## USING ISOTOPES EFFECTIVELY TO SUPPORT COMPREHENSIVE GROUNDWATER MANAGEMENT

# A. Introduction

Many countries are not able to manage their water resources to sustainably meet current and future demands because they lack a comprehensive assessment of the quality and availability of their resources. The need for comprehensive assessments is well recognized, but often the required information is unavailable owing to gaps in hydrological information and understanding. These gaps are particularly acute with respect to groundwater resources.

It is estimated that more than 97% of the Earth's available fresh water is located underground, yet this vital resource is often poorly understood and poorly managed. Stable and radioactive isotope techniques are cost effective tools in hydrological investigations and assessments, and are critical in supporting effective water management. Isotopes are commonly employed to investigate:

- sources and mechanisms of groundwater recharge;
- groundwater age and dynamics;
- interconnections between aquifers;
- interaction between surface water and groundwater;
- groundwater salinization; and
- groundwater pollution.



FIG. III-1. Collecting water samples for hydrochemical and isotopic analysis in Uganda. (Photo credit: Uganda, Ministry of Water, Land and Environment.)

# B. The use of isotopes in groundwater hydrology

#### B.1. Sources and mechanisms of groundwater recharge

A qualitative and quantitative characterization of groundwater recharge is essential to ensure the sustainable development and management of groundwater resources. Aquifers which receive little recharge exhibit only small fluctuations in groundwater levels; a reliable estimate of recharge rate cannot therefore easily be obtained on the basis of classical approaches alone, such as water level monitoring. Isotope techniques are

virtually the only tools which can be used to identify and evaluate present day groundwater recharge under arid and semi-arid conditions.

The isotopic composition of groundwater (expressed as abundance of oxygen-18 and deuterium) is determined by the isotopic composition of recharge. If most of the recharge is derived from direct infiltration of precipitation, the groundwater will reflect the isotopic composition of that precipitation. However, if most of the recharge is derived from surface water (rivers or lakes) instead of from precipitation, the groundwater will reflect the isotopic composition of the contributing river or lake. This isotopic composition is expected to be measurably different from that of local precipitation. The difference arises from the fact that recharge via bank filtration may represent water originating from precipitation in a distant area, for instance in a high mountain region. In high mountain regions the isotopic composition allows for different to that of precipitation sources, and hence of recharge mechanisms. In addition to differences in isotopic composition of groundwater resulting from different recharge sources, there can be differences due to how recently recharge occurred. In hydrological settings in which groundwater is very old (>10 000 years), regional climatic conditions at the time of recharge may have been different from those existing today, and this is reflected in the isotope composition of the groundwater.

It is possible to identify, and in some instances quantify, modern recharge — within 40 to 50 years — by measuring isotopes and dissolved gases (e.g. tritium, tritium and helium-3, chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF<sub>6</sub>)) in soil water in an unsaturated zone or in groundwater from shallow, unconfined aquifers and springs. The tritium–helium-3 method enables bomb tritium from atmospheric testing carried out between 1954 and 1963 to be used to estimate groundwater recharge rates by determining the residence time of different groundwater samples collected at different depths. Even in cases of low vertical flow velocities, identification of the tritium and helium-3 peaks can be used for dating and thus for recharge rate estimation (recharge rate = porosity × vertical flow velocity). In addition, the mere presence of helium-3 derived from the decay of tritium in groundwater with no measurable tritium provides evidence of modern recharge. Tritium and helium-3 data can be modelled to estimate recharge to groundwater and transport parameters of aquifers.

Under certain circumstances, the residence time and thus recharge rate of modern groundwater can also be estimated by measuring the seasonal variations of hydrogen and oxygen isotopes. The applicability of this method is limited to those areas where precipitation shows a pronounced seasonal variation, such as in mountainous areas.

Groundwater in shallow aquifers typically has a residence time of decades to hundreds of years. In contrast, deeper and less permeable aquifers that extend for many kilometres can have through-flow times of thousands of years. If the flow regime is simple and mixing is minimal, such aquifers can serve as archives of information about environmental conditions at the time of recharge. The stable isotopes of hydrogen and oxygen in palaeowaters (groundwater recharged under climate conditions different than today) reflect the air temperature at land surface and the air mass circulation (origin of moisture) at the time of precipitation and infiltration. While palaeotemperatures derived from oxygen–deuterium analyses are useful, recently developed noble gas analytical methods provide greater certainty and precision in palaeotemperature determination.



FIG. III-2. Field work at a coastal aquifer in Peru.

#### B.2. Groundwater age and dynamics

The radioactive decay of environmental radioisotopes and the transient nature of some of these (bomb tritium, anthropogenic krypton-85, bomb carbon-14 and bomb chlorine-36) make such isotopes a unique tool for determining groundwater residence time. Residence time, also called groundwater age, is the length of time water has been isolated from the atmosphere. Recharge of unconfined aquifers usually results in a vertical gradient of groundwater ages (increasing age with depth), while in confined aquifers the dominating feature is a horizontal or lateral gradient (age increasing with distance from area of recharge). In the former case this gradient is approximately proportional to the inverse of the recharge rate (volume/time), while in the latter case the gradient is approximately proportional to the inverse of the flow velocity. Therefore, the hydrogeologically relevant parameters primarily addressed by groundwater dating with radioactive isotopes are the recharge rate and flow velocity of groundwater in unconfined and confined aquifers, respectively.

One of the approaches to determine groundwater flow rate is to estimate flow velocity by measuring the decrease in the radioisotope concentration along the flow path. If the mean porosity value of the aquifer is known, groundwater flow rate can be estimated. This simple approach requires access to at least two wells along the flow path of an aquifer and knowledge of the initial radioisotope concentration in the recharge area.

Under natural conditions, groundwater movement is generally very slow, often in the order of a few metres per year. Water that has moved a few kilometres along the flow path under these conditions is hundreds or thousands of years old; an age beyond the dating range of tritium, tritium and helium-3, and chlorofluorocarbons. Therefore, in large aquifers with long flow paths, the most common radiometric approach to determining groundwater residence times has been carbon-14. Its half-life of 5730 years makes it a suitable tool for the dating of groundwater in an age range of about 2000 to 40 000 years.

Very slow moving groundwater in deep confined aquifers extending over tens and, in some cases, several hundreds of kilometres can reach ages of tens and even hundreds of thousands of years. These ages are beyond the dating range of carbon-14 and require the use of very long-lived radioisotopes. Of the three long-lived radioisotopes used in water studies — krypton-81, chlorine-36 and iodine-129 — only chlorine-36 has been found to have wider practical use so far. However, interpretation of chlorine-36 data to ascertain

groundwater age is often hampered by insufficient knowledge of in situ production of the isotope owing to reactions in the aquifer matrix. Recent developments in sampling and analytical methods suggest that the use of krypton-81 may grow substantially given that it is a reliable tool to date groundwater in the range of 40 000 to 1 million years old.

#### B.3. Interconnections between aquifers

Both groundwater dynamics and groundwater contamination can be influenced by hydraulic interconnections between aquifers. Environmental isotopes, especially stable isotopes, can be used to investigate such interconnections, provided the isotopic composition of groundwater in the aquifers being measured is different. Thus, isotopes can be used to prove a lack of hydraulic interconnections between aquifers based on contrasting compositions. In some settings, hydraulic connections exist naturally between aquifers, and this can be evaluated through variations in isotopic composition. Intense exploitation of an aquifer can induce leakage from overlying and underlying aquifers. Stable isotope data can be used to estimate the flow of groundwater from adjacent aquifers.

#### B.4. Interaction between surface water and groundwater

Groundwater often consists of a mixture of recharge from surface water (lakes or rivers) and local precipitation. It is important to know the proportions of these recharge components in order to increase the sustainable supply of drinking water through bank infiltration, and to prevent drinking water pollution by infiltration of water from a contaminated surface water source. Different recharge components can be identified through the stable isotope compositions of groundwater because evaporation of water in surface water bodies, in particular under semi-arid and arid conditions, leads to an increase in the proportion of the heavy isotopes deuterium and oxygen-18. A simple isotopic balance equation can then be used to estimate the relative proportions of surface water and precipitation in recharge. The accuracy of this determination generally depends on the magnitude of the difference in isotopic composition of the two components and under ideal conditions is in the order of a few per cent.

River water can show a seasonal variation in isotopic composition, usually observed with reduced amplitude and after a time lag in wells near the river. This time lag as well as the change in mean isotopic composition provides the minimum time (transit time) required for river water and possibly its dissolved pollutants to reach a groundwater supply well. Isotope composition also provides insight into the fraction of river water in recharge (possibly polluted) relative to other recharge sources.

In arid climates, river water may be enriched in deuterium and oxygen-18 relative to groundwater if it was replenished under historical conditions with greater humidity. The fraction of river water in groundwater can be estimated based on the differences in isotopic composition of the mixing components.

### B.5. Groundwater salinization

In areas where salinization of groundwater is occurring, it is necessary to identify the mechanism of salinization in order to prevent or alleviate the cause. Isotope techniques can be used to distinguish the importance of the following processes which may lead to the salinization of groundwater:

• leaching of salts by percolating water;

• intrusion, present or past, of salt water bodies such as sea water, brackish surface water or brines; and

• concentration of dissolved salts through evaporation.

#### B.6. Groundwater pollution

Pollution of aquifers by anthropogenic contaminants is of great concern in the management of water resources. Environmental isotopes can be used to trace the pathways of pollutants in aquifers and predict spatial distribution and temporal changes. This information is critical in order to be able to understand the source of contaminants, assess their scale and migration, and to plan for remediation. Measurements of the concentration and stable isotope composition of sulphate and nitrate in groundwater have been widely used to identify sources of sulphate/nitrate pollution. The stable isotope composition of sulphate and nitrate has also been used to evaluate microbial sulphate reduction and denitrification processes, respectively.

Concentration and stable isotope composition of hydrocarbons and their degradation products can together provide a powerful tool for pollution assessment and remediation. The combined use of the stable carbon isotopic composition of carbon dioxide and the oxygen isotope composition of molecular oxygen, nitrate or sulphate provides a robust tracer for the verification and quantification of microbiological processes associated with hydrocarbon contaminated groundwater.

## C. Examples of groundwater management using isotopes

Isotopes are being effectively used in comprehensive groundwater management in many settings around the world. Three recent applications highlight important contributions of isotopic techniques to understanding and managing groundwater resources.

#### C.1. Groundwater dynamics in the Guaraní Aquifer System in South America

The Guaraní Aquifer System (GAS) is one the largest transboundary hydrogeological units in the world, covering about 1.1 million km<sup>2</sup>, mainly within the Paraná river basin in parts of Argentina, Brazil, Paraguay and Uruguay (Fig. III-3). The GAS is formed mainly by sandstone layers and related sedimentary materials of Triassic and Jurassic age, deposited in continental environments. The aquifer crops out along the main western and eastern boundaries of the system, but most of the aquifer is confined by basaltic layers of Cretaceous age (in some places the aquifer is covered by more than 1500 m of basalt and other sediments). The main aquifer units show important differences in thickness (from less than 50 m to more than 600 m, with a mean thickness of 250 m) but it is assumed that there is hydraulic continuity over the whole extension of the aquifer. The GAS exhibits good hydraulic properties for groundwater flow. However, low hydraulic gradients in the deeper part of the aquifer system are responsible for very low groundwater velocities (<1 metre per year), and therefore for old to very old groundwater (in the range of 40 000 to 1 million years old).



FIG. III-3. Map of the Guaraní Aquifer System.

The results of isotope studies indicate the existence of distinct shallow and deep groundwater flows in areas close to the outcrop of the aquifer. Groundwater in the recharge area mainly discharges to local rivers crossing the outcrop area; this shallow groundwater is more prone to pollution by human activities. Isotope data and numerical modelling have indicated that active groundwater recharge to the deep confined aquifer system is very limited, probably in the order of 1% of annual precipitation over the recharge area (10–15

mm/year). Environmental isotopes have been used to address some unresolved hydrological issues that are relevant to the development of a sound conceptual hydrodynamic model of the GAS, including: (a) delineation of major hydrogeological sectors within the GAS, (b) characterization of recharge processes and flow patterns, and (c) groundwater dynamics in the confined part of the aquifer.

The combined use of piezometric, hydrochemical and isotope data has allowed for the identification of areas of recent recharge, discharge and no-flow boundaries. For example, present-day recharge was confirmed in outcrop areas representing 'windows' of aquifer outcrops in the impermeable basalt cover. Hydraulic considerations and numerical modelling indicate that the magnitude of groundwater flow involving the deep aquifer is limited. On the other hand, discharge mechanisms have not been fully studied owing to the difficulties in measuring small discharges of groundwater in areas with large runoff. Besides discharge along the outcrop area on the borders of the aquifer, other factors affecting groundwater flow were studied. For instance, in areas characterized by the presence of dikes, chemical and isotope composition of springs discharging water to major rivers confirmed that deep aquifer water contributes to the flow. Similarly, the chemical and isotope composition of water in extensive wetlands located in Argentina suggest a deep aquifer contribution to baseflow.

Recent work has resulted in a revised conceptual model of the GAS that has important implications for the exploitation of groundwater in the GAS sectors, differentiated based on hydrochemical and isotope data. Groundwater extracted from the unconfined part of the aquifer is fully renewable due to the potential for enhanced recharge under intensive pumping. Water balance considerations indicate potential recharge in the order of 300–500 mm/year. However, these areas are vulnerable to pollution and other impacts of human activity. Groundwater extraction in the confined portion is economically feasible only to certain depths (about 400 m) and, therefore, a substantial amount of the water resources from deep horizons are not available for extraction. Owing to the hydraulic character of the deep confined aquifer, as shown by the long residence time of groundwater, the exploitation of this deep groundwater resource is controlled by the storage coefficient of the GAS. This groundwater usually presents higher mineralization and is well protected against pollution, although extraction would require comprehensive planning.

#### C.2. Improving understanding of hydrogeology in Morocco's Tadla Basin

The Tadla Basin is an important agricultural area situated in the centre of Morocco, where demand for groundwater is increasing greatly. Groundwater provides the majority of the freshwater supply for irrigation and cities and is taken from a multi-layered aquifer system. Early traditional hydrological studies have revealed important relationships between aquifer layers and the locations of recharge and discharge. More recently this aquifer system has been studied as part of several projects undertaken by the Agency, the Moroccan National Centre for Nuclear Energy, Sciences and Technology (CNESTEN), and the Moroccan water authority. Isotope data confirm that sedimentary layers separating the four aquifers of the Tadla Basin allow the hydrological mixing of groundwater between the aquifers, and that some mixing is indeed occurring. Spatial analyses of isotope data have resulted in interpolation maps for oxygen-18, tritium and carbon-14 in the Turonian, Eocene and Quaternary aquifers. These interpolations are important aids for understanding and visualizing hydrological trends across the basin within a given aquifer and also in illustrating differences between the aquifers.

As an example, interpolation of isotope data from the Turonian aquifer, the oldest and deepest aquifer of the multi-layered system and the most important water supply aquifer in the basin, provides very interesting results. Interpolation of carbon-14 data in the Turonian aquifer (Fig. III-4) shows high activity of carbon-14 (expressed as per cent modern carbon (pMC)) in the northeast (green colours) compared to the west side of the basin (coloured red). Greater carbon-14 activities in the northeast are indicative of recent recharge. Interpolation of tritium ages in the Turonian aquifer (not shown) supports the supposition of relatively young water in the northeast part of the aquifer. Carbon-14 and tritium interpolations also show that the confined aquifer zone in the west is characterized by relatively older water (low carbon-14 activity and low tritium content). These interpolations highlight the fact that recharge is greatest in the northeast of the basin and suggest a dominant groundwater flow from northeast to southwest.



FIG. III-4. Spatial distribution of carbon-14 activities in the Turonian aquifer in per cent modern carbon (pMC).

Interpolation of oxygen-18 data for the Turonian aquifer (Fig. III-5) also reveals strong differences across the basin. The effect of high elevation recharge is clearly shown by more negative isotope values along the southern border with the high Atlas Mountains/Tassout area (coloured blue) as compared to more positive values in the northern parts of the basin (coloured orange). Interpolation maps of isotopic data are similarly useful for interpreting details of groundwater movement in the other aquifers of the Tadla Basin.



FIG. III-5. Spatial distribution of oxygen-18 contents in the Turonian aquifer in per mil vs Vienna Standard Mean Ocean Water (VSMOW).

The application of isotope techniques in the Tadla Basin has resulted in a greater understanding of aquifer characteristics and groundwater flow. Specifically, isotopic techniques have provided confirmation of observations obtained using traditional hydrological investigations, have identified the source aquifer for the Tassout Springs (disproving an earlier hypothesis), and have supported a better calibrated numerical model used for the simulation of groundwater dynamics. In these ways, isotopes have been directly used to support the optimization of groundwater management in the Tadla Plain.

#### C.3. New light shed on the Nubian Aquifer

A joint project by the Agency, the United Nations Development Programme (UNDP) and the Global Environment Facility (GEF) on the Nubian Sandstone Aquifer System (NSAS) is primarily aimed at developing a four-country cooperative strategy for the rational management of this transboundary aquifer system. The NSAS — underlying Chad, Egypt, Libyan Arab Jamahiriya and Sudan — is a single, massive reservoir of high quality groundwater (Fig. III-6). Yet the NSAS has very different characteristics in each country and each country has different development objectives for the aquifer.



FIG. III-6. Map showing the location of the Nubian Aquifer.

An essential first step in developing management strategies for the NSAS is to understand both the transboundary and local effects of producing water from the aquifer under present rates of withdrawal as well as under development scenarios in the future. This understanding is being gained through the development of a numerical groundwater flow model of the aquifer system. A critical step in the development of this model has been the use of groundwater age to constrain aquifer parameter values to provide reliable simulations of groundwater flow systems.

The NSAS model has had to meet several unique criteria. It has to be conceptually simple to accommodate limited information on aquifer hydrogeology and sparse observations of water levels. The model also has to provide realistic estimates for this very large aquifer spanning approximately two million square kilometres. And perhaps most importantly, the model has to earn the approval of national coordinators and technical experts from the four participating countries.

A number of previous studies have indicated that groundwater in the NSAS is about 40 000 years old, as indicated by the presence of measurable carbon-14 activity in deep groundwater samples. However, using krypton isotopes (krypton-81), groundwater recovered from production wells near oases in the western desert of Egypt has been estimated to vary in age from about 200 000 to 1.5 million years. To resolve this discrepancy in groundwater age, three samples of groundwater from Sudan were collected and analysed for carbon-14 using two methods: chemically treating 50–200 L of water to extract carbon, and analysis using accelerator mass spectrometry (AMS), which requires only one litre of water and no chemical treatment in the field.

Results indicate large differences between conventional and AMS methods for the same groundwater sample. AMS analysis indicates an age beyond the range of the carbon-14 dating technique (~50 000 years),

whereas traditional, chemical extraction techniques indicate an age of about 20 000 years. This younger age estimate is probably due to contamination with atmospheric carbon dioxide during the sampling and extraction processes. AMS measurements are considered to be much more reliable as they do not require chemical treatment of large samples. Therefore, it was concluded that existing carbon-14 data from the NSAS for deep wells (showing ages of 20 000–40 000 years) are unreliable and that these samples probably have ages of greater than 50 000 years. This conclusion supports the findings from krypton analysis and, as a result, groundwater ages of 200 000 to 1.5 million years have been used in calibrating the groundwater flow model.

A calibrated model (Fig. III-7) was used to simulate groundwater flow in the NSAS for the past three million years, with wet and dry periods represented using approximate palaeoclimate records. The threedimensionality of the model permitted the use of 'particle tracking', or tracing the movement of individual water parcels through the aquifer system. This enabled estimation of the age of water at any location and time during the simulation. By adjusting porosity, the model was refined to correctly simulate the age of water in the aquifer. Thus refined, model simulations provide visualization of groundwater recharge and discharge locations as well as subsurface flow paths. The interpretation of isotope data from NSAS water will continue to play an important role in model refinement and comprehensive groundwater management at both regional and finer scale grid sizes.



FIG. III-7. Oblique views of the geometry for the earlier two-dimensional NSAS groundwater model (above) and the three-dimensional NSAS groundwater model (below). Pumping areas are shown in blue. Two-dimensional models must assume that the effects of pumping reach through the entire thickness of the aquifer. For thick aquifer systems, a three-dimensional model can provide a more accurate depiction of the local influences of pumping.

# D. Role of isotopes in national assessments of water resources as first step in groundwater management

A new initiative has been launched by the Agency to facilitate the integration of isotopes into national water resource assessments conducted by Member States. This initiative, called the IAEA Water Availability Enhancement (IAEA WAVE) project, will assist Member States in identifying gaps in existing hydrological information and understanding, in improving national capacities for collecting, managing and interpreting water resource data, and in using advanced techniques to simulate hydrological systems for resource management. Isotope techniques have an important role to play in providing fundamental information on water resources, as well as providing broader insight into aquifer characteristics and hydrological settings. As a result of addressing these gaps in hydrological information and understanding, the capacity of Member States to conduct comprehensive national water resource assessments will be strengthened. The IAEA WAVE project aims to build on, and complement, other international, regional and national initiatives to provide decision makers with reliable tools for better management of their water resources.

The pilot phase of the IAEA WAVE project is currently under way. In this phase, the Agency is cooperating with selected Member States to identify and characterize gaps in national water resource assessments, and to develop a work programme aimed at strengthening local capacity to address these gaps. Where isotopic techniques are involved, the Agency has a primary responsibility to provide support and training. Other components of the work programme will be met by locating and recommending expert support, technological support, and training within the international hydrological community. Successful IAEA WAVE pilot studies will provide valuable information on water availability as a direct result of increased hydrological expertise and technological capabilities of Member States, with a particular focus on the application of isotopic techniques to groundwater resources. The project will strengthen Member States' capacities to develop and regularly update water resource assessments, and to design and implement resource management strategies.

## E. Summary

Studies using stable and radioactive isotopes are being conducted more frequently in support of comprehensive groundwater management as the time and cost effectiveness of these techniques is recognized. In the Guaraní Aquifer System of South America, the Tadla Basin of Morocco and the Nubian Sandstone Aquifer System of northern Africa, interpretations of isotope data have been used to not only confirm traditional hydrological studies, but also to provide insight into groundwater flows and aquifer dynamics. In particular, isotopes have been used in these areas to define groundwater recharge sources and mechanisms, to determine groundwater age and rate of movement, and to quantify the mixing of groundwater between aquifers. Isotope techniques have additional applications and it is expected that all applications will be considered and potentially employed during the IAEA WAVE project pilot phase. The application of isotopic techniques in hydrological investigations in general and in the comprehensive management of groundwater resources in particular is expected to grow substantially in the coming years.