Dissolved gases in groundwater and groundwater dating methods: How useful for hydrogeological modeling? – Foreword to the special issue

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Introduction

One of the major challenges in hydrogeology is the basic spatial lack of continuous data as this is restricted to available boreholes. Basic information is provided by the measurements of physical parameters (e.g. porosity and permeability) at the well-scale. Information related to a larger part of the aquifer are provided for example, by continuous measurement of piezometric levels or spring flow. Temporal information is extremely powerful in order to characterize aquifer functioning globally. Groundwater dating has thus been developed in order to provide time-constraints in aquifer studies.

For young groundwater (< 50 yrs) tritium measurements were used following nuclear tests during the 1950s and 1960s. Tritium accumulated in the atmosphere and so provided a useful environmental tracer for water originating from this era. Although several monitoring networks from International Atomic Energy Agency provide precise records, seasonal and spatial variations in the tritium precipitation content limit the precision of groundwater dating using this method. Furthermore, tritium levels have decreased gradually and now precipitation concentrations are close to natural background. Groundwater dating using chlorofluorocarbons (CFCs) and more recently sulfur hexafluoride (SF_6) were also widely developed during the last decades (Busenberg and Plummer, 1992; Busenberg and Plummer, 2000; Cook et al., 1995). CFC concentrations have been rapidly increasing in the atmosphere during the second half of the 20th century and their input history is well known with limited spatial variations. Compared with other groundwater dating techniques, CFCs can be rapidly determined, they require no sophisticated sampling equipment and analysis is relatively

simple (Gooddy et al., 2006). Consequently, for more than a decade, a number of laboratories have routinely analyzed groundwaters for these compounds. However, several processes such as contamination, degradation and sorption may modify the CFC concentrations in the soils and aquifers so restricting their use as potential tracers. Furthermore, the prohibition of CFCs by the Montreal protocol (1987) has led to a slow decline of their atmospheric concentrations. This decline increases the uncertainty of their use for modern groundwater. SF_6 is not subject to the Montreal protocol and its continued release from industrial processes has led to a rapid increase in atmospheric concentrations. Although it has even lower concentrations than the CFCs, it is now analyzed by several laboratories. The interest in SF_6 has been limited by potential rock production (Friedrich et al., 2013). ^{85}Kr has also been used as a potential tracer with similar characteristics to CFC although not prone to their associated problems (Cook and Solomon, 1997; Lehmann et al., 1991). The development of new tracers such as ^{39}Ar, ^{81}Kr, (Loosli et al., 1999; Edmunds et al., 2014), SF_5CF_3 and CFC-13 (Busenberg and Plummer, 2008) continues. In recent years and following on from tritium measurements, the tritium-helium ($^3H/^3He$) method has also been used (Solomon et al., 1993). It is based on the measurement of the ^3He produced from the radioactive decay of tritium contained in groundwater. Although it is often preferred to CFCs by hydrogeologist, it implies the precise determination of the atmospheric, terrigenic and mantle-derived helium contributions which might be challenging (Poreda et al., 1988; Schlosser et al., 1988).

Groundwater dating has been used in various type of sub-surface environment, although heterogeneous aquifers such as karstic or fractured aquifers have been less intensively investigated (Ayraud et al., 2008). In young groundwater systems, a combination of groundwater dating techniques has been helpful to investigate important environmental issues such as sources, fate and transport of contaminants, and groundwater surface water interactions for resource management.

"Old" groundwaters can be more problematic (Philips and Castro, 2003). First, there are fewer tools that have the capability to date these groundwater and each tracer has a relatively narrow residence-time range. Second, deep and ancient fluids represent highly complex mixtures including water transported by advection and solutes provided from the rock matrix through dissolution and diffusion processes (Aquilina et al., 2011). In addition very old groundwater may also mix with various amounts of modern groundwater, sometimes through the process of sampling, leading to wide ranges of groundwater residence-times in a single sample (Corcho Alvarado et al., 2007). Carbon-14 has been used for decades but water-rock

interactions with carbonate rocks can make it difficult to interpret. Chlorine-36, radiogenic helium and ^{81}Kr have also been used to investigate groundwater in the range of 10^3 to 10^6 years (Marine, 1979) although the use of an appropriate technique often requires an *a priori* knowledge of the groundwater age.

Beside groundwater dating advancements, the integration of groundwater "ages" in hydrogeological modeling has been developing in parallel. Modeling has prompted some questioning as to the meaning of groundwater dating. Although the concept of "age" appears straightforward and very meaningful to end users, it requires assumptions about hydrogeological functioning. Indeed, the "age" determined from the atmospheric concentration deduced from the groundwater concentration represents a "piston-flow" residence-time. Piston flow is however a highly unlikely model of aquifer functioning. The use of lumped models in order to interpret tracer concentrations has become widely used (Clark and Fritz, 1997). This is a first raw interpretation of tracer concentrations and provides a framework to establish a groundwater flow model. However, mixing at various scales may require much more complex models (Leray et al., 2013). There is still research needed to analyze the relationships between the distribution of tracers in aquifers and the hydrogeological parameters.

As groundwater dating remains an important issue for hydrogeological sciences, two recent workshops have been devoted to groundwater dating (Osenbrück et al., 2010). The second of these was organized in Rennes, western France (October 15-17, 2012). Before the G-DAT meeting, an inter-laboratory comparison exercise was organized. Dissolved gases analyses represent technical difficulties as they require extremely low analytical thresholds. Detailed sampling protocols have been published (IAEA, 2006, 2011; Busenberg and Plummer, 1992, 2000). The International Atomic Energy Agency (IAEA) regularly organizes inter-laboratory comparison of the analytical technics ("TRIC", Gröning et al., 2009). However, different laboratories use various methods for sampling which may induce significant uncertainties between analyses. The aim of the 2012 G-DAT inter-comparison exercise was thus to compare the sampling and analytical protocols from various laboratories.

The inter-comparison exercise was designed by a scientific committee. The idea was to first use a rather simple and homogeneous aquifer and secondly a more complex and heterogeneous one. The first sampling exercise (February 2012) took place in the Fontainebleau Miocene sand aquifer and Dogger limestone deep aquifer. Directly following the G-DAT meeting (October 2012) the second sampling exercise was carried out in a

fractured aquifer (Ayraud et al., 2006). In both cases, a surface shallow aquifer and a deeper aquifer were sampled. Special attention was given to ensure the homogeneity of the groundwater sampled by all of the teams.

The G-DAT meeting was an opportunity to present the results of the inter-comparison exercise on one side and to bring together geochemists and modelers. This special issue "Dissolved gases in groundwater and groundwater dating methods: how useful for hydrogeological modeling?" reflects this meeting between geochemists and modelers as there are three subsections in the special issue. The first section is devoted to the inter-comparison exercise. It includes both the results of the noble gas and tritium inter-comparison (Visser et al., this issue) and those of the CFC and SF_6 inter-comparison (Labasque et al., this issue). A paper presenting the inter-comparison design and the site choice which have been the subject of discussions has been presented previously (Labasque et al., 2014). The second section is devoted to contemporary application of groundwater dating methods. It includes multi tracer studies in Austria (Kralik et al., 2014) and Italy (Mayer et al., 2014), and papers investigating pesticide transport (Akesson et al., 2014), helium fluxes (Mahara et al., 2014) as well as karstic systems (Delbart et al., 2014). The third section is devoted to the integration of groundwater dating data in hydrogeologic models in order to investigate the physical meaning of residence time/age concepts. It includes a paper advocating that the term “groundwater age” is misleading (Suckow, 2014), two papers illustrating the use of Bayesian modeling (Massoudieh et al., 2014a,b) and two papers devoted to ^{36}Cl use in paleoclimate studies (Petersen et al., 2014; Rebeix et al., 2014).

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