Reactive transport modelling of groundwater chemistry in a chalk aquifer at the watershed scale

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ABSTRACT

This study investigates thermodynamics and kinetics of water–rock interactions in a carbonate aquifer at the watershed scale. A reactive transport model is applied to the unconfined chalk aquifer of the Champagne Mounts (France), by considering both the chalk matrix and the interconnected fracture network. Major element concentrations and main chemical parameters calculated in groundwater and their evolution along flow lines are in fair agreement with field data. A relative homogeneity of the aquifer baseline chemistry is rapidly reached in terms of pH, alkalinity and Ca concentration since calcite equilibrium is achieved over the first metres of the vadose zone. However, incongruent chalk dissolution slowly releases Ba, Mg and Sr in groundwater. Introducing dilution effect by rainwater infiltration and a local occurrence of dolomite improves the agreement between modelling and field data. The dissolution of illite and opal-CT, controlling K and SiO_2 concentrations in the model, can be approximately tackled by classical kinetic rate laws, but not the incongruent chalk dissolution. An apparent kinetic rate has therefore been fitted on field data by inverse modelling: $1.5 \times 10^{-5}\ mol_{chalk}\,L^{-1}_{water}\,year^{-1}$. Sensitivity analysis indicates that the CO_2 partial pressure of the unsaturated zone is a critical parameter for modelling the baseline chemistry over the whole chalk aquifer.

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1. Introduction

Chalk aquifers are important water resources in several European regions, specifically in Belgium, Great-Britain, France and Northern Germany (Brouyères et al., 2004; Ireson et al., 2009; Kloppman et al., 1998). The accurate determination of the baseline hydrochemistry at a watershed scale is a key point for their best water resources management, in particular for assessing any long-term or accidental contaminations. As a general trend the baseline hydrochemistry progressively evolves along a flow line, from the recharge areas, through the unsaturated zone, towards the deepest saturated zones of the aquifer. The main geochemical mechanisms are relatively well-known in chalk aquifers. They are primarily controlled by the infiltration of diluted water enriched in carbon dioxide and calcite equilibrium under open conditions in the vadose zone, and closed conditions in the saturated zone (Appelo and Postma, 2005). Since the kinetics of calcite dissolution is rapid, a relative homogeneity of the aquifer baseline chemistry is reached in terms of pH, alkalinity and Ca concentration (e.g. Edmunds et al., 1987; Kloppman et al., 1998; Moral et al., 2008).

A main objective of this paper is to quantitatively analyze the space and time distribution of the natural baseline chemistry of the chalk groundwater. Reactive transport models are more and more frequently applied to investigate the mechanisms involved in contaminant migration in aquifers, investigation that generally requires the modelling of the hydrochemistry of the pristine aquifer. This is not a trivial task due to the coupling between mass-transport processes and water-rock interactions. Firstly, the transport process follows a complex pattern induced by the dual porosity nature of chalk formations where a network of interconnected fractures crosses the porous carbonate matrix (Mathias et al., 2006; Price et al., 1993). Secondly, the incongruent dissolution of trace alkaline-earth elements trapped

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in calcite typically takes place in chalk aquifer systems (Edmunds et al., 1987, 1992; Elliot et al., 1999; Gillon et al., 2010; Kloppman et al., 1998; Schürch et al., 2004). This process has been evidenced from the evolution of Mg/Ca, Sr/Ca ratios as well as isotopic contents of Sr–C along the flow line. Such an incongruent contribution to the baseline water chemistry is known to increase with the residence time of groundwater in the aquifer (Edmunds et al., 1987). Furthermore, the very low rate of such incongruent processes cannot be determined in the laboratory. The issue of quantifying natural chemical weathering rates requires an inverse modelling approach applied to field systems. On the contrary, the dissolution of illite and opal-CT, controlling K and SiO_2 concentrations is tackled by classical kinetic rate laws in the present model.

Classical inverse calculations with transport have been done for estimating dolomite dissolution at field scale in limestone aquifer (e.g. Deike, 1990; Plummer et al., 1990), but not for calcite incongruent dissolution in chalk aquifers. Moreover, this approach cannot capture the full complexity of chemical reactions occurring in chalks, from both thermodynamic and kinetic points of view, as well as the present reactive transport model does. A geochemical model of the processes taking place along a flow line in a Spanish carbonate aquifer has been recently proposed by Moral et al. (2008), with emphasis on dolomite incongruent dissolution. Gillon et al. (2010) has proposed a thermodynamic model of the incongruent dissolution of impure calcite (Mg and Sr contents) in an unconfined chalk aquifer, the Champagne Mounts (Eastern France) that is also investigated in this study. The recent paper of Gillon et al. (2012) goes a step further by considering water flow along a given 1D line. Classical mass-balance calculations similar to Deike (1990) have allowed the authors to estimate effective rates for the chalk incongruent dissolution. Sensitivity analysis of such rates vs. flow velocity has been made.

Modelling studies that couple chemistry and transport in carbonated aquifers at the scale of a watershed are scarce. Especially, if one aims at extending the model to investigate contaminant migration. This paper attempts to such a simulation benefiting from a wide set of field data. The classical mass-balance approaches, quoted in the previous paragraph, cannot capture the full complexity of chemical reactions occurring in chalks, from both thermodynamic and kinetic points of view, as well as the present reactive transport model does. For instance there is neither modelling of 2D-profiles of chemical elements and pH (a key parameter for contaminant speciation and mobility), nor any explicit modelling of p_{CO2} differential effect between the unsaturated and saturated zones. In a step by step approach, the modelling study develops a two-dimensional (2D) reactive transport model applied to the unconfined chalk aquifer of the Champagne Mounts, by considering both the unsaturated zone (in a simplified manner) and the saturated zone in a dual porosity pattern as well as the inverse determination of incongruent dissolution rate of impure calcite with trace contents in Mg, Sr and Ba. Insights into the dissolution kinetic rates of illite, kaolinite and opal-CT embodied in the chalk are given. In a second stage, the paper addresses the additional contributions to the baseline water chemistry of local dolomite occurrence in the chalk deposit. A sensitivity analysis of the modelling results is also performed in terms of CO_2 partial pressure in the unsaturated zone from the one hand, and dilution by rainwater infiltration from the other hand.

2. Site description and sampling

2.1. Geological context

The study area is localized in the Champagne Mounts, at 20 km on the east of Reims (Marne, France) and covers approximately 160 km^2 between the river Suippe (northern boundary) and the river Prosne (southern boundary). Geological and hydrogeological description of the area can be found elsewhere (Bourdon et al., 2009; Gillon et al., 2010; Hubert et al., 2006; Renard and Jeannée, 2008).

The present study focuses on the upper unconfined aquifer, constituted by Santonian (C5) and Campanian (C6) chalks (Fig. 1). A lower, captive and confined aquifer, in Coniacian (C4) and Turonian (C3), is covered by the upper aquifer (Gillon et al., 2010). A highly unfractured and very poorly permeable level of C4c chalk prevents interactions between the two aquifers and is considered as the substratum of the upper aquifer (Gillon et al., 2010). Along the northern side, the Champagne chalk is overlaid by clay layers, from the Tertiary at the summit of the Mont Haut and colluviums, resulting from in situ weathering of chalk. Moreover, the first 10–20 m of the Champagne chalk below the topsoil are significantly fractured and can reach 10 fractures per meter. Fracturing of the Champagne chalk decreases with depth (Vachier et al., 1987); average fracture to fracture spacing is about 0.2 fracture per meter.

2.2. Hydrogeology, hydrochemistry and sampling

The Champagne chalk is characterized by a total porosity of 40% (Crampon et al., 1993), including about 1% vol. related to the fracture network (Vachier et al., 1987). The meteoric precipitations (700 mm per year in average) occur over the entire studied area and constitute the only aquifer recharge. Globally, groundwater flows along the two flow lines reported in Fig. 1, particularly in the Southern-East and in the Northern-East. Approximately 15% of the groundwater recharge takes place through fractures (Price et al., 1993). The hydraulic conductivity of the matrix, at water saturation, ranges between 10^{-9} and 10^{-7} ms^{-1}. The overall hydraulic conductivity of the Champagne chalk can reach 10^{-6} ms^{-1} due to the presence of fractures (Bourdon et al., 2009). The unsaturated zone has been measured up to a depth ranging from 10 to 115 m beneath the surface, the maximum thickness being found in the Champagne Mounts. The mean annual groundwater temperature is 12 °C.

Groundwater samples were collected in 24 monitoring wells from 2002 to 2007 by pumping after purge of the water column. The well screens were only opened to the saturated zone of the upper aquifer at known depths. Chalk levels and the associated sampled water at each borehole are available in the Supporting Information of Gillon et al. (2010). Globally, the composition of the groundwater is of Ca–HCO$_3$ water type with a circumneutral pH. Water collection were done twice a year, during respectively high and low water level, which could explain the significant variability of field data (Tables A and B, in Supporting Information). The pH was measured on-site in boreholes. In the figures of this paper, the data are plotted versus the distance of monitoring wells from the groundwater divide line without any reference to seasonal fluctuations.