BULLETIN

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GROUNDWATER DATING AND THE BOTTLED WATER INDUSTRY

INTRODUCTION

Many water bottlers want to know the age of the water obtained from their source. The main reason is often as part of a marketing strategy, to show that the water is old – it adds to the "story".

However, the age of groundwater also provides important technical information to the hydrogeologist which provides greater insight and understanding of aquifer processes, recharge and flow system. Thus an understanding of the age of groundwater can provide significant benefit in the management and sustainable use of an aquifer.

The purpose of this note is to provide background on dating techniques, with a particular focus on isotope based dating.

GROUNDWATER AGE

The age of groundwater ranges from less than a month up to around a million years. Groundwater up to around 50 years old is generally referred to as 'young' groundwater. During the last 50 years, an array of chemical and isotopic substances have been released to the atmosphere as a result of human activities that can be used to date groundwater. Young groundwater is typically found at depths up to 30m in unconsolidated sediments and up to 300m (or more) in fractured rock and karstic systems.

Groundwater in excess of 50 years old is generally referred to as 'old' groundwater. Isotopes that occur naturally in the environment are used for dating old groundwater.

DATING TECHNIQUES

There are a range of techniques that can be used to date groundwater over a wide range of timescales:

- Aquifer hydraulic properties (hydrogeological analysis)
- Chemical tracers
- Radioactive isotope analysis

AQUIFER HYDRAULIC PROPERTIES

The type and distribution of rocks and unconsolidated sediments within a groundwater system can be a major factor affecting the rate and movement direction of water. The hydraulic properties of an aquifer can be used to provide an estimate of the age of groundwater at a particular location.

The rate at which water moves through the ground is dependent on the permeability of the aquifer and the hydraulic gradient. If these, together with the distance to the recharge area are known, then the age of the groundwater can be calculated.

This method provides an indication of the groundwater flow rate, and therefore the time it takes for rainfall recharge at the outcrop area to travel to the point of abstraction. However, the accuracy of this method is low as aquifer hydraulic properties are often poorly quantified and can also vary considerably spatially; and the distance to the recharge area can be very difficult to define. While this method can work reasonably for young water, the older the water gets and the more complex the geological setting, the less accurate the assessment.

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CHEMICAL TRACERS

Chemical tracers can be used to date young groundwater and include chlorofluorocarbons (CFCs), sulphur hexafluoride (SF_6) and nitrate. In all cases these chemical tracers have been introduced by man, and while at low concentrations and below regulatory limits, are detectable. Because it is known when these chemicals were introduced, and records of atmospheric concentrations or application concentrations have been established, it is possible to use them to identify age. For example:

- CFCs – CFC gases were added to the atmosphere from refrigeration uses during the 1950's to the 1980's. CFCs are well mixed in the atmosphere and are a convenient way to date groundwater. However CFC concentrations are falling and therefore other methods will ultimately need to be used to date young groundwater.
- SF_6 – Industrial production of SF_6 began in the 1950's for gas filled high voltage electrical switches. SF_6 is a very stable gas, is well mixed and accumulating rapidly in the atmosphere, and therefore offers a convenient way to date groundwater.
- Nitrate – The heavy use of nitrogen fertilisers began in the early 1970's, therefore elevated concentrations of nitrogen in groundwater in agricultural areas can provide an indication of recent recharge and therefore that the groundwater is relatively young.

RADIOACTIVE ISOTOPE ANALYSIS

Radioactive and stable isotope tracers are increasingly used to study groundwater age and movement, covering time spans from a few months up to a million years. In essence, the concentration of the isotope is a function of the half-life of the isotope and the starting concentration.

Isotopes for dating young groundwater include ^{3}H (tritium), $^{3}H/^{3}He$ (tritium/helium-3) and ^{85}Kr (krypton-85):

- Tritium and Helium-3 – Tritium was added to the atmosphere from nuclear bomb testing in the 1950's and 1960's. Tritium has a half-life of 12.4 years and concentrations have therefore now been reduced by a factor of 16. Tritium will continue to drop to natural background levels therefore the use of tritium for age dating groundwater will soon come to an end. It is also area specific, i.e. not well mixed in the atmosphere. It is difficult to evaluate age information from tritium data alone therefore tritium is commonly used together with its decay product helium-3 (^{3}He).
- Krypton-85 – Added to the atmosphere from the reprocessing of fuel rods from nuclear reactors. However ^{85}Kr is not a practical dating method in groundwater studies due to difficulties in collection and analysis.

Isotopes for dating old groundwater include ^{14}C (radiocarbon), ^{81}Kr, ^{36}Cl, ^{4}He and uranium isotopes:

- ^{14}C – Used to date groundwater between 1,000 and 40,000 years old.
- ^{81}Kr – Used to date groundwater between 50,000 and 1,000,000 years old.
- ^{36}Cl – Used to date groundwater between 50,000 and 1,000,000 years old.
- ^{4}He – Used to date groundwater between 100 and 1,000,000 years old.
- Uranium isotopes – Used to date groundwater between 10,000 and 1,000,000 years old.

These isotopes are all produced naturally in the environment. ^{14}C is most commonly used to date old groundwater.

DATA ANALYSIS

An age estimate based on a single isotope or chemical tracer at a single location may not be very informative as each dating technique has limitations. Multiple estimates based on more than one tracer and at multiple locations are therefore necessary to meaningfully use groundwater age data.

It should be remembered that water abstracted from a source is a mixture of water from different flow paths. Because each flow path is a different length and passes through different geology, the time taken

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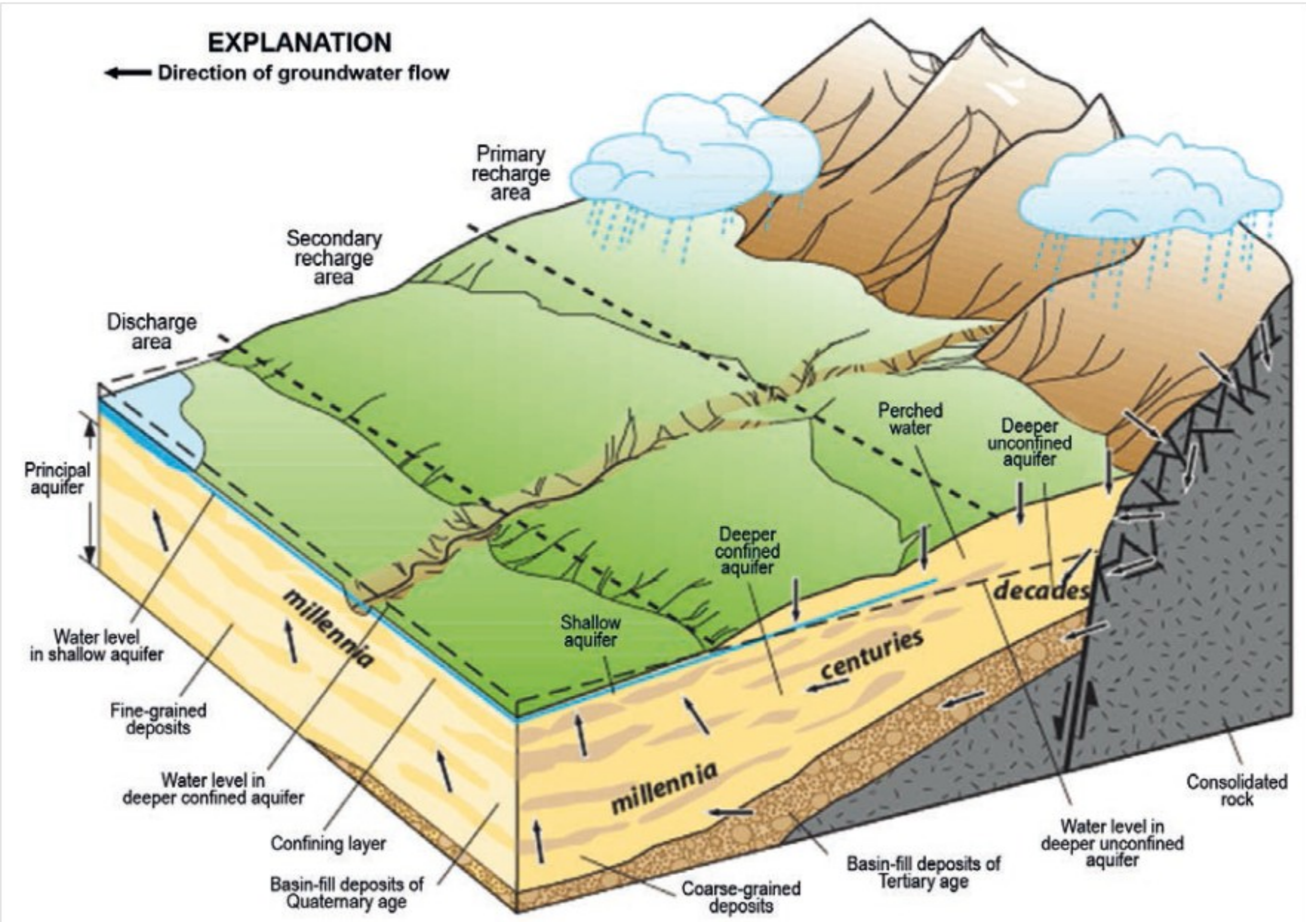
to follow each path and therefore the age of water from each path will be different. The age frequency distribution and mean age of the mixture affect the interpretation of the groundwater dating methods. A whole set of tracers is generally required to cover the entire age range of an aquifer or a set of different aquifers.

The amount of analysis undertaken is dependent on the objective of the age determination. If it is simply to demonstrate that some of the water is “old”, then less than 5 analyses for long half life isotopes may suffice. If the objective is to determine the “ages” of the water, with a view to understanding flow paths, which in turn might be used to define catchment areas and develop a source protection plan for the long term, then 10’s of analyses at different times of the year for different tracers and isotopes will be needed.

The figure below illustrates the different ages of water within a hydrogeological system. Abstracting water from a well or borehole will draw on waters of different ages.



Generalized block diagram showing conceptualization of groundwater recharge, discharge and groundwater age in a basin fill groundwater flow system (from Ref. 1).

LABORATORY ANALYSIS

The British Geological Survey is the UKs leading organisation for groundwater dating and tracer analysis, and uses a wide range of environmental agents for this work including CFCs, SF_6, tritium, radiocarbon (^{14}C) and stable isotopes.

To provide an indication of costs, CFC and SF_6 analysis should be undertaken together and will cost ~£100 and ~£120 respectively per sample. ^{14}C analysis costs ~£400 per sample. A minimum of 10 samples is often required per analytical technique.

Therefore, a dating exercise is likely to cost in the order of £6000 in laboratory costs, plus data interpretation.

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University research departments may also provide analysis, and may take smaller sample batches.

SUMMARY

Before embarking on groundwater dating consider the following:

- ✓ Why are you doing it?
- ✓ How accurate do you need the dating to be?
- ✓ What is the most appropriate method?
- ✓ How old is the water likely to be?
- ✓ How mixed is the water – how much young water and how much old?
- ✓ How will you use the analysis?
- ✓ How much sampling needs to be done?

REFERENCES

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3. USGS Fact Sheet 134-99. Tracing and Dating Young Groundwater. US Geological Survey. September 1999.
4. Gooddy, D. C. Using Man Made Gases as Groundwater ‘Age’ Tracers. British Geological Survey.