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Research papers

Recharge processes and vertical transfer investigated through long-term monitoring of dissolved gases in shallow groundwater

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We investigated temporal variations and vertical evolution of dissolved gaseous tracers (CFC-11, CFC-12, SF_6, and noble gases), as well as $^3H/^3He$ ratio to determine groundwater recharge processes of a shallow unconfined, hard-rock aquifer in an agricultural catchment. We sampled dissolved gas concentration at 4 locations along the hillslope of a small experimental watershed, over 6 hydrological years, between 2 and 6 times per years, for a total of 20 field campaigns. We collected groundwater samples in the fluctuation zone and the permanently saturated zone using piezometers from 5 to 20 m deep. The purpose of this work is *i*) to assess the benefits of using gaseous tracers like CFCs and SF6 to study very young groundwater with flows suspected to be heterogeneous and variable in time, *ii*) to characterize the processes that control dissolved gas concentrations in groundwater during the recharge of the aquifer, and *iii*) to understand the evolution of recharge flow processes by repeated measurement campaigns, taking advantage of a long monitoring in a site devoted to recharge processes investigation.

Gas tracer profiles are compared at different location of the catchment and for different hydrologic conditions. In addition, we compare results from CFCs and $^3H/^3He$ analysis to define the flow model that best explains tracer concentrations. Then we discuss the influence of recharge events on tracer concentrations and residence time and propose a temporal evolution of residence times for the unsaturated zone and the permanently saturated zone. These results are used to gain a better understanding of the conceptual model of the catchment and flow processes especially during recharge events.

1. Introduction

As nitrates have become a major environmental threat in agricultural areas, numerous works evaluate mechanisms controlling NO_3^- exportation from catchment and emphasize the key role of the shallow groundwater (Böhlke and Denver, 1995; Creed and Band, 1998; Martin et al., 2006; Molenat et al., 2002). In particular, these studies show that catchment can present an important time lag in response to variation of the NO_3^- input signal. Although physical characteristics of shallow groundwater are pointed out to explain this delay, mechanisms involved are still debated. A better knowledge of this time lag, through the evaluation of the residence time of groundwater is thus crucial for managing groundwater in small agricultural catchments.

Recent results obtained using natural solutes and/or their isotopic composition as tracers, pointed out that small catchments show variable residence times that can surprisingly exceed several years (Hrachowitz et al., 2013; Kendall and McDonnell, 1998; Kirchner et al., 2001; Ruiz et al., 2002a). These methods were based on opposite trends observed between the nitrate concentrations in drainage water and in stream water (Ruiz et al., 2002a) or on spectral analysis of the input–output signal of chemical compound (Kirchner et al., 2001; Molénat et al., 2000; Neal and Kirchner, 2000) that require a high frequency monitoring of rain inputs for a long period which is rarely available.

Another approach to estimate response time to changes in agricultural practices consists in numerical modelling. Again, transit times greater than one year and up to 14 years in headwater catchments have been derived from mechanistic groundwater modelling (Basu et al., 2012; Martin et al., 2006; Molénat and Gascuel-Odoux, 2002) or lumped and parsimonious model and time series of nitrate concentration in streams (Fovet et al., 2015; Ruiz et al., 2002b). All these approaches use the approximation of Dupuit-Forsheimer which reproduces the water dynamic of the catchment, but assume a perfect and instantaneous vertical mixing

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of groundwater neglecting vertical flows. In addition, in numerous models, individual storm events are neglected and only base flow is considered (Fovet et al., 2015; Ruiz et al., 2002b). Although these models reproduce seasonal and inter-annual nitrate variations, processes inducing temporal concentration variations at shallow depth are still poorly understood, especially after storm events.

An interesting alternative to obtain additional information on water dynamics is to analyze anthropogenic atmospheric gases. Industrial production of CFCs and SF_6 started in the 1940s and 1960s respectively which makes these dating tracers suitable for the study of post-war diffuse pollution in agricultural catchments (IAEA, 2006). However, following Montreal protocol in 1987, stagnation and then decrease of atmospheric CFCs concentrations over the past two decades have induced higher uncertainties in dating of young shallow groundwater since two different recharge dates can be derived from a single gas concentration (rising or falling part of the atmospheric curve (CMDL/NOAA)). Therefore, the combined use of other dating tracers like SF_6 (whose input atmospheric function is always rising) and $^3H/^3He$ (a radioactive parent/daughter clock method which does not require the knowledge of the ^3H input function) allows reducing uncertainties (Darling et al., 2012; Newman et al., 2010; Suckow, 2014). Another advantage of the anthropogenic gas tracers is to help conceptualizing flow and mixing processes of the studied groundwater system (Darling et al., 2012; Suckow, 2014). It is common to use lumped parameter models which fit the data to a conceptual model of defined flow, among which the most commonly used are piston (PFM), binary mixing (BMM) or exponential mixing (EM) (Maloszewski and Zuber, 1982). While each different tracer will give an apparent tracer age, stating the model used to interpret tracers concentrations will allow defining a Mean Residence Time (MRT) corresponding to the weighted average of the age distribution (Suckow, 2014).

Numerous authors used CFCs and SF_6 to obtain a better understanding of pollutant-transfer processes and to predict the most likely evolution of groundwater quality with respect to diffuse agricultural pollution (Böhlke, 2002; Gooddy et al., 2006; Katz et al., 2001; Koh et al., 2006). Gooddy et al. (2006) used the comparison of the spatial distribution of different tracers and lumped parameter models to discriminate groundwater flow regimes in different parts of the aquifer and thus improved their conceptual model. Kolbe et al. (2016) coupled groundwater modelling with CFC age dating to classify local groundwater circulation in an unconfined aquifer. Recent studies in hard-rock aquifers in Brittany provided a potential regional distribution of residence times as well as a reconstruction of NO_3^- concentration in recharge water (Aquilina et al., 2012; Ayraud et al., 2008).

Temporal variability of residence time in the first meters of the aquifer usually receives less attention though being essential to further assess recharge processes in the critical zone. For instance, few studies focus on vertical variation of CFCs in shallow groundwater although it is a key parameter to constraint solute transfer from soil to the water table and within the aquifer (Cook et al., 1996, 1995; Le Gal La Salle et al., 2012). Moreover, no study to date investigates the temporal variability of dissolved CFCs and SF_6 concentrations at a single location over several hydrologic cycles nor how robust is the conceptual model over time. Such information can be used to evaluate how residence time changes with varying recharge conditions.

In this context, the scope of this paper is *i*) to assess the benefits of using gaseous tracers like CFCs and SF6 to study very young groundwater with flows suspected to be heterogeneous and variable in time, *ii*) to characterize the processes that control dissolved gas concentrations in groundwater during the recharge of the aquifer, and *iii*) to understand the evolution of recharge flow processes by repeated measurement campaigns, taking advantage of a long monitoring in a site devoted to recharge processes investigation (Legout et al., 2005; Rouxel et al., 2011).

To address these issues, we focus on a shallow unconfined aquifer in a small experimental catchment in Brittany (West of France) where flow processes and nitrate dynamic have been extensively studied giving a strong knowledge on water quality (Martin et al., 2006, 2004; Rouxel et al., 2011; Ruiz et al., 2002b). We investigate dissolved CFCs and SF_6 gases concentrations during 6 hydrological cycles at different depths ranging from 4 to 20 m below ground level. Gas tracer profiles are compared at different locations of the catchment and for different hydrologic conditions. We compare CFCs and $^3H/^3He$ apparent ages and discuss flow model that best explains tracer concentrations and origin of apparent age discrepancies between age dating tracers. Then we discuss the influence of recharge events on tracer concentrations and residence time and propose a temporal evolution of residence times for the unsaturated zone and the permanent groundwater of the catchment. These results are used to gain a better understanding of the conceptual model of the catchment and flow processes especially during recharge events.

The originality of this work is thus *i*) to use a detailed analysis of long-term time-series of dissolved gas tracers (CFC-11, CFC-12, SF_6 as well as recharge temperature and excess air deduced from noble gases concentrations); *ii*) to investigate their temporal evolution in vertical profiles ranging from 0 to 20 m below ground level.

2. Methods

2.1. Site description

Kerrien site is a small experimental catchment (0.095 km^2) located closed to the sea in an intensive agricultural area southwest of Brittany, France (Fig. 1). This site is part of the French observatory network RBV (http://rnbv.ipgp.fr/) and belongs to the Environmental Research Observatory AgrHys (http://www6.inra.fr/ore_agrhys_eng/) devoted to studies of response times of hydro-chemical fluxes under changing agriculture.

The study site is representative of hard rock catchments. It has been previously described by Martin et al. (2004). The fissured and fractured granitic bedrock is overlain by a regolith of an estimated average thickness of 20 m (Martin et al., 2004). The regolith constitutes the main unconfined, shallow aquifer, with a hydraulic conductivity ranging from 9.10^{-6} to $5.10^{-4} m \cdot s^{-1}$ and a total porosity of 0.4% (Rouxel et al., 2012). The hillslope of the catchment shows a topographic gradient varying from 14% upslope to 5% downslope. Groundwater table roughly follows the topographic slope. It comes up to the ground level downslope while upslope, a zone of about 2 m thickness remains permanently unsaturated. The surface runoff is negligible on the hillslopes and the shallow groundwater provides most of the stream flow with a base flow index about 90% (Ruiz et al., 2002b). Groundwater table level displays large seasonal fluctuations ranging from less than one meter downslope to 4 to 6 m upslope.

The climate is oceanic. Mean annual rainfall for the period 2003–2010 was 1033 ± 186 mm, slightly lower than the mean annual rainfall of 1185 mm over the decade 1992–2002 (Molenat et al., 2008). The interannual variability is large with rainfall in 2005 (616 mm) being half of rainfall in 2010 (1220 mm). Mean annual PET is less variable with a mean annual value of 704 ± 19 mm. The average maximum and minimum monthly rainfall occurs in November and September (143 mm and 47 mm respectively). Recharge period extends from November to March but it can vary slightly depending on the yearly rainfall pattern.

Groundwater chemical composition has been extensively studied since the early 1990s in this site (Martin et al., 2004;