Chemical Geology 276 (2010) 284–293

Contents lists available at ScienceDirect

Chemical Geology

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

Interaction of dissolved and sedimentary sulfur compounds in contaminated aquifers

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ARTICLE INFO

Article history:
Received 9 March 2010
Received in revised form 14 June 2010
Accepted 22 June 2010

Editor: B. Sherwood-Lollar

Keywords:
Sulfate
Sulfide
Sedimentary reduced sulfur
Bacterial sulfate reduction
Biodegradation
Stable isotopes

ABSTRACT

A sulfate rich Quaternary urban aquifer is contaminated with a variety of different petroleum hydrocarbons. To reveal the details of the sulfur cycling and to prove the occurrence of bacterial sulfate reduction (BSR), as one major process of anaerobic biodegradation, geochemical and isotope investigations of different dissolved (sulfate and sulfide) and reduced inorganic sedimentary sulfur compounds (monosulfide, disulfide, and elemental sulfur) were conducted. In order to recognize possible biodegradation, the carbon isotopic composition of dissolved inorganic carbon was examined as well.

The local significant depletion of ^{13}C in DIC is a first indicator for the occurrence of biodegradation at the site. The enrichment of both heavy sulfur and heavy oxygen isotopes in dissolved sulfate and the simultaneous decrease of sulfate concentrations at several sampling locations provide clear evidence for the occurrence of BSR in the aquifer. The isotope distribution pattern of sulfate suggests a straightforward bacterial reduction process. However, the isotopic composition of dissolved sulfide indicates the occurrence of secondary processes superimposed on BSR.

Primary or secondary pyrite is the dominant sedimentary sulfur species in the aquifer matrix. The ubiquitous occurrence of sedimentary monosulfide is further evidence for the important role of BSR. However, the presence of elemental sulfur and the isotope distribution pattern of sedimentary sulfur species point to a temporal variability of the hydrochemical conditions at the site with the occurrence of secondary sulfur transformations such as partial re-oxidation. Nevertheless, isotope and hydrochemical data indicate an overall high natural attenuation potential of the investigated aquifer.

1. Introduction

Sulfur cycling in anoxic aquifers contaminated with petroleum hydrocarbons is closely related to basic processes controlling biodegradation of the organic pollutants. The most straightforward link between biodegradation and sulfur transformations is bacterial sulfate reduction (BSR) when sulfate reducing bacteria oxidize organic contaminants utilizing dissolved groundwater sulfate as a terminal electron acceptor (e.g. Vroblesky et al., 1996; Reinhard et al., 1997; Davis et al., 1999). Beyond that, certain sulfur transformations such as oxidation of dissolved sulfide at geochemical gradients may compete with biodegradation processes for electron acceptors including dissolved oxygen, nitrate or ferric iron (Knöller et al., 2008).

Stable isotope tracers have been proven to be valuable tools for assessing biodegradation in contaminated aquifers. In that context, the most straightforward approach (direct approach) focuses on the investigation especially of carbon and hydrogen isotope ratios in organic reactants (i.e. contaminants) and their intermediate and final degradation products. An extensive pool of recent literature is available dealing with the isotope fractionation related to certain degradation mechanisms and pathways (e.g. Hunkeler et al., 2001, Morasch et al., 2001, Morasch et al., 2002, Meckenstock et al., 2004, Mancini et al., 2006, Mancini et al., 2008a) and the successful field application of the direct approach for recognizing and quantifying intrinsic biodegradation (e.g. Mancini et al., 2002, Richnow et al., 2003a,b, Griebler et al., 2004, Abe and Hunkeler, 2006, Fischer et al., 2006, Fischer et al., 2007, Mancini et al., 2008b). In contrast to the examination of the isotopic composition of contaminants by the direct approach, the indirect method focuses on the isotopic investigation of potential electron acceptors such as dissolved sulfate and nitrate. The reduction of different electron acceptors decisively controls in situ biodegradation by respiration reactions.

The preferential utilization of the lighter sulfur isotopes by sulfate reducing bacteria usually results in the enrichment of the lighter sulfur isotope in the produced sulfide and of the heavier sulfur isotope in the remaining sulfate (e.g. Kaplan and Rittenberg, 1964, Canfield, 2001). This significant discrimination of sulfur isotopes enables the detection and quantification of the reduction process by stable isotope measurements.

In several field studies, stable sulfur isotopes of dissolved sulfate were used to identify BSR in contaminated aquifers (Schroth et al., 2001, Spence et al., 2001, Spence et al., 2005). Nevertheless, only a few approaches have been attempted to quantify the reduction process and to interpret field derived enrichment factors with respect to interferences of BSR with

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0009-2541/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemgeo.2010.06.013

Fig. 1. Location of the investigated aquifer in Germany.

secondary sulfur transformation processes (Knöller et al., 2008). However, the potential contribution of information derived from the isotopic investigation of sediments for the assessment of the natural attenuation potential of contaminated aquifers has not been acknowledged appropriately yet.

In this study we combine the results of the commonly conducted isotopic investigation of dissolved sulfur compounds with knowledge that originates from the examination of the isotopic composition of sedimentary sulfur compounds. We show that this combination reveals crucial details of the temporal hydrochemical evolution of a contaminated aquifer that may be utilized for a more reliable assessment of the overall natural attenuation potential.

2. Local setting and analytical methods

2.1. Study site

The investigated section of the contaminated Quaternary urban aquifer is situated on the site of an abandoned gasoline station in central eastern Germany (Lat. 51°20′32″ N; Long. 12°21′47″ E, Fig. 1). The extension of the contamination with petroleum hydrocarbons had previously been contoured as the result of several conventional sampling campaigns carried out by means of soil and groundwater sampling and analysis.

At the investigated site the aquifer is stratified into two lithologically different sections. The upper layer, reaching down to a depth of about 6 m, is dominated by fine sands with silt lenses. The lower layer, consisting of sandy gravel, displays a significantly higher hydraulic conductivity than the fine sands above. Neither of the two aquifer sections contains carbonate minerals. The unsaturated zone that covers the site is lithologically comparable to the upper aquifer layer. At the investigated site and beyond, the subsurface is almost completely concealed by buildings and pavement preventing local groundwater recharge.

The contaminant plume consists of BTEX species only. The average composition is 32% benzene, 18% toluene, 10% ethylbenzene, and 40% xylene. The highest total BTEX concentrations of 29,000 μg/L were measured in the center of the contaminant plume (wells P2 and P9, Fig. 2).

2.2. Sampling

The 11 accessible wells (Fig. 2), which go down to a depth of at least 8 m, are fully screened across the saturated zone, which complicates groundwater sampling from defined depths. However, all 11 groundwater samples were taken from a depth of 7 m, i.e. from the lower layer of the aquifer. Due to the mentioned considerable differences in hydraulic conductivity between the two aquifer sections, all samples can be considered as representative for the lower (sandy gravels) layer of the contaminated aquifer portion.

During pumping, the water quality parameters dissolved oxygen, electric conductivity, redox potential, pH, and temperature were monitored at the respective well heads by using the appropriate electrodes (Oxi 325, LF 325, pH 330, and pH 196 T, WTW, Germany) and a flow cell. Samples were not taken before constancy of the parameters was reached. Water samples for stable sulfur isotope analyses were immediately stabilized on site with Zn-acetate to prevent any re-oxidation of dissolved hydrogen sulfide.

At four locations each situated within a few cm distance of sampling wells P1, P3, P8, and P9 (Fig. 2) sediment samples were taken from two distinct depths (6.7 m and 7.3 m). Sediment samples were instantly transferred into gas-tight plastic bags that were thoroughly flushed with nitrogen gas before closing. The samples were stored at −20 °C until further handling.

2.3. Chemical and isotope analyses

Groundwater samples were filtered through a 0.45 μm membrane filter. BTEX concentrations were determined with a gas chromatograph (Perkin-Elmer, USA) equipped with a flame ionization detector.

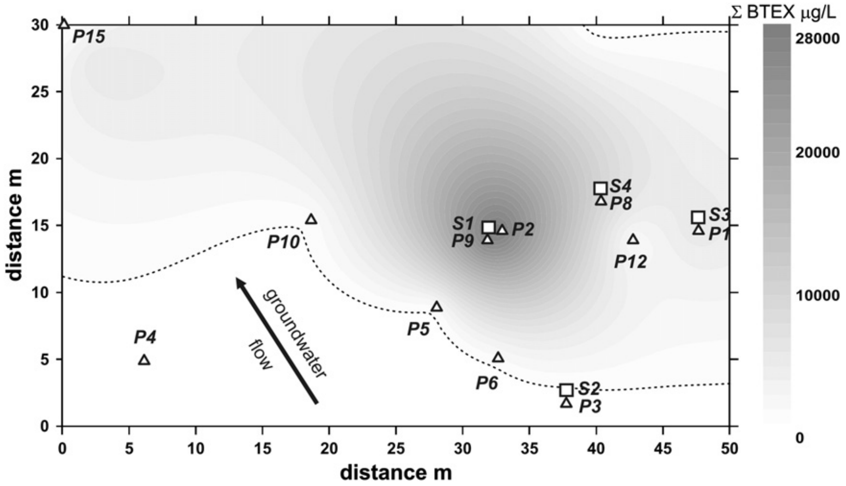

Fig. 2. Location of the groundwater sampling wells (triangles), of the sediment sampling locations (rectangles) and of the BTEX plume (modified after Schubert et al. (2007)).