4.12 Environmental tracers, groundwater age and vulnerability

Since about 1970 a wide range of agricultural and industrial contaminants such as nitrate, pesticides and chlorinated solvents have been found in an increasing number of aquifers, globally (e.g. Singh & Sekhon 1979, Alley 1993, Foster 2000). Human impacts on groundwater quality can generally be recognised by the contents of environmental tracers back to about 1950. Before 1950 anthropogenic influence on the groundwater quality were very limited (Hinsby et al. 2001). The increasing pressure on both groundwater quality and quantity (over-exploitation) leads to increasing pressures on the vulnerable water resources and the aquatic environment. This calls for efficient tools for development of sustainable integrated water management policies based on scientific sound knowledge.

Important factors controlling the evolution of groundwater quality and quantity include how fast groundwater is recharged, how fast it flows and how it interacts with sediments and rocks in the groundwater bodies (Sect. 4.13). The computation of these parameters requires detailed geological information, which is commonly not available for the subsurface.

Direct information about groundwater age, flow paths, flow velocities, contaminant transport mechanisms etc. can be obtained by the analysis of environmental tracers in groundwater. Hence, environmental tracers are important tools for developing a sustainable management policy for the protection of the water resources and the aquatic environment. This chapter shortly describes the most common environmental tracers used for groundwater age estimation (Fig. 4.12.1) and their application in water resources management and research.

**Fig. 4.12.1:** Illustration of the aging of groundwater along a flow line in an aquifer, and the most common environmental tracers used for groundwater dating. Courtesy R. Purtschert, modified after Hinsby (2001).
4.12.1 The definition of environmental tracers and groundwater age

Environmental tracers are defined as: “Natural or anthropogenic compounds or isotopes that are widely distributed in the near-surface environment of the Earth, such that variations in their abundances can be used to determine pathways and timescales of environmental processes” (Cook & Böhlke 2000).

Groundwater age is generally considered as the average travel time for a water parcel from either the surface or from the water table (point of recharge) to a given point in the aquifer. Groundwater dating (age estimation) is the estimation of the groundwater age by one or more available techniques. The term “residence time” is here used synonymously with “age”. Hence, the residence time of groundwater is here defined as the average travel time between the point of recharge and the point of discharge, e.g., to a river or a lake or to any monitoring point in the groundwater zone.

The tracer age estimate is normally considered and described as the average age of the water sample. This is a good approximation in cases where the flow system is simple, and can be approximated by a piston flow model (insignificant mixing and dispersion). However, where significant mixing and dispersion occur, e.g., in long screens in water supply wells or in groundwater bodies with a significant volume of low permeability units (“stagnant zones”) the estimated tracer model age may either underestimate or overestimate the actual mean age of the water parcel (Weissmann et al. 2002, Bethke & Johnson 2002). A sound knowledge of the geological setting and both physical and chemical processes in the aquifers is therefore important for the right interpretation and application of the environmental tracers and computed groundwater ages.

4.12.2 Groundwater age estimation

There are basically three different ways of estimating groundwater age at a groundwater well or monitoring point: (1) by environmental tracers (e.g. Plummer et al. 1993), (2) by groundwater flow modelling (e.g. Engesgaard & Molson 1998) and (3) by a combination of both (Bauer et al. 2001, Trolldborg 2004).

This chapter focus on the application of environmental tracers as groundwater dating tools.

Dating young groundwater. It is common to distinguish between young (modern) groundwater and old groundwater. Young groundwater is considered to be groundwater with a human impact recharged since about 1950, while old groundwater recharged the aquifers before 1950 and generally do not exhibit any significant human impact (e.g. Plummer et al. 1993, Cook & Herczeg 2000, Hinsby et al. 2001a). Research during the past decade has introduced several new environmental tracers for dating of young groundwater. Especially the tracers tritium (\(^{3}\)H), CFCs, SF\(_6\) and \(^{85}\)Kr are all applied in an increasing number of studies for recognition of modern water components possibly containing contaminants, and for groundwater dating (e.g. Hinsby et al. 2001a, Manning et al. 2005, Hinsby et al. 2006). Figure 4.12.2 shows the atmospheric concentrations of the most common tracers for the identification of human impacts and groundwater dating. The radionuclides \(^{36}\)Cl, \(^{14}\)C and \(^{3}\)H are introduced into the atmosphere by nuclear test bombing in the 1950’s and early 60’s, while \(^{85}\)Kr escapes into the atmosphere by the processing of fuel rods from nuclear power plants. CFCs and SF\(_6\) are gases used in the industry (although the use of CFCs is now banned due to its Ozone depletion capacity).

The tracers \(^{85}\)Kr, CFCs and SF\(_6\) may be used for estimation of absolute ages i.e. under optimal conditions they can estimate the recharge year of a given water sample or the average residence time (age) of the sample in groundwater. The tracers \(^{36}\)Cl, \(^{14}\)C and \(^{3}\)H are in this context considered as event markers (Plummer et al. 1993, Cook & Böhlke 2000), and may only be used for identification of human impacts or a relative age (e.g. younger than 1960, 1990 etc.). However, \(^{3}\)H (tritium) can be used together with its daughter nuclide \(^{3}\)He to estimate absolute groundwater ages (Solomon & Cook 2000, Manning et al. 2005).
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Fig. 4.12.2: Evolution of the concentration of environmental tracers in the atmosphere during the period 1940–2000. All tracers may be applied as relative or absolute groundwater dating tools. Modified after Clark & Fritz (1997) and Hinsby et al. (2001a).

**Dating old groundwater.** Tracers such as $^{39}$Ar, $^{14}$C, $^{8}$He and $^{81}$Kr are used for dating groundwater of preindustrial age up to a million years old or more, e.g., in combination with groundwater flow modelling (e.g. Hinsby et al. 2001b, Lehmann & Purtschert 1997). Groundwater without measurable $^{14}$C content is sometimes specified as “very old groundwater” (Fröhlich et al. 1991).

In small countries with short distances between recharge and discharge points (like Denmark) the groundwater used for drinking water supply is generally less than 1000 years old, although in rare cases it may be even very old (up to >10,000 years, Hinsby et al. 2001b). In large countries with large sedimentary basins as, e.g., Canada and Australia (Fröhlich et al. 1991, Lehmann & Purtschert 1997, Sturchio et al. 2004), and even France (Marty et al. 1993), the groundwater used for water supply may be up to a million years old or more. These are often described as very old groundwaters, and defined as groundwater without measurable $^{14}$C (Fröhlich et al. 1991). Old or perhaps even very old groundwaters may also be found in deep well protected buried valleys, such as the Ellerbeker Rinne northwest of the city of Hamburg (Hinsby 2006), one of the BurVal pilot areas (Chap. 5.4).

**4.12.3 Applications of environmental tracers and groundwater dating**

Groundwater vulnerability. The content of environmental tracers in groundwater, and groundwater dating at wells or monitoring points, provide valuable information on recharge rates and the risk of contamination at these points, i.e. they indicate the vulnerability of the groundwater. If groundwater contains one or more of the environmental tracers shown in Figure 4.12.2, the groundwater probably also contains other contaminants, depending on the land use in the area, and such groundwater can be considered as vulnerable to surface pollution. If a groundwater body does not contain any environmental tracers indicative of a human impact, this groundwater body is not vulnerable to pollution from the surface. An analysis of the contents of a modern water component in a water sample gives a first indication of possible contamination at a monitoring point (Hinsby et al. 2001, Manning et al. 2005). Analyses of the contents of environmental tracers in groundwater provide a detailed understanding of subsurface flow systems including the groundwater age distribution and the possibility of evaluating degradation rates and the history and fate of groundwater contaminants (Plummer et al. 1993, Böhlke & Denver 1995, Hinsby et al. 2006a, b).
The quality and the quantity of the subsurface water resources are closely linked to the age of groundwater. The aquifers have a considerable attenuation potential for many contaminants (Christensen et al. 2000), and the risk of contaminant appearance therefore decreases with increasing groundwater age along flow paths. On the other hand old groundwater may dissolve elements and substances from geological layers, which can also be of health concerns. Arsenic is a good example.

Table 4.12.1 suggests three vulnerability classes for groundwater primarily based on the contents of tritium. The table should be used only as a guideline and a first rough approximation and should never stand alone. However, it may serve as an initial screening and provide a first overview of the vulnerability to surface pollution of a groundwater body at a given point.

Note that there is some overlap between the different vulnerability groups as defined by $^{14}$C. This reflect the fact that the $^{14}$C activities ("concentrations") in groundwater are highly affected by subsurface chemical and physical processes, which affect the concentrations and introduce quite high uncertainties in the groundwater dating results if the subsurface conditions are not known in detail (Buckau et al. 2000, Hinsby et al. 2001). Hence, the $^{14}$C ranges given above are relatively uncertain and special caution are needed in the interpretation of this tracer. For instance $\delta^{13}$C should always be measured together with $^{14}$C and taken into account in the interpretations.

Figure 4.12.3 illustrates the measured tritium values in all five areas investigated in the BurVal project. The figure indicates that about half of the sampled wells (with $^3$H > 1 TU) can be considered to have high to medium vulnerability to surface pollution, while the other half (with $^3$H < 1TU) may be considered to have low vulnerability to surface pollution according to Table 4.12.1.

More sophisticated methods may be applied e.g. for subdiving the high or low vulnerability groups in subgroups. For instance Hinsby (2006) used the method suggested by Manning et al. (2005) applying $^3$H/He for assessing the susceptibility ("vulnerability") of wells sampled in the BurVal project. All environmental tracers mentioned in the table below and in this chapter in general (see e.g. Fig. 4.12.1) were used for groundwater dating or as groundwater age indicators in the BurVal project (Hinsby 2006).

### Other specific applications

The environmental tracers have many important applications for instance as an important part of the characterisation of groundwater bodies as requested by the Water Framework Directive:

Table 4.12.1: Groundwater vulnerability classes as defined by the contents of selected environmental tracers in monitoring wells. Assuming short well screens and/or no significant mixing of water types. Tritium units are TU, $^{39}$Ar and $^{14}$C units are percent modern (pmc).

<table>
<thead>
<tr>
<th>vulnerability</th>
<th>high</th>
<th>medium</th>
<th>low</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater age (yr)</td>
<td>0 – 35</td>
<td>35 – 55</td>
<td>&gt; 55</td>
</tr>
<tr>
<td>$^3$H (12.32)$^1$</td>
<td>5 – 25</td>
<td>&lt; 1 or &gt; 25</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>$^{39}$Ar (269)$^2$</td>
<td>&gt; 90</td>
<td>70–90</td>
<td>&lt; 70</td>
</tr>
<tr>
<td>$^{14}$C (5730)$^2$</td>
<td>&gt; 50</td>
<td>40–60</td>
<td>&lt; 50</td>
</tr>
</tbody>
</table>

$^1$Half-life in years for $^3$H (Lucas & Unterweger 2000) $^2$Half-life in years from Cook & Herczeg (2000)
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Fig. 4.12.3: Tritium concentrations in wells investigated in the BurVal project. Wells above the 1 TU line are considered to have high or medium vulnerability to groundwater pollution, while wells below this line have a low vulnerability. Results from all five investigated buried valleys are presented. From left to right these are: Bording, Tyrsting, Reede Kro, Ellerbeker Rinne and Cuxhaven as indicated with the bold letters in the top of the diagram and the background colour. Data from Hinsby (2006).

a) For identification of pristine groundwater without human impact and hence for the assessment of the composition of these and of natural background levels (NBLs) for relevant elements and substances

b) To support the derivation of threshold values for groundwater based on the chosen NBL and a reference value (e.g. for a dependent ecosystem or for drinking water) for a given substance

c) To evaluate timescales and history of contaminant inputs

d) To evaluate the interaction between a groundwater body and dependent ecosystems.

Other applications include:
- As indicator of leaks through or along water supply or monitoring wells
- As a tool for evaluation of results from groundwater flow models or for calibration of groundwater flow models
- Identification and quantification of mixing of different groundwater types
- As a tool for evaluating contaminant degradation rates especially in combination with groundwater flow models.
4.12.4 Conclusion

Environmental tracers and groundwater dating are important tools in the sustainable management of water resources and protection of the aquatic environment, e.g., for evaluation of groundwater vulnerability and groundwater interaction with dependent ecosystems. The best and most certain estimations of groundwater travel times and velocities are obtained if multiple tracers are used and compared to results from numerical groundwater modelling. Environmental tracers are also important tools when the natural background levels of different dissolved substances in groundwater have to be estimated, e.g., in connection with the derivation of groundwater threshold values for substances characteristic of the groundwater body as being at risk according to the requirements of the EU Water Framework Directive. Finally, the environmental tracers provide valuable data for evaluation of the history and fate of contaminants in the subsurface, and for evaluation of the results from groundwater flow models.

4.12.5 References


Hinsby K (2001): Freshwater – our most important resource. – In: Hinsby and Binzer "Freshwater our most important resource – Geology and groundwater models", special issue of Geologi – Nyt fra GEUS, nr.1 – 2001 (available in English and Danish at: www.geus.dk).


