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Extended Abstracts

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title: **Evaluation of environmental tracer data to estimate the transit time of water under saturated conditions**

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INTRODUCTION

Many problems in hydrogeology require some understanding of the timescales of groundwater flow and contaminant transport. Over the past five decades, a powerful suite of environmental isotope and tracer methods has been developed to address the question of groundwater residence time on a wide range of timescales (Fig. 1).
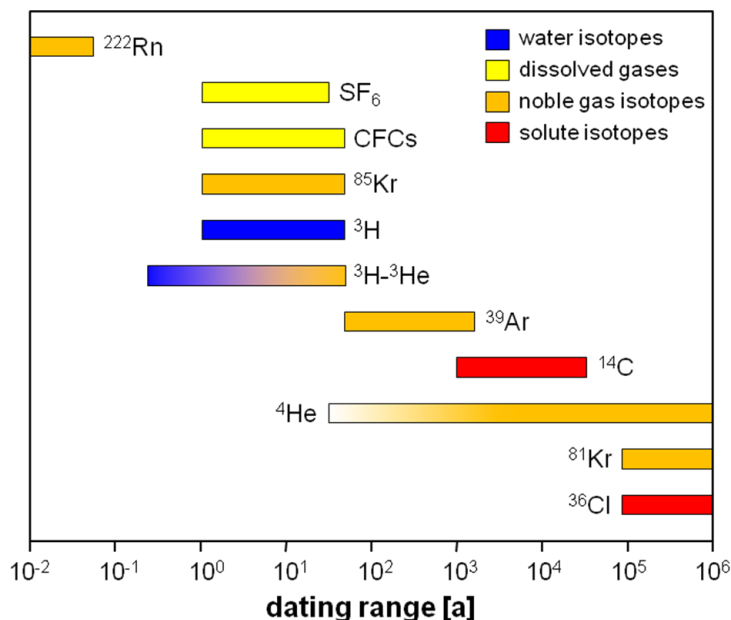
Figure 1. Overview of environmental tracer methods and their dating ranges.

A short review of these methods is provided here, covering their strengths and weaknesses, examples of their applications, and ways to evaluate and interpret the resulting data sets – often comprising multiple tracers. More detailed reviews and various case studies can be found in two special issues on environmental tracer and dating methods in hydrogeology, which are due to appear soon in Hydrogeology Journal and Isotopes in Environmental and Health Studies. Another great resource was provided a decade ago by Cook and Herczeg (2000).

One goal of these publications is to raise awareness of the potential and requirements of environmental tracer methods, as despite their successful use in many research studies, they remain underutilized in practical applications in groundwater management. As groundwater models are often calibrated only by hydraulic data, despite the well-known shortcomings of this approach, it is important to note that tracer dating provides valuable independent constraints, even though the dating methods also have limitations.

The available dating methods together cover a time range from days (^{222}Rn) to millions of years (^{81}Kr, ^{36}Cl, Fig. 1). However, the coverage of this age range is uneven. Several methods (so-called transient tracers — ^{3}H, CFCs, SF$_6$, ^{85}Kr) are based on the anthropogenic release of compounds and radioisotopes to the environment over the past five decades, leading to a time-dependent input into groundwater. Therefore, this young age range is well covered. On the longer time scales, methods based simply on the radioactive decay of solute isotopes (^{14}C, ^{36}Cl, ^{39}Ar, ^{81}Kr)

are available. However, while the complex geochemistry of the elements C and Cl can substantially complicate the respective methods, the use of the more ideally behaving noble gas radioisotopes is hampered by the difficulty of their analysis. The accumulation of the stable isotope ^{4}He is an alternative tool in the range of high ages and potentially also for the younger range, but the He accumulation is rarely known sufficiently well to provide quantitative age information. Finally, the ^{3}H-^{3}He method, combining the decay of the water-bound ^{3}H with the accumulation of the stable noble gas isotope ^{3}He, is a powerful tool but also limited essentially to the period since the tritium bomb-peak in the 1960s.

As the young age range (up to 50 years) is of particular importance in many applications related to groundwater quality and abstraction, the present contribution will focus on this range in the following. The wide choice of methods in this range enables multi-tracer studies and a comparison of the different methods.

DISCUSSION OF SELECTED METHODS AND THEIR APPLICATIONS

Tritium is the classical dating tool in hydrology, but it has lost much of the power it had in the decades after the bomb peak, as concentrations in precipitation have returned almost to natural levels. Quantitative dating based only on tritium is hardly possible, but a distinction of pre-bomb and post-bomb water is still very effectively possible. More promising than ^{3}H alone is its combination with ^{3}He. The ^{3}H-^{3}He method has proven to be particularly reliable and has in many case studies been used to compare with other methods and to detect effects influencing CFCs or SF_6 (e.g., Horneman et al. 2008; von Rohden et al., 2010a). The biggest disadvantage of the ^{3}H-^{3}He method is probably that it requires a rather large experimental effort.

The transient trace gases CFCs and SF_6 are cheaper and easier to apply than the ^{3}H-^{3}He method. Another advantage of the CFCs is that several compounds are available, which can compensate for the fact that some of them may be affected by contamination or degradation. As the atmospheric concentrations of the CFCs have leveled off since the 1990s (due to the ban of these ozone-destroying compounds), SF_6 has gained increased attention. However, it is becoming increasingly clear that SF_6 excesses of natural, terrigenic origin, are quite wide-spread, occurring not only in crystalline or volcanic rocks and hydrothermal environments (Busenberg and Plummer, 2000; Koh et al., 2007), but also in sedimentary aquifers (Deeds et al., 2008; von Rohden et al., 2010a). Therefore, recent proposals for new tracers such as SF_5CF_3 and CFC-13 (Busenberg and Plummer, 2008) are very welcome.

Despite some problems mentioned above, successful applications of the established dating tracers abound. ^{3}H-^{3}He ages have been used to determine groundwater flow velocities both horizontally and vertically. Vertical ^{3}H-^{3}He age profiles enable the determination of recharge rates (e.g. Solomon et al. 1993; von Rohden et al., 2010b). Horizontal transects of ^{3}H-^{3}He ages have been used to study river infiltration (Stute et al. 1997) or to provide a time-scale for the propagation of contaminant plumes (Shapiro et al. 1999). Another important application of the method is to provide chronologies of past environmental change, in particular histories of groundwater contamination including the retrospective proof that trend reversals have taken place (e.g., Aeschbach-Hertig et al. 1998; Tesoriero et al., 2007; Visser et al., 2007a). Another straightforward use of age information obtained by ^{3}H-^{3}He dating is the determination of the rates of chemical processes such as oxygen depletion (Beyerle et al., 1999) or denitrification (Singleton et al., 2007).

Applications of CFCs include among many other topics the study of water exchange between groundwater and lakes or rivers (e.g., Katz et al. 1995; Modica et al., 1998). Detailed vertical CFC profiles were used to assess vertical recharge velocities in a shallow sandy aquifer (Cook et al., 1995) as well as to study groundwater flow in fractured rock (Cook et al., 2005). As other dating tools, the CFCs were also used to reconstruct histories of contamination, e.g. by nitrate in agricultural watersheds (Böhlke and Denver, 1995).

DATA EVALUATION: EFFECTS TO CONSIDER

Many dating methods for groundwater are based on gas tracers, which inescapably are affected by gas/water partitioning in the subsurface. Interaction with a gas phase leads to excesses or deficits of dissolved gas concentrations relative to atmospheric solubility equilibrium, referred to as excess air or degassing. Excess air has long been recognized and various models accounting for the effect of air entrapment on dissolved gas concentrations have been proposed and applied (Aeschbach-Hertig et al., 2000). Atmospheric noble gases can be used to constrain excess air and its composition by fitting the different models to the data (Aeschbach-Hertig et al., 1999).

In contrast to excess air, the phenomenon of degassing has only recently received more attention. In particular, it has been encountered in studies of contaminated or naturally anoxic aquifers, where it occurs as a result of biogeochemical gas production in the subsurface (e.g., Visser et al., 2007b). The equations of the closed-system equilibration (CE) model, which has been quite successful in describing excess air, can also describe the case of equilibrium degassing (Aeschbach-Hertig et al., 2008). The feasibility of modeling the effects of degassing on conservative gases suggests that reasonable dating is possible even in cases of considerable degassing.

Many transient tracer methods used for dating young groundwater are affected by "contamination", i.e., the presence of tracer components in addition to the expected atmospheric sources. Such excesses can have a variety of causes, even natural ones as mentioned above for SF_6. Thus, the term contamination may not always seem appropriate, but dating is hampered irrespective of the origin of the excess. Contamination in the strict sense is commonly associated with waste disposal or industrial effluents. Such contamination is most prominent for the CFCs. Apart from leakage from landfills, sewer lines, underground storage tanks, and disposal of industrial wastes, another source of contaminated recharge can be rivers (IAEA, 2006). A further complication for CFC dating is degradation in anaerobic environments, which has frequently been observed (IAEA, 2006). Finally, sorption may affect CFC transport, but this process has received comparatively little attention.

With regard to the complicating effects of excess air, degassing, contamination, degradation, and sorption, the noble gas radioisotopes ^{39}Ar, ^{85}Kr, and ^{81}Kr are exceptionally robust among the gas tracers. Groundwater dating with these isotopes is not affected by gas/water partitioning, as only the ratio of the radioisotope to a stable isotope of the respective noble gas is required for dating. Degradation, sorption, and contamination appear highly unlikely for these inert gases. Particularly useful among these radioisotopes is ^{39}Ar, because it is uniquely able to close the gap in the dating ranges between about 50 and 1000 years (see Fig. 1). The applicability of the noble gas radioisotopes is currently limited by the requirement of very large samples and sophisticated analytical methods due to their extremely low abundance. A new analytical technique (ATTA: Atom trap trace analysis) has recently been demonstrated for the case of ^{81}Kr (Sturchio

et al., 2004). Progress is currently being made towards implementing ATTA also for [39]Ar (Welte et al., 2009).

The best practical way to deal with the various effects that may disturb the different groundwater dating tools is to combine several methods in multi-tracer studies. Such combinations enable the identification of problems affecting the single methods. Moreover, attempts can be made to consistently interpret the multi-tracer data sets in terms of mixing and transport models. The most direct approach is to estimate parameters of lumped-parameter models by optimizing the fit of modeled and measured tracer concentrations (Corcho Alvarado et al., 2005; 2007). A more sophisticated approach includes distributed-parameter models, whose spatially variable parameters are constrained by the requirement of consistency with the tracer data. The combination of environmental tracers with numerical groundwater flow and transport models clearly is the way to go to extract the maximum benefit from tracer studies. This approach has been demonstrated successfully for almost two decades (e.g., Reilly et al., 1994; Sheets et al., 1998; Mattle et al., 2001), but it still is not used as often as it would seem appropriate.

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