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Tracing effects of decalcification on solute sources in a shallow groundwater aquifer, NW Germany

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SUMMARY

δ^{87}Sr values and Ca/Sr ratios were employed to quantify solute inputs from atmospheric and lithogenic sources to a catchment in NW Germany. The aquifer consists primarily of unconsolidated Pleistocene eolian and fluviatile deposits predominated by >90% quartz sand. Accessory minerals include feldspar, glauconite, and mica, as well as disperse calcium carbonate in deeper levels. Decalcification of near-surface sediment induces groundwater pH values up to 4.4 that lead to enhanced silicate weathering. Consequently, low mineralized Ca–Na–Cl- and Ca–Cl-groundwater types are common in shallow depths, while in deeper located calcareous sediment Ca–HCO_3-type groundwater prevails. δ^{87}Sr values and Ca/Sr ratios of the dissolved pool range from 7.3 to -2.6 and 88 to 493, respectively. Positive δ^{87}Sr values and low Ca/Sr ratios indicate enhanced feldspar dissolution in shallow depths of less than 20 m below soil surface (BSS), while equilibrium with calcite governs negative δ^{87}Sr values and elevated Ca/Sr ratios in deep groundwater (>30 m BSS). Both positive and negative δ^{87}Sr values are evolved in intermediate depths (20–30 m BSS). For groundwater that is undersaturated with respect to calcite, atmospheric supplies range from 4% to 20%, while feldspar-weathering accounts for 8–26% and calcium carbonate for 62–90% of dissolved Sr^{2+}. In contrast, more than 95% of Sr^{2+} is derived by calcium carbonate and less than 5% by feldspar dissolution in Ca–HCO_3-type groundwater. The surprisingly high content of carbonate-derived Sr^{2+} in groundwater of the decalcified portion of the aquifer may account for considerable contributions from Ca-containing fertilizers. Complementary tritium analyses show that equilibrium with calcite is restricted to old groundwater sources.

Introduction

During the Pleistocene glaciations, eolian and fluvial sands were deposited over wide areas in Northern Europe (e.g. Ehlers et al., 1984; Eissmann, 2002; Walter, 2007). Today, the unconsolidated sediments represent economically important but vulnerable groundwater reservoirs that are exploited for drinking water supply. Particularly, unconfined aquifers, shallow water tables, and decalcification of soils increase the potential risk for environmental and anthropogenic contamination (e.g. Dahl and Dörhöfer, 1991; Dörhöfer et al., 2001).

Soils dominated by quartz sand have naturally low acid-neutralization capacities, and decalcification caused by natural and anthropogenic processes produces low pH values in shallow groundwater systems. As a consequence, the mobility of aluminum and other heavy metals increases, and leaching and transfer of toxic compounds may affect the quality of potable water resources. The effect of base cation loss on forested watersheds resulting from the impact of soil acidification in Europe and North America was intensely studied throughout the past decades (e.g. Falkengren-Grerup et al., 1987; Shortle and Bondietti, 1992; Bricker and Rice, 1993; Likens et al., 1996; Lawrence et al., 1999; Huntington et al., 2000; Driscoll et al., 2001; Hrkal et al., 2006; Fenn et al., 2006).

^{87}Sr/^{86}Sr and Ca/Sr ratios are useful natural tracers to discriminate sources of base cations and quantify inputs to hydrological systems (e.g. Bullen et al., 1996; Katz and Bullen, 1996; Probst et al., 2000; Wiegand et al., 2001; Négrel et al., 2004). Both tracers are reactive along flow paths and are controlled by the sources contributing to the dissolved Sr^{2+} and Ca^{2+} loads. While the Sr isotope composition is not affected by changes in Sr^{2+} concentrations, the Ca/Sr ratios may be altered, e.g. by precipitation of secondary minerals and cation-exchange processes (e.g. Sposito, 1989; Capo et al., 1998).

In near-surface groundwater systems, dissolved Sr^{2+} and Ca^{2+} pools generally represent mixtures of atmospheric inputs and releases from mineral weathering. In addition, anthropogenic sources including fertilizers may be of importance (e.g. Böhlke and Horan, 2000; Soler et al., 2002; Vitòria et al., 2004). Under favorable conditions, the contributing sources have different Sr isotope and Ca/Sr ratios permitting the determination of origin

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and mixing proportions of solute inputs along flow paths. For example carbonate and silicate minerals are usually characterized by considerable differences in their isotope and concentration ratios. Studies focusing on experimental dissolution rates of Sr-bearing minerals include Åberg (1995), Brantley et al. (1998), and Taylor et al. (2000), while applications to water–rock interactions and weathering processes in the natural environment were reported by Miller et al. (1993), Johnson and DePaolo (1994), Bullen et al. (1997), Peterman and Wallin (1999), Quade et al. (2003), Jacobson et al. (2002), Bau et al. (2004), Shand et al. (2007) and others.

The present study is focused on a shallow groundwater aquifer located in Pleistocene siliciclastic deposits in NW Germany to assess changes in the chemical composition of the water caused by decalcification (carbonate dissolution) processes. A decrease in the acid-neutralization potential of soils and declining depths of decalcification are probably linked to a combination of natural and anthropogenic processes including fluctuating water tables, redox processes, agricultural exploitation, nitrification, acid rain deposition of the past decades, and increased groundwater withdrawal. Considerable variations in groundwater pH and alkalinity imply changes in the weathering regime across the aquifer. To trace the effects of decalcification on solute sources and quantify replenishing cation inputs from mineral and atmospheric sources, $^{87}Sr/^{86}Sr$ (here reported as $\delta^{87}Sr$ values) and Ca/Sr ratios of groundwater, rainwater, bulk sediment, and mineral separates were evaluated. A model for the evolution of groundwater with respect to the origin of dissolved Ca^{2+} and Sr^{2+} and quantification of solute fluxes from atmospheric and mineral sources is presented.

Geology and hydrology

The water works of Ristedt is located about 10 km south of the city of Bremen in Lower Saxony, northwestern Germany (Fig. 1). About 20-million m^3 of groundwater are pumped annually from depths between 18 and 30 m for local drinking water supply by the Harzwasserwerke GmbH, Germany. The catchment area has a size of about 100 km^2, extending between the towns of Syke and Weyhe. The average yearly precipitation is 691 mm yr^{-1} (source: Deutscher Wetterdienst/German Meteorological Service; www.dwd.de). Groundwater recharge is between 100 and 300 mm annually, corresponding to about 133-million m^3 yr^{-1} (source: EG-WRRL Report 2005).

The aquifer is composed of Quaternary unconsolidated siliciclastic sediments (sands, intercalated with silt and gravel) that were deposited during the Pleistocene (mainly Elsterian and Saalian glaciations) (e.g. Ehlers et al., 1984; Grube et al., 1986; Meyer, 2005). In the northern catchment area, periglacial deposits created by solifluction during the Weichselian glaciation form a transition to sand-loess deposits in the south, and eolian sands in the west (Kartenserver des NIBIS, 2008a). Streams draining the catchment are bordered by peaty-clayey fens. Deposits of the northern catchment area show variable permeabilities from $>10^{-4}$ to $<10^{-5}$ m/s, while to the south medium permeabilities with coefficients between 10^{-5} and 10^{-4} m/s prevail. The western catchment surrounding the water works of Ristedt shows highest permeabilities of $>10^{-4}$ m/s (Kartenserver des NIBIS, 2008b). Groundwater drains largely through the streams Hache and Hombach both discharging to the river Weser.

Groundwater flows from the higher plains in the southwest (German "Geest") to the northeast (Weser marshlands) (Fig. 1). During the sampling campaign in summer 2001, the water table was between 20 and 25 m below the surface at the rim of the Geest plains, and between 1 and 4 m in the Weser marshlands. Groundwater in monitoring wells of the Geest is mostly oxic in contrast to the marshland where anoxic conditions prevail. Reducing conditions are linked to intercalations of organic-rich layers and coal fragments in the sand deposits. Alternating groundwater dynamics and redox processes in organic-rich sediments of the Weser marshland cause acidic conditions that contribute to natural decalcification of the soils.

Methods

Groundwater samples ($n = 32$) were collected from monitoring wells in defined depths between 6 and 54 m below the soil surface (BSS). In addition, sediment from the unsaturated and saturated zone was collected (Fig. 1). In the unsaturated zone, sediment cores ranging between 2 and 5 m in depth were drilled with a piston corer. An additional core of 30 m length (B16) from the saturated zone located in the Weser marshlands was provided by the Harzwasserwerke GmbH. Water samples were filtered through 0.45 μm cellulose-nitrate filters, stabilized with 1% distilled HNO_3 and stored in pre-cleaned polyethylene bottles prior to analysis of Sr concentrations and $^{87}Sr/^{86}Sr$ ratios. A separate set of samples was collected for major elements and analyzed by standard procedures including ion-chromatography and graphite-AAS at the Central Laboratory of the Harzwasserwerke GmbH, Langelsheim, Germany. Saturation indices were modeled with the computer code PHREEQC (Parkhurst and Appelo, 1999). Tritium analyses were performed on 2 L of untreated groundwater samples using the liquid scintillation technique at the University of Goettingen, Germany. Selected samples were analyzed at the Hydroisotop GmbH, Germany.

Bulk sediment samples were dried (40 °C) prior to geochemical analysis. Selected sediment samples were pulverized and analyzed by X-ray fluorescence spectroscopy for major and trace components at the Geoscience Center, University of Goettingen, Germany. For Sr isotope analysis, about 100 mg of sediment powders were digested in a mixture of $HF–HNO_3–HClO_4$ at 120 °C over night. The digestion of mineral separates (~10 mg) followed the same procedure. After complete dissolution and evaporation, the sample residue was dissolved in 6 N HCl at 120 °C and again evaporated. The sample residue was then re-dissolved in 2.5 N HCl for ion exchange chromatography. Separation of Sr from other cations was carried out on quartz glass columns using Biorad AG50 × 8 (200–400 mesh) resin and 2.5 N HCl. Groundwater (~10 mL) was pre-concentrated by evaporation before ion exchange chromatography. Sr concentrations were determined by isotope dilution technique using an ^{84}Sr-enriched spike solution. Purified Sr fractions were loaded onto out-gassed Ta single filaments using 0.25 N H_3PO_4 and measured on a Finnigan MAT262 thermal ionization mass spectrometer (TIMS) at the Geoscience Center, University of Goettingen, Germany. $^{87}Sr/^{86}Sr$ ratios were corrected for instrumental fractionation using the natural $^{88}Sr/^{86}Sr$ ratio of 8.375209. Routine standard measurements yield 0.71026 ± 0.00002 (2σ: $n = 32$) for the NBS987 Sr standard. Only distilled reagents were used for chemical sample preparation. Blanks were less than 0.5 ng for Sr. The reproducibility of the individual $^{87}Sr/^{86}Sr$ ratio is equal to or less than 0.00002 (2σ). All analyzed $^{87}Sr/^{86}Sr$ ratios were normalized to the average $^{87}Sr/^{86}Sr$ ratio of rainwater 0.710 (Wiegand et al., 2001) and are reported in delta notation according to the equation:

$$\delta^{87}\mathrm{Sr} = \left(\frac{^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{sample}}}{^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{rainwater}}} - 1\right) \times 1000 \qquad (1)$$

Results

Hydrogeochemical parameters

Changes in the physical and chemical properties across the aquifer (e.g. acid-neutralization capacity, redox conditions, resi-