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Quantifying chemical reactions by using mixing analysis

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HIGHLIGHTS

- Urban aquifer is infiltrated by a polluted river that is the main recharge source.
- Three end-members are necessary to explain the temporal variability of river water.
- Departures from ideal mixing line are attributed to chemical processes.
- Mixing calculations are used to quantify chemical processes in urban groundwater.
- The processes quantified are redox processes and carbonate dissolution.

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ABSTRACT

This work is motivated by a sound understanding of the chemical processes that affect the organic pollutants in an urban aquifer. We propose an approach to quantify such processes using mixing calculations. The methodology consists of the following steps: (1) identification of the recharge sources (end-members) and selection of the species (conservative and non-conservative) to be used, (2) identification of the chemical processes and (3) evaluation of mixing ratios including the chemical processes. This methodology has been applied in the Besòs River Delta (NE Barcelona, Spain), where the River Besòs is the main aquifer recharge source. A total number of 51 groundwater samples were collected from July 2007 to May 2010 during four field campaigns. Three river end-members were necessary to explain the temporal variability of the River Besòs: one river end-member is from the wet periods (W1) and two are from dry periods (D1 and D2). This methodology has proved to be useful not only to compute the mixing ratios but also to quantify processes such as calcite and magnesite dissolution, aerobic respiration and denitrification undergone at each observation point.

1. Introduction

Ensuring good water quality is a major challenge in urban areas. Urban aquifers may suffer pollution from recharge sources such as water leakage from sewer and septic systems, seepage from rivers, seawater intrusion, and losses from water supply network etc. As a result, a wide range of organic pollutants are found in urban aquifers. Since these pollutants reach groundwater environment, their occurrence depends on simultaneous transport and biogeochemical processes. For a quantitative assessment of groundwater quality a sound understanding of all these processes affecting these pollutants is essential. However, the quantification of these processes is not an easy task.

In order to quantify such processes, modelling tools that provide extensive biogeochemical capabilities are necessary (Prommer et al., 2000). Reactive transport models quantify the spatial and temporal evolution of a number of chemical species subjected to transport phenomena and chemical reactions. Numerous codes have been developed in recent years. They have been applied to problems such as leachate attenuation (Islam et al., 2001; Van Breukelen et al., 2004), pollution plumes (Brun et al., 2002), microbially mediated reactions (Schäfer et al., 1998a,b; Hunter et al., 1998; Tebes-Stevens et al., 1999; Wang and Papenguth, 2001), carbon cycle modelling cases (Greskowiak et al., 2005) and the quantification of redox processes in aquifers (Keating and Bahr, 1998; McGuire et al., 2002; Massmann et al., 2004; Miotlinski, 2008) and in the hyporheic zone (Miller et al., 2006; Zarnetske et al., 2011). However, simpler approaches are required since these techniques are tedious and time consuming because of the need for a reliable flow and conservative transport models.

Mixing calculations constitute an alternative to reactive transport models. Mixing calculations typically involved: (1) End-Member Mixing Analysis (EMMA) (Hooper et al., 1990; Hooper, 2003) to find the minimum number of end-members required to explain a set of chemical analyses, and (2) mixing ratios defined as the proportion of

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mixing waters in a sample (Schemel et al., 2006). Mixing ratios are useful because they can be quantified using conservative species even when the end-members are uncertain (Carrera et al., 2004; Rueedi et al., 2005). Their application is easier than that used for transport modelling because only chemical data and a previous conceptual model of the study zone are needed. Mixing calculations are advantageous in a number of hydrogeological tasks such as groundwater recharge sources in urban environments (Rueedi et al., 2007; Houhou et al., 2010; Vázquez-Suñé et al., 2010; Jurado et al., 2013; Tubau et al., 2014) or the interaction between groundwater and surface water bodies (Plummer et al., 1998; Beyerle et al., 1999; Crandall et al., 1999; Lambs, 2003; Petitta et al., 2010; Cánovas et al., 2012a,b) and hydrograph separation (Subagyono et al., 2005; Ladouche et al., 2001). However, mixing calculations do not shed much light on hydrogeochemical reactions.

The concentration of conservative solutes in a mixture is obtained by linear combination of the end-members (Fig. 1). Assuming two conservative species C_1 and C_2, the concentrations of these species are a linear combination of the end-members (EM1 and EM2) with weights given by the mixing ratios (δ). However, if species C_1 is not conservative there is a departure from the ideal mixing line that can be attributed to chemical processes (Fig. 1). This concept has often been the subject of speculation (Pitkänen et al., 1999; Laaksoharju et al., 1999; Balistrieri et al., 2003; Morell et al., 2008; Barros et al., 2008; Panagopoulos, 2009; Tubau et al., 2014), but never formalised. As an example, Fig. 2 shows the average concentrations at the River Besòs versus the average concentrations in the aquifer for major and minor ion, metals, pesticides, drugs of abuse (DAs, Jurado et al., 2012) and pharmaceutical active compounds (PhACs, López-Serna et al., 2013; Jurado et al., 2014). It can be observed that some species (redox indicators and some organic compounds) have higher concentrations in the River Besòs than in the aquifer, suggesting that chemical processes can occur when river water infiltrates the aquifer.

In summary, mixing models have been widely used in all branches of hydrology but they have never been used to quantify chemical reactions. The aim of this work is to present an approach to quantify chemical processes using mixing calculations. This methodology is applied in the Besòs River Delta aquifers in Barcelona, Spain. It is assumed that the composition of the observation points is the sum of river water mixing (conservative) and groundwater–aquifer interactions (non-conservative). The evaluation involves the identification of the recharge sources and the identification and quantification of the chemical processes undergone at each observation point.

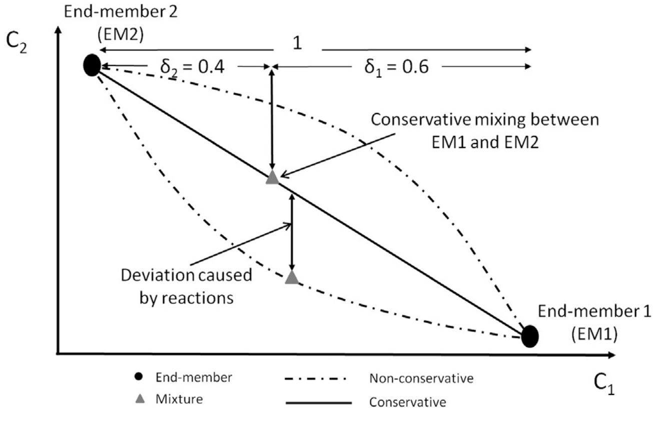

Fig. 1. Plot of species C_1 over species C_2 considering two end-members. Note that the concentration of the conservative solutes in a mixture is obtained by the linear combination of the end-members depicted by the black straight line (conservative mixing), but deviations from mixed solutions should they exist may be due to chemical processes.

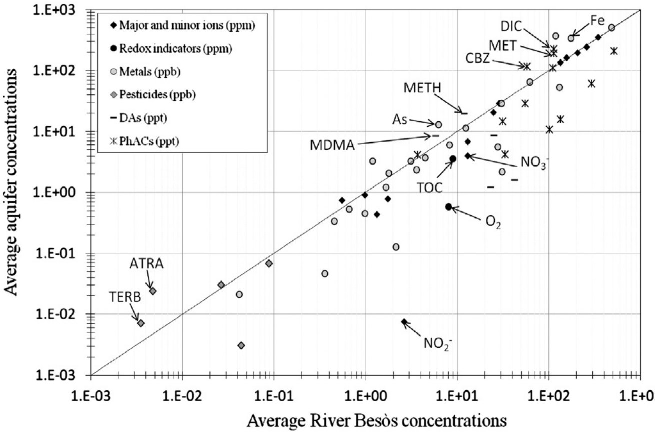

Fig. 2. Average concentrations in the River Besòs and in the aquifer for major and minor ion, metals, redox indicators, pesticides, drugs of abuse (DAs, Jurado et al., 2012) and pharmaceutical active compounds (PhACs, López-Serna et al., 2013; Jurado et al., 2014).

2. Materials and methods

2.1. Site description

The study area is located in NE Barcelona, at Sant Adrià del Besòs in the Besòs River Delta, and has an extension of 0.16 km^2. The area is bounded by the River Besòs and it is close to the underground car park at Plaça de la Vila (Fig. 3).

The geology of the River Besòs catchment was carried out by MOP (1966). It was updated by Velasco et al. (2012) using new information obtained from civil work projects performed in the delta area. It is a small asymmetric delta that occupies an area of 17.4 km^2 (Riba and Colombo, 2009). From the geological point of view, the study area is placed in the Quaternarian Besòs Delta. The aquifers are constituted by Quaternary sediments that rest unconformably over a basement formed by Paleozoic and Cenozoic rocks. The Palaeozoic lithology consists mainly of slates and granites. The Cenozoic rocks are mostly made up of Miocene matrix-rich gravels and sandstones as well as massive grey marls from the Pliocene. On top of this basement are the fluvio-deltaic sediments of the Besòs Delta River that make up two superposed aquifer layers that constitute two aquifers: (1) the shallow aquifer, is an unconfined aquifer made up of siliceous sands and carbonate gravels (limestones and dolomites) (2) the main aquifer, formed of siliceous and carbonate sands (siliceous sands dominate over the carbonate ones). These aquifers are separated by an aquitard made up of clays and silts (Fig. 4).

The hydrology of the Besòs River Delta aquifers is highly dependent on the River Besòs flow regime. The River Besòs presents a typical Mediterranean hydrogeological pattern characterised by the rainfall variability. These events vary within the year and from one year to another. Average streamflow is 4 m^3/s at the Santa Coloma gauging station (located 2.5 km upstream from Plaça de la Vila site), which is part of the Catalan Water Agency (ACA). The streamflow reached values of up to 30 m^3/s in rainy periods and it exceeded 100 m^3/s in strong events. Generally, in summer the River Besòs flow rate is caused exclusively by the WWTP effluents worsening the river water quality. In the study area, river water is a mixture of raw and treated sewage water, rainfall, waters from other part of the catchment, etc.

The river is hydraulically connected to the shallow aquifer at the Delta. Most of the groundwater extracted between the river and the parking area is recharged from the river (Ondiviela et al., 2005). Groundwater flows from the River Besòs to the car park because of the continuous pumping of about 150 L/s to avoid seepage problems (Fig. 3). This aquifer–river system is very dynamic due to short