cationic solute in such soils. Al^{3+} is counter balanced essentially by the anions SO_4^{2-} and NO_3^- which illustrates the importance of H_2SO_4 and HNO_3 as the cause of the mobilization of Al. The levels of dissolved Al frequently encountered in soil solutions (e.g. between 1 and 50 mg L^{-1}) are potentially toxic to many trees and other plants (Godbold *et al.*, 1988), and far exceed the limit of 0.2 mg L^{-1} fixed in the German drinking water standards (TWVO, 1986).

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In general the pH increases at some depth in the soil profile or in the substratum, which may cause precipitation of dissolved Al, as is illustrated by decreasing Al concentrations with increasing depth (Böttcher *et al.*, 1985; Mulder *et al.*, 1987) and by an increase in oxalate extractable Al (Süsser and Schwertmann, 1991).

The nature of the precipitated Al has been the subject of much debate. On the basis of a near constancy of the activity product $(Al)(OH)(SO_4)$ in the order of the theoretical value for the solubility product of the mineral jurbanite $((Al)(OH)(SO_4) \cdot 5H_2O, K_{SO} = 10^{-17.8})$, the precipitation of this mineral has been hypothesized by several authors (Nordstrom, 1982; Prenzel, 1983; Khanna *et al.*, 1987). On the other hand, close inspection of solution data and the lack of evidence for coupled mass transfers of Al and SO_4 between solid phases and soil solution has led others to dismiss the jurbanite hypothesis (Mulder *et al.*, 1987). Reactive, poorly ordered Al hydroxides have also been suggested to be precipitated in the sub soil and to determine the Al activity in soil solutions (Süsser and Schwertmann, 1991). Lükewille *et al.* (1984) observed Al precipitates from groundwater in a forested area affected by acidic atmospheric deposition, which provided an opportunity to test the jurbanite hypothesis. This paper gives further details on the nature of the Al precipitates first described by Lükewille (1989).

2. Geological and Hydrochemical Settings

The Senne is located at the south-western slope of the Teutoburger Forest in northern Germany. The quartziferous parent material, originating from Saale glaciation, is on average 25 m thick and is underlain by an almost impervious layer of marl (Emscher Marl). Coarse limestone gravel is sporadically embedded in the lower part of the sandy ground (Figure 1).

The aquifer is divided into two parts by generally impermeable incorporated moraines, which are decalcified. Several streams arise in the Senne, running in

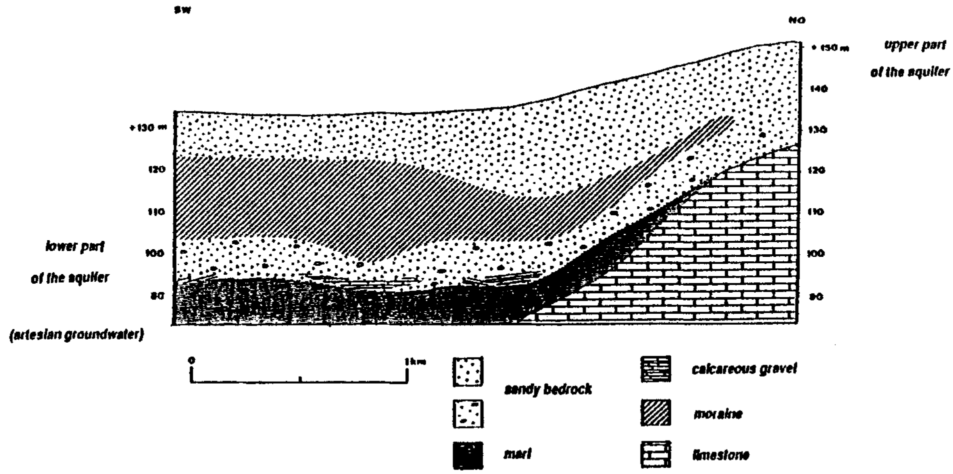

Fig. 1. The Senne aquifer.

small ravines. Groundwater from the upper part of the aquifer feeds the streams by percolation through the bottom of the valleys. In some instances the partly artesian groundwater from the lower part of the aquifer fills the streams by pushing up through the moraines.

The area is mainly forested by *Pinus sylvestris* L. which were planted around 1890 when the former heathland was turned into woodland (Lükewille, 1989). The soils are predominantly humus podzols.

Acidic deposition in the Senne area is in the order of 2 to 3 kmol H^+ ha^{-1} yr^{-1}. The poorly-buffered aquifer is strongly acidified down to about 10 m depth with groundwater pH levels ranging from 4.4 to 3.8 and mean Al (Al^{3+}) concentrations of 5.0 mg L^{-1}. Sulfate is the major anion with concentrations averaging 40 mg L^{-1}. Because of the embedded limestone gravel groundwater originating from the lower part of the aquifer still is well-buffered. Becarbonate (HCO_3^-) is the major anion and the pH level is about 7.0 (Lükewille, 1989).

Thousands of private wells in the Senne draw drinking water from the upper part of the aquifer. The city of Bielefeld is pumping about 13×10^6 m^3 of groundwater yr^{-1}. The waterworks draw water from both parts of the aquifer simultaneously. During pumping, the acidified, Al rich groundwater from the upper part of the aquifer is mixing with the well-buffered from the lower part of the aquifer, resulting in the precipitation of whitish compounds. The precipitation starts at pH values of about 4.5. The temperature is in the order of 5 to 8 °C. Water-filters, casings and pipes in the municipal wells are coated or even blocked by the compounds. The water output can be considerably reduced (Baudisch, 1989).

The same phenomenon can be observed in streams where water from the two different spring types meets: flocky precipitates are coating the stream beds (Lükewille *et al.*, 1984).

3. Materials and Methods

White precipitates collected from different water tubes (S1, S2, S3) and from a stream bed (Ölbach; S4) were analyzed. S1, S2 and S3 were taken from a water tube in about 15 m depth where water from the upper and lower parts of the sandy aquifer is mixing. Sample 4 was collected directly at the confluence of two different spring types (see para. 2).

Quantitative and qualitative analysis of elements was performed by x-ray fluorescence (XRF) on $Li_2B_4O_7$ glass disks. Total S was determined as sulfate by HPLC after fusion on the sample with Na_2CO_3-KNO_3. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on 25 mg subsamples at a heating rate of 10 °C min^{-1}, using a Dupont 1090 thermal analyzer. X-ray diffractograms were made using a Philips PW 1050 / PW 1710 machine. For the qualitative and semi-quantitative electron microprobe analysis (EMPA) a Philips 515 scanning electron microscope (SEM) and an Edax 9100 microanalyser were used. The energy-dispersive spectra were acquired by point analyses from various regions of the samples at 10 KeV. Infrared rotation-vibration transition spectroscopy was performed using a FTS-7 Bio-Rad analyser.

4. Results

X-ray diffraction analyses (XRD) of the white compounds show them to be mainly amorphous. Broad bands (at position 10, 4.5, 2.2 a) are observed in samples S1, S4 and indicate some order. Data from Infrared spectroscopy (IRS) indicate the presence of SO_4^{2-}. Electron microprobe analyses (EMPA) and the x-ray fluorescence (XRF) spectra show that the samples mainly contain aluminium and H_2O, in much smaller quantities Si, S, P, Fe and Ca (Table I). The differential thermal analyses (DTA) show a strong endothermic peak between 100 and 300 °C and a small exothermic peak at about 950 °C (Figure 2). The endothermic peak is associated with a mass loss of about 40%.

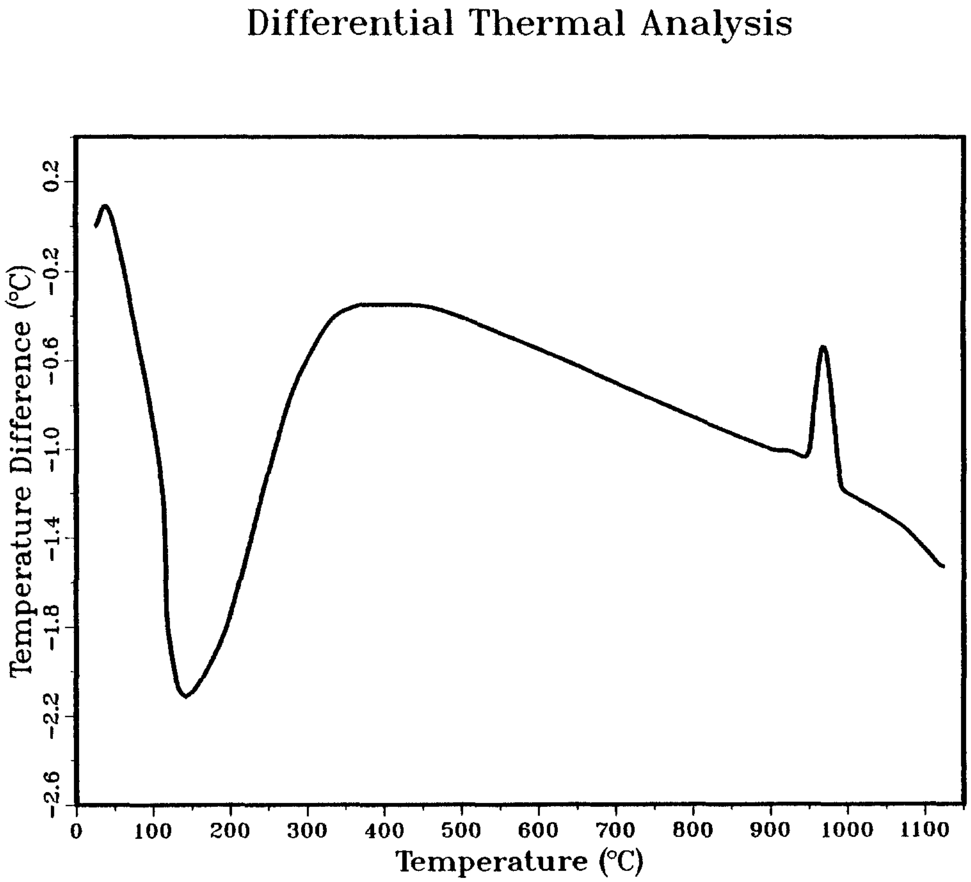

Fig. 2. Differential thermal analysis graph of sample S3 (24.3 mg, heated at 10 °C min^{-2}).

TABLE I

Quantitative elemental analyses by X-ray fluorescence (XRF)

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	P_2O_5	SO_3	H_2O[a]	Sum
S1	3.04	47.8	0.05	0.03	2.09	7.20	40.5	100.7
S2	5.15	47.4	0.06	0.15	1.71	3.28	42.3	100.0
S3	5.48	41.8	0.11	0.06	3.11	5.15	43.3	99.0

[a] The H_2O content was estimated from loss ignition, corrected for SO_3.

5. Discussion

The analytical data show that the precipitates consist of amorphous aluminium hydroxide. The DTA graphs are quite similar to those reported by Mackenzie (1970) for alumina gels formed by adding 9N NaOH to $Al_2(SO_4)_3$. Apparently, where shallow acidic groundwater rich in Al and SO_4 is mixed with near-neutral Ca- and HCO_3-rich water from the $CaCO_3$ bearing lower part of the Senne aquifer, $Al(OH)_3$ is precipitated from solution. The precipitation starts at pH values of about 4.5. A similar process has been described by NORDSTROM (1982) for locations directly below the confluence of an acidic stream draining pyritic mine spoils with a stream of neutral pH. The stoichiometry of the reaction that takes place can be written as:

$$Al^{3+}(aq) + 3\ HCO_3^-(aq) \rightarrow Al(OH)_3(s) + 3\ CO_2(g \text{ or } aq).$$

As a result, the two water types were transformed into a single Ca and SO_4 containing water. Appreciable amounts of silica, phosphorous and sulfate apparently coprecipitated with the Al, or were sorbed later on the aluminous precipitate.

The precipitate clearly cannot be identified as a basic aluminium sulfate: the molar Al/S ratio varies from 10.4 to 22.7, whereas it is 1.0 in jurbanite and 4.0 in a high Al/S basic aluminium sulphate such as basaluminite. These results prove that essentially amorphous $Al(OH)_3$ compounds can be formed during *in-situ* neutralization of acidic Al-SO_4 waters derived from soils acidified by acidic atmospheric deposition. Similar amorphous products could be involved in precipitation of Al in soils. These results, however, do not exclude the possibility that jurbanite is formed as a secondary Al phase in the deeper horizons of soils acidified by acidic deposition. Maybe the conditions in the Senne aquifer, where relatively large amounts of water of very contrasting composition are mixed rather abruptly, are particularly favorable for the formation of amorphous Al hydroxide.

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