

# Physical and Chemical Tracers in the Environment

Yazeed van Wyk and Dr Eunice Ubomba-Jaswa

## 1. Introduction

Environmental tracers are physical properties and chemical components of water whose spatiotemporal differentiation is used to infer information on the flow paths and dynamics of water and contaminant movement through the environment (Käss, 1998). In general, a tracer is a substance that is experimentally measured in a given system of interest for the purpose of deducing process information from the tracer signal. Tracer testing can provide insight into groundwater flow characteristics and contaminant transport processes that are not provided by conventional aquifer testing methods and are best suited for assessing water quality issues associated with contaminant migration. The appropriate choice of tracer can help identify the dominant transport mechanisms. Ideally, one of the tracers should move at the same velocity as the water. The tracer under consideration should not decay, adsorb onto the rock matrix or react with other tracers (i.e. it should be chemically inert)(National Research Council, 1996). The Water Research Commission (WRC) and the Council for Scientific and Industrial Research (CSIR) has been at the forefront of initiating research on the use of isotopic tracers as groundwater dating tools since the 1970's (Levin M. et al., 1990), (Vogel and van Urk, 1975a),(Vogel et al., 1982),(Midgley and Scott, 1994, Weaver et al., 1999). In addition, environmental tracers have found widespread application in hydrogeology to determine groundwater ages. For the purpose of this paper however, it is necessary that we distinguish upfront the difference between artificial and environmental tracers. An artificial

tracer is deliberately released or injected for the purpose of gaining information on environmental processes. In contrast, an environmental tracer is either naturally present in groundwater or produced as a result of human activity, but not specifically released for tracing purposes. Many of the commonly used environmental tracers are not natural, but have been produced anthropogenically and either deliberately or accidentally released into the environment (Cook, 2015). The main differences between environmental and artificial tracers are the spatial and temporal timescales about which they provide information on. For artificial tracers, the period between injection and observation is usually measured in days, and they are released only over a relatively small area. Because of the short time frame of artificial tracer studies, they are most useful for providing information on processes that occur very rapidly, such as for identifying flow pathways in fractured rock and karst aquifers. There is also increased use of simultaneous injection of conservative and nonconservative tracers, including the injection of contaminants to assess the potential for sorption and degradation within aquifer systems, and the use of bacteriophage to obtain information on the survival of viruses (Cook, 2015). In contrast, environmental tracers usually provide information on processes that have occurred over many years. Most environmental tracers have been widely distributed across the surface of the earth, and so they can also provide information on processes that occur over much larger spatial scales. Environmental tracers have been used to assess surface water groundwater interaction and for measuring rates of recharge and evaporation. Environmental tracers are also used to fingerprint water or contaminant sources—either by identifying signals typical of particular geological units or aquifers, or of particular manufacturing processes for contaminants. Other tracers can provide information on chemical reactions such as sulphate reduction or denitrification. An important application of environmental tracers is to estimate the age (or residence time) of groundwater, and there are a range of different environmental tracers that have been used for this purpose. Measurement of groundwater age allows determination of water velocities and aquifer recharge rates and also of the susceptibility of water supplies to contamination.

## **2. Physical and chemical tracers: Principles of application**

The basic concept of tracer application is that within the bulk of water or of solutes present in the studied system some portions of these substances can be distinguished by their characteristic tracer signatures (concentration, isotopic composition, etc). A prerequisite for application of tracers is that the spatial or temporal differentiation of tracer signatures exceeds the sampling and analytical precisions. These differentiated isotopic signatures can be inherited from the infiltrating water or acquired during passage of water through soils and rocks where the composition of dissolved substances is formed. Concentrations of tracers in groundwater may vary with time due to variable inputs or because they are subject to the radioactive decay. Such tracers can be used to derive the age of groundwater. However, the simplest mode of tracer application is purely qualitative and relies on a simple comparison of the isotopic signatures between different parts of the groundwater system or between groundwater and infiltrating water. Such comparisons can provide information on the internal structure of the system or on the presence or lack of hydraulic connections between its parts, e.g. between the recharge and discharge areas which is a basic factor of most vulnerability assessments. In a quantitative sense, tracers can be used to derive time scales of water flow, estimate the relative contributions of different flow components at the groundwater receptor or characterize aquifer properties (Kendall and McDonnell, 2012). The quantitative interpretation of tracer data requires application of the mathematical models describing how tracer signatures change along the groundwater flow paths due to mixing, dispersion and removal processes. Fitting of the tracer data to such models provides quantitative characteristics of flow velocity, groundwater volumes and hydrodynamic dispersion. Below are briefly described applications of the most common tracers (Table 1.)

**Table 1.** The use of environmental tracers in hydrogeology.

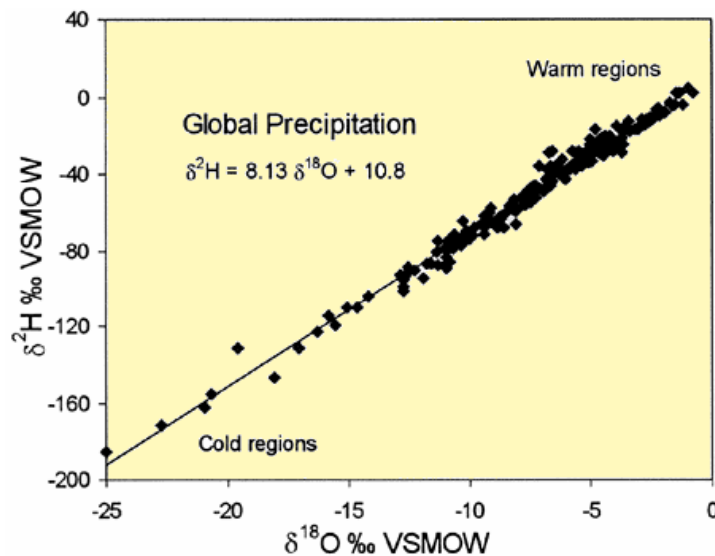
<b>Tracer</b>	<b>Applications</b>
$\delta^{18}\text{O}$ , $\delta^2\text{H}$ ( $\text{H}_2\text{O}$ )	Origin and mixing of waters; mean residence time of water in the saturated/unsaturated zone and estimation of recharge rates.
$^3\text{H}$	Identification and dating of young groundwaters; estimation of recharge rates.
Freon, $\text{SF}_6$ , CFC's	Identification and dating of young Groundwaters.
$^{14}\text{C}$	Discrimination between young and older Groundwater. Age of waters.
Water temperature	Quantification of groundwater-surface water exchange, fracture characterisation.
$^{222}\text{Rn}$	Identification of groundwater outflows to surface water bodies.
$\delta^{18}\text{O}$ , $\delta^{15}\text{N}$ ( $\text{NO}_3^-$ )	Identification of sources; evidence for denitrification.
$\delta^{13}\text{C}$ (organic compounds)	Identification of sources; characterization of degradation processes.

### 3. Stable Isotopes composition of water

Stable isotopic signatures of water expressed as  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  ( $\delta\text{D}$ ) are the most commonly used environmental tracers due to their wide applicability, easy sampling procedures and moderate costs of analyses. The “delta” notation is a way to express the relative abundances of the oxygen ( $^{16}\text{O}$ ,  $^{18}\text{O}$ ) and hydrogen ( $^1\text{H}$ ,  $^2\text{H}$ ) isotopes in water molecules. The differentiation of the stable isotopes of water in the hydrological cycle arises in two stages. Firstly, the spatial and temporal differentiation of atmospheric precipitation is driven by rainout processes. Isotopic composition of precipitation depends generally on air temperature through the so called seasonal, altitude, latitude and continental effects (Clark and Fritz, 1997). Secondly, evaporation from the surface water bodies and from the ground shifts isotopic signatures of infiltrating water towards higher delta values. The resulting spatial and temporal (mainly seasonal) differentiation in isotopic composition of infiltrating water provides a basis to infer pathways and timescales of groundwater flow. Typical applications of this isotopic differentiation are related to identification and delineation of recharge zones and to identification and quantification of mixing between isotopically different parts of groundwater systems, including surface water bodies. Temporal differentiation of stable isotopic composition in infiltrating or recharging water is used to derive timescales of flow and the values of transport parameters (i.e. dispersivities) in the unsaturated, and even the saturated zone. Analysis of isotopic composition of meteoric waters from different parts of the world reveal that their  $^{18}\text{O}$  and  $^2\text{H}$  isotopes vary in a uniquely characteristic, predictable manner and undergo linear correlation defined by the following equation:

$$\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$$

This equation is commonly known as the “global meteoric water line (GMWL) and was first derived by (Craig, 1961a), where he traced the isotopic compositions of all natural waters originating from atmospheric precipitation and not subjected to surface evaporation (*Figure 1*).



**Figure 1** GMWL derived for weighted average annual values for precipitation monitored at GNIP stations (From Clark, I. and Fritz, P, 1997.)

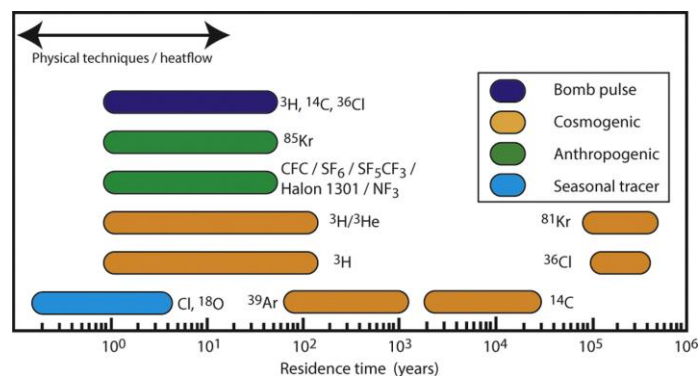
#### 4. Residence time tracers

Since recharge involves addition of water to aquifers over time, tracers that estimate groundwater residence times are invaluable in determining recharge rates. The radioactive isotopes,  $^3\text{H}$ ,  $^{14}\text{C}$ , and  $^{36}\text{Cl}$  have been most commonly used (Clark and Fritz, 1997), while recent advances in analytical techniques are increasing the applicability of the radioactive isotopes of the noble gases  $^{39}\text{Ar}$ ,  $^{81}\text{Kr}$ , and  $^{85}\text{Kr}$  as residence time tracers. These radioactive isotopes have half-lives between 10.76 years ( $^{85}\text{Kr}$ ) and 301,000 years ( $^{36}\text{Cl}$ ), which permits their use in determining groundwater residence times that range from a few years to several hundred thousand years (Figure 2). By extension, these tracers may be used to determine recharge rates over timescales proportionate to their half-lives (Scanlon et al., 2002). The most important representative classes of tracer applications in groundwater is the  $^3\text{H}$  and  $^{14}\text{C}$  method. Notwithstanding, the importance of the other radioactive tracers such as ( $^{238}\text{U}$ ,  $^{36}\text{Cl}$ ,  $^{222}\text{Rn}$ ,  $^{39}\text{Ar}$ ,  $^{81}\text{Kr}$ , and  $^{85}\text{Kr}$ ), however such interpretations are beyond the scope of this



paper and we will therefore limit our discussion to only tritium and Carbon 14.

Tritium is a dating isotope of young waters and has a half-life of 12.32 years natural produced in the atmosphere by cosmic radiation (Käss, 1998). In the atmosphere,  $^3\text{H}$  is primarily oxidised to water and enters the water cycle as precipitation. The  $^3\text{H}$  activities of rainfall increased during the atmospheric nuclear tests in the 1950s and 1960s. Because most of the atmospheric nuclear tests took place in the northern hemisphere, bomb pulse  $^3\text{H}$  activities in the northern hemisphere were much higher than in the southern hemisphere. The occurrence of tritium in groundwater indicates the extent of migration of modern post-1950s recharge. Its short half-life of about 12.32 years does not provide an exact dating for the old waters. In this case, the radiocarbon isotope is used as an excellent tracer for groundwaters with medium and long residence time (Clark and Fritz, 1997).



**Figure 2.** Approximate residence time range of tracers used in determining recharge rates Clark and Fritz (1997) and (Scanlon et al., 2002).

The radioactive isotope  $^{14}\text{C}$  has a life of 5730 years. It is produced by the interaction of cosmic rays with atmospheric gases in the upper atmosphere and mixing within the upper atmosphere produces uniform  $^{14}\text{C}$  content across the Earth (Clark and Fritz, 1997). The use of  $^{14}\text{C}$  in dating groundwater was first applied by Muennich (1957), and has subsequently been widely used due to the ubiquitous presence of dissolved inorganic carbon (DIC) in groundwater (Cartwright and

Morgenstern, 2012);(Clark and Fritz, 1997). DIC is a ubiquitous component of groundwater and  $^{14}\text{C}$  may be used to estimate groundwater residence times in the range of 2000–30,000 years (Clark and Fritz, 1997). The calculation of  $^{14}\text{C}$  ages may be complicated if groundwater DIC is derived from a mixture of sources (Clark and Fritz, 1997)(Kendall and McDonnell, 2012). Where a large proportion of DIC is derived from the dissolution of  $^{14}\text{C}$ -free carbonate minerals in the aquifer matrix, the  $^{14}\text{C}$  originating from the atmosphere or soil zone will be significantly diluted. Additional sources of  $^{14}\text{C}$  free DIC include old geogenic carbon from igneous degassing or  $\text{CO}_2$  produced together with methane from old organic carbon in the aquifer matrix. However, interpreting  $^{14}\text{C}$  data is not as straightforward as one will need to account for the correct input function. If this is not determined accurately, the  $^{14}\text{C}$  residence times can be overestimated and recharge rates underestimated. While studies have addressed this, it is difficult to determine the contribution of old C in some groundwater systems where multiple sources of old carbon might be present. This limits the precision to which groundwater residence times can be calculated using  $^{14}\text{C}$ . Despite the potential problems in its interpretation,  $^{14}\text{C}$  is the most widely used tracer for estimating long-term recharge rates in regional aquifer systems (Clark and Fritz, 1997).

In addition to using Tritium, Chlorofluorocarbons (CFCs) are a suite of dominantly anthropogenic halogenated alkanes that have a similar age range to that of  $^3\text{H}$  and are thus commonly viewed as an alternative to  $^3\text{H}$  for calculating residence times and recharge rates as the bomb-peak  $^3\text{H}$  activities declined(Kendall and McDonnell, 2012). CFCs degrade slowly and the atmospheric residence times are approximately 44 years (CFC-11), 90 years (CFC-113), and 180 years (CFC-12). The long residence times result in uniform distributions of atmospheric CFCs in both the northern and southern hemispheres. CFC concentrations in water may be routinely determined at low levels (<1 pg/L) and the solubilities are also well known. Complications in using the CFCs are that the solubilities are temperature dependant and the temperature of groundwater in the recharge zone needs to be determined(Cook, 2015)). Additionally, entrapment of excess air during recharge (or during well



construction or sampling) results in higher than predicted CFC concentrations in water.

## **5. Summary and Future Opportunities**

Environmental tracer techniques have been shown to provide both qualitative and quantitative information on hydrological processes in the environment, particularly with respect to groundwater. An advantage of the tracer methods, compared to the more traditional methods used in hydrogeology, lies in their ability to convey detailed information on groundwater system functioning integrated over a wide range of spatial and temporal scales. Some examples articulated above: (1) stable isotopes of water in conjunction with  $^3\text{H}$  and  $^{14}\text{C}$  demonstrate that many groundwaters are either meteoric or palaeowater, and are recharged often through a number of different mechanisms, (2) long-lived natural radionuclides such as  $^{14}\text{C}$  are used routinely to estimate recharge and horizontal flow rates on a regional scale, and provide information that is not easily obtained through conventional hydrogeological approaches. A new class of environmentally friendly and highly fluorescent nanomaterial called carbon quantum dots (CQDs) are already being applied as next generation hydrogeological tracers for bio-imaging and catalytic applications. The fluorescence emission and surface functionalization of the CQDs as parameters are used to study flow of water in simulated laboratory columns and in field. As we continue into the twenty-first century, it can be foreseen that environmental tracers will continue to be an important tool for better understanding of groundwater systems and one that should become standard practice in any hydrogeological study. These methods are now being used more frequently and widely than ever, and their development continues to be dynamic. This is especially true within the context of the 4IR, on how we can extract more information from complex datasets through using machine learning and artificial intelligence.

## References

- CARTWRIGHT, I. & MORGENSTERN, U. 2012. Constraining groundwater recharge and the rate of geochemical processes using tritium and major ion geochemistry: Ovens catchment, southeast Australia,. *Hydrology* 475, 137-149.
- CLARK, I. D. & FRITZ, P. 1997. Environmental isotopes in hydrogeology. *CRC press*.
- COOK, P. G. 2015. The Role of Tracers in Hydrogeology. *Groundwater* 53.
- CRAIG, H. 1961a. Standard for reporting concentration of deuterium and oxygen-18 in natural waters. *Science*, 133, 1833–1834.
- KÄSS, W. 1998. *Tracing Technique in Geohydrology* Netherlands, A. A Balkema Publishers.
- KENDALL, C. & MCDONNELL, J. J. 2012. Isotope tracers in catchment hydrology. *Elsevier*.
- LEVIN M., WALTON, D. & VERHAGEN, B. T. 1990. Environmental isotope, hydrological and hydrogeochemical studies of ground water pollution associated with waste disposal. *Joint Water Research Commission project of the AEC and the Schonland Research Centre, Wits . Water Research Commission Project K5/311*.
- MIDGLEY, J. J. & SCOTT, D. F. 1994. The use of stable isotopes of water (D and 18O) in hydrological studies in the Jonkershoek Valley. *Water SA*, 20, 151-154.
- NATIONAL RESEARCH COUNCIL 1996. Rock fractures and fluid flow – Contemporary understanding and applications. Washington, D.C: National Academy Press.
- SCANLON, B. R., HEALY, R. W. & COOK, P. G. 2002. Choosing appropriate techniques for quantifying groundwater recharge. *Hydrogeology Journal*, 10, 18-39.
- VOGEL, J. C., TALMA, A. S. & HEATON, T. H. E. 1982. The age and isotopic composition of groundwater in the Stampriet artesian basin, SW Africa. *CSIR Research Report*.

VOGEL, J. C. & VAN URK, H. 1975a. Isotopic investigation of Lake St Lucia. .  
*Unpublished CSIR report.*

WEAVER, J. M. C., TALMA, A. S. & CAVE, L. 1999. Geochemistry and Isotopes  
for Resource Evaluation in the Fractured Rock Aquifer of the Table  
Mountain Group. *Water Research Commission Report, Pretoria*  
481/1/99.

**Yazeed van Wyk <sup>1\*</sup> and Eunice Ubomba-Jaswa<sup>1</sup>**

<sup>1</sup> Water Research Commission, Private Bag X03 Gezina, Pretoria 0031,  
South Africa

\* Correspondence: yazeedv@wrc.org.za; Tel.: (+27661773637)