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Using Isotopes for Design and Monitoring of Artificial Recharge Systems

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USING ISOTOPES FOR DESIGN AND MONITORING OF ARTIFICIAL RECHARGE SYSTEMS

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FOREWORD

Over the past years, the IAEA has provided support to a number of Member States engaged in the implementation of hydrological projects dealing with the design and monitoring of artificial recharge (AR) systems, primarily situated in arid and semiarid regions. AR is defined as any engineered system designed to introduce water to, and store water in, underlying aquifers. Aquifer storage and recovery (ASR) is a specific type of AR used with the purpose of increasing groundwater resources. Different water management strategies have been tested under various geographical, hydrological and climatic regimes. However, the success of such schemes cannot easily be predicted, since many variables need to be taken into account in the early stages of every AR project.

As often occurs in the case of the assessment and management of groundwater and aquifers, information on hydrological behaviour and response to human-made actions is difficult to obtain and often very costly, especially if only conventional hydrological methods are used. Classical methods in AR and ASR are meant to provide information on changes in the volume and quality of the artificially introduced water to ensure its sustainability. Although the use of isotopes and geochemical tracers to plan and monitor AR and ASR has been limited, there is a growing number of publications reporting the successful application of tracers in the different phases of AR and ASR schemes.

This publication discusses several theoretical aspects important to the understanding, planning and monitoring of AR and ASR schemes and presents a selected number of examples illustrating the usefulness of isotopes and other tracers. One section presents the list of available isotope tracers, indicating the type of information that can be obtained from each. The case studies presented in this publication illustrate the use of these tools in the different stages of AR and ASR schemes.

The publication is expected to be of interest to hydrologists and water managers in areas where intensive exploitation of available water resources leads to shortages of water and where AR is being considered or is being implemented.

The IAEA officers responsible for this publication were B. Newman and L. Araguás-Araguás of the Division of Physical and Chemical Sciences.

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CONTENTS

1. INTRODUCTION

1.1. BACKGROUND

Water scarcity and water quality problems continue to be major societal concerns around the world. Population growth, increased need for food production and other pressures are expected to substantially increase the need for fresh water supplies. An additional consequence of rising demands will be increasing reliance on groundwater supplies. Therefore, many countries and local to regional water agencies are looking for ways to augment the amount of groundwater available for use. Promotion of surface water transfer (e.g. from reservoirs, ponds, springs, treated wastewater, etc.) to groundwater can be accomplished using a variety of engineering designs and there are many different terms used to describe this process. Artificial recharge, aquifer storage and recovery, aquifer recharge, managed recharge, and engineered recharge have all been used to describe ways of augmenting groundwater supplies. It is not the purpose of this guidebook to discuss the intricacies of the similarities and differences between these terms (partly because definitions can vary). However, the reader should be aware that many different terms are used and that in some countries or districts these terms can have very specific legal meanings and implications. For this guidebook we will restrict usage to the terms artificial recharge, and aquifer storage and recovery. Artificial recharge (AR) is probably the most commonly used term historically and for the purpose of this publication it means any engineered process (passive or active) that promotes transfer of surface water to groundwater regardless of the intended use or benefit. Aquifer storage and recovery (ASR) is more specific and refers to systems where the major objective is to store water in an aquifer system for later use as, for example, a drinking water supply or for agriculture. AR and ASR systems typically involve either injecting water into an aquifer through wells (an active design) or by surface spreading and percolation (a passive design). For ASR, the aquifer is essentially used as a water bank where surplus water is stored and withdrawn in times of need. ASR is also used to improve water quality because the process of unsaturated and saturated flow can promote reduction of contaminant concentrations through geochemical or biogeochemical processes.

There are various methods used for AR and ASR. Introduction of water into the subsurface can be promoted via reservoirs, river banks, channels or trenches, sprinkling networks, infiltration basins or injection wells. Depending on the quality of the infiltrating water and purpose of the managed recharge, different methods may be applied. Direct pumping of excess fresh water into a targeted aquifer using injection wells is also used to store water for later recovery. Periodic storing of surplus rainwater or surface runoff for later use is the main reason for AR in arid and semi-arid regions. Another objective of AR is water treatment, because soil, sediments, and rock provide natural purification media for surface waters. However, it is necessary for the injected or percolated water to have sufficient residence time in the subsurface so that the proper reactions and interactions occur. In this case, surficial infiltration techniques are generally used. A residence time of a few weeks to a couple of months between the infiltration area and the wells is typically needed in order to obtain the required purification level. Commonly applied infiltration methods include basin and bank infiltration as well as sprinkling infiltration, which is enhanced through continuous pumping directly onto forested soil. This method is commonly used for water treatment in regions with abundant surface water resources and many glaciofluvial deposits, such as in northern Europe.

The main benefits and uses of AR include treatment, storage, adjustment of groundwater levels, aquifer recharge, and prevention of saltwater intrusion. Substantial amounts of water can be stored deep underground which may reduce the need to construct large and expensive surface reservoirs. Subsurface storage systems are considered to be more environmentally friendly than surface reservoirs. They also offer more protection from tampering. In addition, AR may restore and expand the function of an aquifer that has experienced long term declines in water levels due to heavy pumping necessary to meet growing urban and agricultural water needs.

1.2. OBJECTIVES

Isotopes are underutilized in AR and ASR projects, but are very powerful tools for: (1) planning projects; (2) monitoring and improving efficiency/optimization; and (3) understanding water quality aspects. The objective of this publication is to encourage greater use of isotope methods for AR and ASR projects by providing discussion and examples of the kinds of issues that isotopes can address.

1.3. SCOPE OF THE REPORT

This report discusses the use of a wide variety of stable isotope and radioactive isotopes for AR and ASR studies. It covers applications relevant to passive recharge approaches (e.g. ponded infiltration) as well as active approaches (direct pumping of water into an aquifer system). It is intended to be a resource not only for hydrologists, but also for water managers and policy makers who are interested in knowing how isotopes may be effectively used as part of AR and ASR investigations and monitoring programmes.

1.4. STRUCTURE

This report contains five sections (including this introduction section) which are arranged by topic. Section 2 focuses on basic isotope systematics to provide the necessary background to understand the terminology and discussion in subsequent sections. Section 3 focuses on how isotopes can be used to improve planning at future artificial recharge sites and highlights how valuable isotope studies can be before actually implementing the artificial recharge process. Section 4 describes how isotopes can be used to monitor and evaluate the effectiveness of actual ASR processes which are critical aspects of managing a site or facility. Section 5 discusses how isotopes can be used to understand important water quality and geochemical aspects related to AR and ASR. In addition to general discussion about the various isotope methods, the last three sections contain descriptions of case studies which help illustrate how isotopes are actually applied and demonstrate the benefits of incorporating isotopes in the planning, monitoring, and evaluation stages of implementing AR or ASR schemes at a particular site.

2. BASIC ISOTOPE SYSTEMATICS

2.1. STABLE ISOTOPE NOTATIONS AND EXPRESSIONS

Stable isotopes are powerful tracers of hydrological processes and as such, will be discussed extensively in this guidebook. As their name implies, stable isotopes are 'stable' meaning that they do not undergo radioactive decay. Because stable isotope values only change as a result of certain processes (e.g. evaporation or mixing) they are very useful tools for identifying sources of water, evaluating interactions between different water types (e.g. surface water and groundwater), and for understanding geochemical reactions that might occur in groundwater systems. Stable isotope values for oxygen, carbon, and hydrogen are not reported as concentrations, but instead are expressed as relative isotope ratios in units of per mil (‰) using what is known as delta (δ) notation [1]:

$$\delta^{i}E = \left[\frac{R_{\text{sample}}}{R_{\text{reference}}} - 1\right] \times 1000‰ \qquad (1)$$

where i is the atomic mass of the heavier isotope of the element E (O for oxygen, C for carbon, H for hydrogen), R_{sample} is the ratio of the abundance of the heavier isotope of the element (^{18}O, ^{13}C, ^{2}H) to the lighter isotope of the element (^{16}O, ^{12}C, ^{1}H) in the sample and, $R_{\text{reference}}$ is the ratio of the abundance of the heavier isotope of the element to the lighter isotope of the element in the reference material.

The reference material for oxygen and hydrogen is Vienna Standard Mean Ocean Water (VSMOW), which is assigned δ^{18}O and δ^{2}H values of 0‰ (note that δ^{2}H is sometimes written as δD because the common name of the heavier isotope of hydrogen, hydrogen-2, is deuterium). The reference material for carbon is Vienna Pee Dee Belemnite (VPDB), which is assigned a δ^{13}C value of 0‰. Positive values indicate enrichment of the heavier isotope and negative values indicate depletion of the heavier isotope, compared to the ratios observed in the standard reference material.

2.2. SYSTEMATICS OF OXYGEN AND HYDROGEN STABLE ISOTOPES IN HYDROLOGY

A starting point in any isotope hydrology study is to examine the isotopic composition of local surface waters. Precipitation and groundwater have distinct stable isotopic ratios based on their location as a result of natural fractionation processes. Most of atmospheric moisture is produced by evaporation at the surface of subtropical oceans [2]. Because the VSMOW international standard approximately represents 'mean ocean water', it is often (but not always) close to the δ values of oxygen and hydrogen in ocean water (e.g. ~0‰). Isotopic fractionation during the evaporation of ocean water and subsequent condensation of water in clouds leads to a depletion of ^{18}O and ^{2}H and thereby negative δ values in fresh waters compared to ocean waters [3]. The gradual rainout process preferentially removes the heavier isotopes ^{18}O and ^{2}H from the air mass [2]. This can be recognized as a gradual decrease in the δ^{18}O and δ^{2}H values in atmospheric vapour and precipitation as an air mass moves towards the poles and is known as the *latitude effect* [4]. A similar depletion of the heavier isotopes takes place as moist air masses move inland or to a higher altitude, known as the *continental effect* and the *altitude effect*, respectively [4–10]. In tropical marine regions the *amount effect* leads to a strong depletion of ^{18}O and ^{2}H in connection with intense rain events [4, 10–12]. The amount effect is a form of *seasonality* in equatorial areas. In the mid and high latitudes of the northern hemisphere, the most distinctive source of seasonal variation is related to temperature, which causes greater depletion of ^{18}O and ^{2}H in precipitation during the cold winter months [7]. In continental interiors, seasonal variations in the isotopic composition of precipitation are much more pronounced than that of coastal areas [11]. Paleoclimate reconstructions based on $\delta^{18}O$ and $\delta^{2}H$ groundwater records rely upon evaluating these different effects in order to accurately quantify the temperature and humidity changes over time (e.g. [13, 14]).

Groundwater is formed from percolation of atmospheric precipitation and thereby it is essential to understand at some level the factors affecting the isotopic composition of precipitation occurring in a basin. A certain aquifer may, for example, have a broad catchment area which collects recharge waters from different altitudes with distinct isotopic compositions. Seasonal $\delta^{18}O$ and $\delta^{2}H$ variations in precipitation are generally smoothed out during groundwater infiltration. However, some seasonality may exist depending on the hydrological properties, size and thickness of the vadose zone of the aquifer [15, 16]. Alternatively, groundwater may become isotopically distinct from precipitation through *selective recharge* or *isotopic fractionation* effects related to *evapotranspiration* and *runoff* (e.g. [15, 17]). Evapotranspiration and runoff mechanisms are related to climate and, especially in higher latitudes, to changing seasons. In low temperature, shallow aquifers, the isotopic compositions of oxygen and hydrogen are conservative parameters, which can generally only change by mixing with isotopically different water masses [18, 19]. Meteoric waters — referring to waters circulated through the atmosphere, including precipitation, groundwater, surface water, pore water, ice caps and glaciers — globally show a linear correlation between $\delta^{18}O$ and $\delta^{2}H$ values. This relationship is called the global meteoric water line (GMWL) [3]. The line is defined by the equation:

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

This relationship, presented in Fig. 1, has been confirmed in many later studies [11]. The isotope data of meteoric waters from Finland have been illustrated against the GMWL in Fig. 1. The global line is actually a combination of numerous local meteoric water lines, as any given locality will have a characteristic local meteoric water line (LMWL) with somewhat different slope and intercept. A local line can reflect the origin of the water vapour and subsequent modifications by secondary processes of re-evaporation and mixing [15]. It is recommended that any detailed hydrogeological study using $\delta^{18}O$ and $\delta^{2}H$ should attempt to define the LMWL as best as possible. Additional information about the global distribution of stable isotopes and tritium in precipitation can be found through the IAEA Water Resources Programme Website www.iaea.org/water through the IAEA Global Network of Isotopes in Precipitation (GNIP) link.

In isolated surface water reservoirs, such as lakes and rivers, the water mass is exposed to evaporation, which leads to isotopic enrichment and to an offset of the $\delta^{18}O$ and $\delta^{2}H$ values to the right of the meteoric water line. Compared to the GMWL or a LMWL, the slope of the evaporation line varies from 3.9 to almost 8, depending on local relative humidity, h [20]. In practice, significant differences are often recorded in $\delta^{18}O$ and $\delta^{2}H$ between local groundwater and surface water reservoirs.

2.3. SYSTEMATICS OF TRITIUM IN HYDROLOGY

When tritium, a radiogenic isotope of hydrogen, is incorporated into the hydrologic cycle, it provides information about residence time and movement of water in the subsurface. As a hydrologic tracer, tritium can be used to investigate groundwater movement resulting from applied or managed aquifer recharge.

Tritium (^{3}H) is a short lived radioactive isotope of hydrogen with a half-life of 12.32 years [21]. Tritium concentrations are expressed as tritium units (TU), where the ^{3}H activity of 1 TU denotes 0.118 Bq/kg of water in the SI system or 3.19 picocuries per liter (pCi/L). Tritium is produced naturally in the atmosphere from the interaction of cosmogenic radiation with nitrogen [22], by above ground nuclear explosions, and by the operation of nuclear reactors. Following the release of large amounts of tritium into the atmosphere from nuclear bomb testing in the 1950s and 1960s, the International Atomic Energy Agency (IAEA) implemented a global monitoring programme of tritium in precipitation [12], and since then tritium has been used extensively as a tracer in hydrology [23, 24].

Tritium is a useful hydrologic tracer because it rapidly oxidizes into tritiated water (HTO) and enters the hydrological cycle. HTO typically resides in the atmosphere less than one year before it is removed, primarily through precipitation. HTO acts very similarly to other water molecules, which makes it a useful tracer of the water cycle. Knowledge of the distribution of tritium, and its calibrated rate of decay, enables the estimation of the timing and rates of groundwater recharge, flow and mixing.

Natural levels of tritium were from 1–20 TU in continental precipitation and 0.5 TU in the surface ocean prior to nuclear bomb testing in the 1950s [25]. Nuclear weapons testing in the 1950s and 1960s increased the level of tritium (bomb-tritium) in the atmosphere by two to three orders of magnitude, overwhelming naturally produced tritium [24, 26]. Tritium is a transient, relatively short-lived radiogenic isotope; as such, bomb tritium was removed from the atmosphere and entered the hydrologic cycle; decaying into ^{3}He at a constant rate. Precipitation data collected by the IAEA allowed for a subsequent estimate of the tritium input function, or yearly tritium deposition for a given location [12, 24] (Fig. 2). Consequently, the presence of ^{3}H in ground water can identify water that has undergone exchange with the atmosphere over the past ~50 years .

The use of bomb tritium in hydrologic investigations includes studies of circulation and mixing in oceans (e.g. [27–30]), and lakes (e.g. [31, 32]), as well as for groundwater movement, mixing, and timing of recent recharge (e.g. [33–39]). Bomb tritium is introduced as a transient tracer at the atmospheric interface and subsequently mixes into the aqueous system. Interpretation of tritium distributions in marine or freshwater systems is complicated by variations in the tritium input function, and the dispersion and radioactive decay of the bomb tritium signal. In order to use tritium as a tracer, it is thus necessary to determine the tritium concentration of the input source (precipitation or surface water) to the system (e.g. Fig. 2). These challenges are overcome by the construction of historical cumulative deposition maps based on data from networks which monitored monthly tritium in precipitation. Where temporal data are missing at a given site, deposition estimates can be obtained, for example, based on correlation with the Ottawa tritium precipitation function [24]. With these methods it is possible to calculate the yearly tritium deposition and precipitation (input function) for any given latitude and longitude [24]. Tritium inputs can also be estimated using the model of Doney et al. [40] (see also Ref. [41]).

Tritium is a useful tracer in ASR studies because groundwater samples which contain greater than 0.3 TU may be classified as ‘modern’ water, that is, groundwater that was recharged after 1950. As such, ASR water is tritium ‘live’ (>0.3 TU) and often distinct from older native groundwater that is tritium ‘dead’ (~0 TU), allowing the movement and distribution of ASR water to be determined.

2.4. ^{3}H–^{3}He QUANTITATIVE GROUNDWATER DATING

Tritium-helium-3 (^{3}H–^{3}He) determinations of groundwater samples allow for the quantification of groundwater residence times for groundwaters less than ~60 years old. Tritium–helium-3 groundwater residence times (ages) provide information about the rates of water movement in the subsurface resulting from applied or managed aquifer recharge.

The use of ^{3}H, combined with its daughter ^{3}He, to study groundwater flow was first proposed by Tolstikhin and Kamenskiy [42], however analytical challenges slowed the application of the ^{3}H–^{3}He method to hydrological systems. Measurement of ^{3}H by the mass spectrometric determination of its daughter ^{3}He [43] advanced the widespread use of the ^{3}H–^{3}He method. Early studies of marine and lacustrine systems made use of this method (e.g. [44–47]). A decade later, the calculation of groundwater residence times (ages) using ^{3}H–^{3}He dating was made possible when the ^{3}He from tritium decay ($^{3}He_{tri}$) was successfully distinguished from other sources (e.g. [48–50]). The determinations of water residence times through ^{3}H–^{3}He dating in lakes and groundwaters are now used extensively to study transport and mixing processes.

The ^{3}H–^{3}He method provides a quantitative determination of groundwater residence time based on accumulation of the inert gas ^{3}He, the β-decay product of tritium. When tritiated groundwater decays, the released ^{3}He ($^{3}He_{tri}$) remains dissolved until the groundwater interacts with the atmosphere. The tritium–helium clock thus starts when $^{3}He_{tri}$ is no longer lost from the system, and begins accumulating with the decay of ^{3}H. The time the water has resided in the aquifer can be calculated by determining $^{3}He_{tri}$ (e.g. [48, 50]). This technique, based on measuring the ratio of $^{3}H/^{3}He_{tri}$, is more precise than using tritium alone because it does not depend on the tritium input function or atmospheric tritium content at the time of recharge. Instead, the ^{3}H–^{3}He method is based on the assumption that groundwater is a closed system, and that the $^{3}He/^{3}H$ ratio increases with time. Thus, the calculated ^{3}H–^{3}He age can be determined from the equation:

$$\tau = \frac{1}{\lambda}\left[1 + \frac{[^{3}\mathrm{He}_{\mathrm{tri}}]}{[^{3}\mathrm{H}]}\right] \qquad (3)$$

Where τ is the^{3}H–^{3}He age in years, λ is the decay constant, and the other terms are as defined above. This approach only depends upon the initial ^{3}H activity and its daughter product $^{3}He_{tri}$, which may be isolated from the total ^{3}He dissolved in groundwater (e.g. [48, 50]).

Determining groundwater age distribution is useful in ASR studies in order to better understand the subsurface movement of recharged water. The age structure of an aquifer may be delineated by ^{3}H–^{3}He groundwater ages from wells distributed around a recharge site.

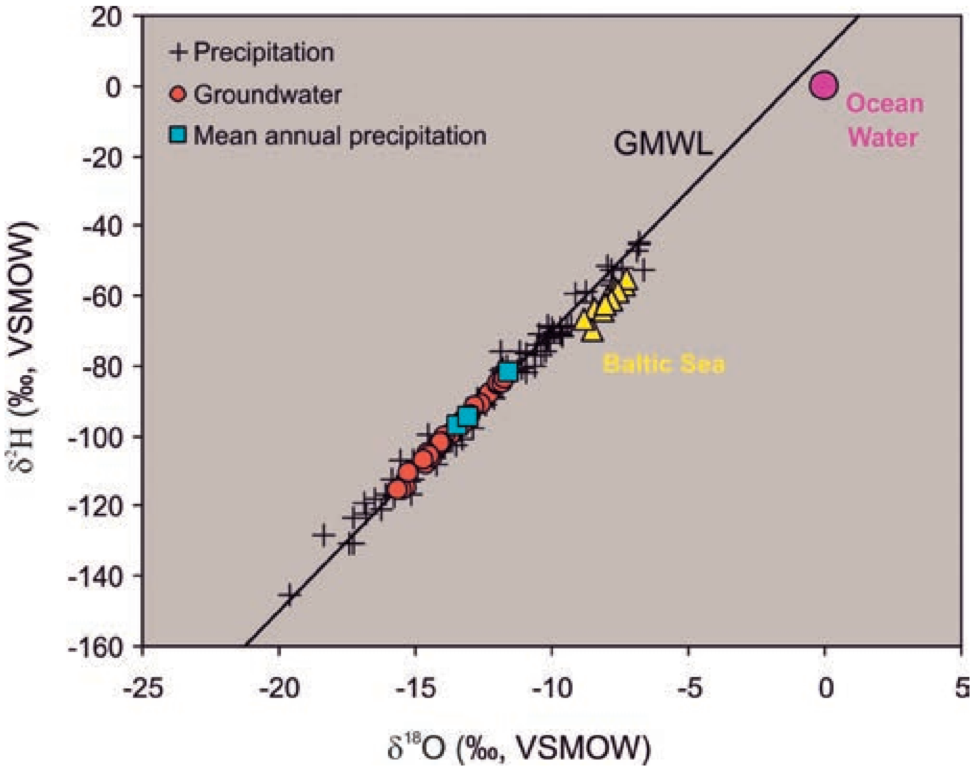


FIG. 1. Linear correlation of oxygen and hydrogen ratios in global meteoric waters (GMWL). Isotopic composition of Finnish precipitation and groundwater plot on the GMWL; Baltic Sea water is slightly displaced from global line. Brackish Baltic Sea water is mixture of evaporated surface waters from surrounding areas and sea water from the Atlantic Ocean.

2.5. NOBLE GAS RECHARGE TEMPERATURE AND EXCESS AIR (ΔNe)

Noble gas (He, Ne, Ar, Kr and Xe) concentrations, and the parameters derived from these values (noble gas temperature, recharge altitude, recharge salinity, fractionation by diffusive gas loss, and entrained air), provide tools to study groundwater recharge processes including the extent and movement of ASR groundwater. A thorough discussion of the calculation of groundwater noble gas temperature (recharge temperature) and the various models that describe the dissolution and/or diffusive processes governing bubble fluid interactions is provided in [51–54] also discuss some key issues related to the use of noble gas tracers and the use of ‘young’ groundwater tracers in general.

Noble gases dissolved in groundwater provide a measure of water temperature at the time of recharge. As such, groundwater noble gas paleoclimate reconstructions provide a unique absolute temperature record. These low resolution records are based on knowledge of noble gas solubilities in water, which increase in a non-linear fashion as water temperature decreases, as described by Henry’s Law (e.g. [51, 53, 55, 56]). Xenon exhibits the greatest sensitivity to temperature changes, and Ne the least (He is not used as its solubility is virtually insensitive to temperature). These solubility characteristics enable creation of a soil temperature record, and consequently the localized climate, at the time of groundwater recharge, to be derived from the concentrations of noble gases in groundwater. The method of deriving recharge temperatures using four independent parameters (Ne, Ar, Kr, Xe) also allows for calculation of the amount of any gas in excess of its atmospheric solubility equilibrium concentration; in this respect, Ne is the most sensitive noble gas because of its relatively low solubility in water and dominantly atmospheric origin. Thus, neon in excess of solubility (ΔNe) can be used as a proxy for ‘entrained air’: as such, it has successfully identified periods of increased aquifer recharge when large fluctuations in the water table have been accompanied by air entrainment [13–14, 53, 57]. ΔNe is calculated by the following equation:

$$\Delta Ne = \left[\frac{Ne_{\text{sample}}}{Ne_{\text{eq}}} - 1 \right] \times 100 \tag{4}$$

where $\mathrm{Ne_{sample}}$ is the concentration ($\mathrm{cm^3STP\ Ne/g\ H_2O}$) of neon measured in the sample and $\mathrm{Ne_{eq}}$ is the concentration of neon from air equilibration of the recharging groundwater. $\mathrm{Ne_{eq}}$ is calculated from the noble gas recharge temperature derived from concentrations of Ne, Ar, Kr, and Xe in the groundwater sample.

Laboratory experiments have provided evidence in support of the excess air mechanism [58–60]. In this respect, noble gases also provide a record of paleohumidity.

2.6. CARBON IN NATURAL WATERS

Dissolved species of organic and inorganic carbon are involved in important redox reactions taking place in hydrogeochemical processes. In subsurface waters, the two main isotopically distinct sources of DIC are soil CO_2 derived from respiration and microbially decomposed organic matter, and dissolved carbonate species resulting from the dissolution of carbonate minerals [15]. In open water bodies an atmospheric carbon source also exists. The expected $\delta^{13}C_{DIC}$ value for rainwater in equilibrium with atmospheric CO_2 is around –9‰, as the $\delta^{13}C$ for the present atmospheric CO_2 is –8‰ [61].

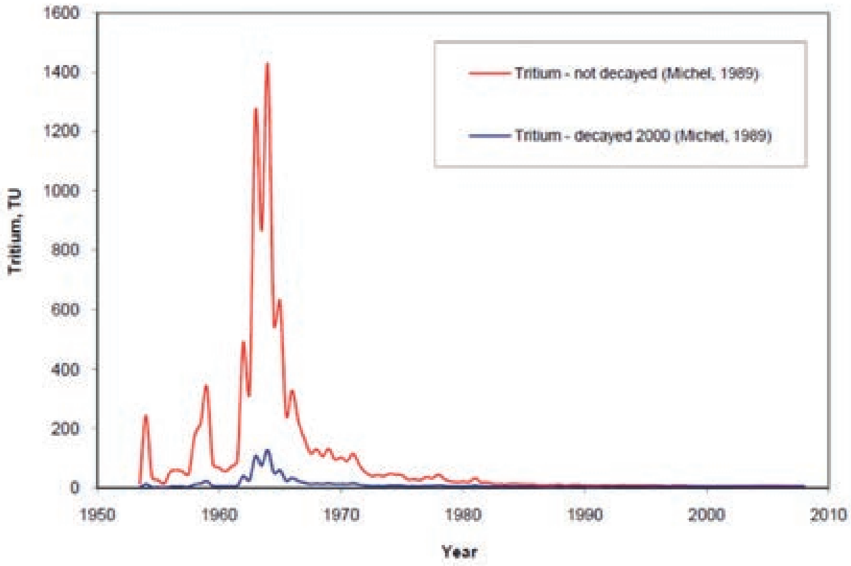


FIG. 2. Plot of Santa Maria tritium precipitation curve and tritium concentration decayed to the levels in year 2000.

Total dissolved inorganic carbon is a pH dependent mixture of carbonate species in varying dissociation stages and is expressed as $\sum CO_2 = mH_2CO_3 + mHCO_3^- + mCO_3^{2-}$. Besides other isotopically distinct DIC sources, the $\delta^{13}C_{DIC}$ of water is dependent on fractionation between the dissolved carbonate species and CO_2. In surface water, dissolved organic carbon (DOC) generally comprises about 90% of total organic carbon (TOC) [62]. In most groundwaters DOC contents are generally below 2 mgC/L [62]. DOC is comprised of humic substances (80–90%), fatty acids, carbohydrates, amino acids and hydrocarbons. The isotopic composition of DOC is controlled by the vegetation type dominating in the area [15]. For example, in terrestrial high latitude regions the $\delta^{13}C$ value of C_3 vegetation is typically around –27‰ [63–65]. Diffusive loss of soil CO_2 from soil profiles fractionates carbon, and the $\delta^{13}C$ values of soil CO_2 are thereby generally about –23‰ [66, 67]. Groundwaters in crystalline bedrock terrains have a low pH (< 7), and generally record nearly the same $\delta^{13}C$ as that in soil CO_2 [67–69]. The existence of carbonate minerals in aquifer materials brings an additional carbon source to the DIC pool. The carbon isotope composition of sedimentary marine carbonates has generally remained at 0 (±3) ‰ throughout geological history [70]. In diagenetic carbonates $\delta^{13}C$ values are typically lower than those in marine carbonates. Generally, the dissolution of carbonate minerals tends to shift the $\delta^{13}C_{DIC}$ to higher values compared to those of the initial DIC in water.

Carbon-14 (^{14}C) activities (radiocarbon) can be used to date older groundwaters and to understand sources of DIC in the geochemical evolution of groundwater. The radioactive isotope ^{14}C is formed in the upper atmosphere by cosmic radiation. The half-life of ^{14}C is 5730 years [71]. Carbon-14 activities are expressed as percent modern carbon (pmC). The fractions of CO_2, DIC and DOC derived from the living biomass record of ^{14}C activities is close to the modern atmospheric level of ~100 pmC [63]. The ^{14}C method has been widely used to date groundwaters from the late Quaternary period [15]. Carbon matter older than this is generally free of ^{14}C, i.e. the ^{14}C activity of 'dead carbon' is 0 pmC.

The $\delta^{13}C_{DIC}$ values and the activities of $^{14}C_{DIC}$ can be used to evaluate the degree of openness of a groundwater system with respect to soil CO_2 (e.g. [15, 63]). In a carbonate-free environment, under both open and closed system conditions, the isotopic composition of soil CO_2 defines the $^{14}C_{DIC}$ activity and the $\delta^{13}C_{DIC}$ value in groundwater [67]. In carbonate terrains, however, DIC is derived from isotopically distinct carbon sources. Under both open and closed system conditions, the dissolution of calcite increases the $\delta^{13}C_{DIC}$, but the magnitude of the shift in $\delta^{13}C_{DIC}$ is dependent on the amount of CO_2 available to promote calcite dissolution. In open systems, regardless of calcite dissolution, soil CO_2 prevails, and $^{14}C_{DIC}$ activities remain at around 100 pmC. Under closed system conditions, however, modern $^{14}C_{DIC}$ composition is diluted by ^{14}C-dead carbon sources. Similarly, the decomposition of organic matter with a distinct ^{14}C signature would affect the activity of $^{14}C_{DIC}$ in groundwater. In addition, the decay of DOC may add isotopically light DIC to groundwater, thus decreasing the $\delta^{13}C_{DIC}$. Mixing of waters with distinct $^{14}C_{DIC}$ and $\delta^{13}C_{DIC}$ may also affect the isotopic composition of DIC. All these processes may be investigated and quantified using analyses of $\delta^{13}C_{DIC}$ and $^{14}C_{DIC}$.

2.7. ISOTOPE SAMPLING AND ANALYSIS

Prior to sampling, wells should be pumped continuously until water parameters (temperature, specific conductance, pH, and turbidity) stabilize (generally about three casing volumes of water are purged). Clean Teflon tubing with stainless steel fittings attached to a sampling point on the well discharge pipe as close to the well head as possible are recommended. The sampling point should be located as close as possible to the well head, upstream from water storage tanks, and from the well head treatment system (if any).

Collecting water samples for deuterium and oxygen-18 analyses is simple and has no special requirements. Water samples are collected in ~50 mL, high-density polyethylene (HDPE) plastic or glass screw cap bottles. Do not field rinse the bottles. Do not add chemical treatment. Fill bottles two-thirds full with water so that if a sample expands or freezes during shipping, the bottle will not break. Cap each bottle with a Polyseal or double cap. Store at ambient temperature until shipment to the laboratory. Bottles should be tightly sealed to prevent evaporation which can substantially alter the stable isotope composition. Sealing caps with plastic tape or other impermeable material also helps prevent accidental leakage of the sample water.

Isotopes of oxygen and hydrogen are measured using isotope ratio mass spectrometer (IRMS) techniques or recently introduced techniques based on laser spectroscopy (e.g. [72, 73]). Compared to traditional IRMS techniques which measure isotope ratios, laser methods measure absolute abundances of ^{2}HHO, HH^{18}O and HHO. For a traditional IRMS analysis of δ^{18}O, water samples are equilibrated with CO_2 gas and the isotopic composition of CO_2 is analyzed [1, 74]. The isotopic composition of hydrogen is analyzed after the high temperature reduction of water to H_2 on metal [75], using either specially prepared zinc metal [76], chromium or uranium. An isotope exchange technique can also be adapted for hydrogen. In this case, a water sample is equilibrated with H_2 gas in the presence of platinum powder and the isotopic composition of H_2 is analyzed. Isotopic ratios of the produced CO_2 (for δ^{18}O) and H_2 are measured with an isotope ratio mass spectrometer. The values of δ^{18}O and δ^2H are reported based on the VSMOW–SLAP scale in per mil (‰); to values of –55.5‰ and –428‰, respectively, for SLAP (Standard Light Antarctic Precipitation) relative to VSMOW [1]. The repeatability of IRMS analyses is generally ≤ 0.1‰ for oxygen and ≤ 1.0‰ for hydrogen in water. With the laser spectroscopy technique, similar or slightly larger values are obtained (e.g. up to 0.2‰ for oxygen) depending on the method used [72, 73].

Carbon isotope samples are filtered prior to collection. For samples to be analyzed for δ^{13}C or ^{14}C (by accelerator mass spectrometry, AMS) groundwater is diverted through a 0.45 μm pore size vented capsule filter before bottom filling two 500 mL glass bottles. The bottles are overfilled with three bottle volumes of groundwater to purge atmospheric contamination and a small amount of preservative is added to prevent microbial growth. These samples are capped with no headspace, and are sealed with a conical or Teflon lined cap to avoid atmospheric contamination. The bottles are placed in a foam sleeve, and then refrigerated prior to analyses.

The analysis of δ^{13}C in dissolved inorganic carbon (DIC) in a water sample generally takes place either using a gas evolution technique or conventional precipitation techniques. An automated method for δ^{13}C analysis of DIC on continuous-flow IRMS has also been introduced [77]. In the gas evolution technique, DIC in a water sample is converted to CO_2 gas under vacuum conditions using a phosphoric acid reaction [78]. For this, alternative sampling and extraction techniques exist. In general, it is essential to avoid degassing of CO_2 and exchange with air in the sampling process of DIC for isotopic analyses. In the vacutainer gas evolution technique, water samples are filtered (<0.2 μm) into pre-evacuated glass septum tubes, loaded with 85% H_3PO_4 [79]. Often water samples are just placed into amber glass or heavy plastic bottles with tight caps and then taken to the laboratory for DIC extraction. No preservation of water samples is required if they are stored in cold and dark conditions and analyzed within a few days at the most after sampling. Microbial activity within a water sample can be reduced significantly by filtering the sample (<0.2 μm). However, for longer term storage, the addition of a preservative is recommended. In precipitation techniques, DIC is sampled for ^{13}C measurements by precipitating it from solutions such as Ba or Sr carbonate. The precipitate is reacted with phosphoric acid under closed system conditions. Depending on the method, certain purification and 'drying' procedures for collected CO_2 are followed and the isotopic ratio of carbon is measured on isotope ratio mass spectrometer. The repeatability of analyses is generally ≤ 0.2‰ for carbon in DIC. Carbon-14 analysis can be made using precipitates collected in the field or on water samples. Both accelerator mass spectrometry and liquid scintillation methods can be used to measure these samples [15] Carbon-14 activities are usually expressed as percent modern carbon (pmC). For more information about the extraction of DIC in natural waters for isotopic analyses see e.g. [15] or [80]. For sampling and analysis of ^{14}C in DIC and the $^{87}Sr/^{86}Sr$ ratio in water, see e.g. [15, 78, 81].

Groundwater samples for tritium analyses are collected by bottom filling a one liter glass or HDPE bottles. The sample bottles are bottom filled and allowed to overflow several times the amount of the bottle volume to purge atmospheric contamination before capping. Sealing the cap with tape prevents sample leakage. Tritium may be measured using liquid scintillation [82] with electrolytic enrichment [83], in which case the detection limit is a function of the statistics associated with the liquid scintillation counter. In general, the longer the counting time the greater the precision and the lower the detection limit. Alternatively, tritium may be measured using the mass spectrometric determination of its daughter isotope helium-3 [15], in which case the analytical error principally reflects counting statistics on the helium-3 ion beam. Tritium concentrations are often expressed as tritium units (TU), where the ^{3}H activity of 1 TU denotes 0.118 Bq/kg of water in the SI system, or 3.19 pCi/L.

For more information on sampling and analysis methods see Refs [15] and [73, 84, 85]. Note that the IAEA documents and videos are available through the IAEA Water Resources Programme webpage at www.iaea.org/water.

3. PLANNING ARTIFICIAL RECHARGE AND AQUIFER STORAGE AND RECOVERY SYSTEMS

3.1. INTRODUCTION

An artificial recharge (AR) project must sometimes overcome both years of consuming environmental and legal disquisitions as well as strong public opposition. The main concerns among citizens seem to be the threat of destruction of the original natural environment, aquifer contamination and the availability of groundwater in the surrounding area in light of artificial recharge activities. The types of AR projects are various, but longtime issues remain more or less the same; water companies struggle to fulfill the demands of permission procedures and, in the worst case, must go through all legal requirements. Naturally, environmental demands vary from country to country and state to state. Vulnerability of the surrounding environment/ecosystem also varies, depending on the location of an AR project. The extent of construction work is different in each operation area depending on the infiltration method chosen.

The most visible activities are likely surficial infiltration methods using ponds or ditches as well as sprinkling infiltration through forest floors. Where applicable, riverbank or lake bank filtration or infiltration wells can reduce the need to disturb the ground surface. The breaking of any ground changes the original scenery but eventually becomes a part of the landscape. The real challenges of managed recharge remain hidden underground. The volume and composition of infiltration water and natural recharge are usually significantly different and will change natural conditions in an aquifer. This is especially the case in active AR, where surface water is continuously introduced into an aquifer. Water companies and agencies should meet these challenges through thorough research prior to infiltration activities i.e. adopting the IAEA's 'fact before act' approach to planning. An effective artificial groundwater recharge scheme requires understanding of various fields including hydrogeology, sedimentology, geochemistry and geophysics. Isotope geology offers a very effective addition, in connection with these other methods.

Isotopic applications in AR may aid in coordinating: (1) planning of recharge plants, including infiltration methods and locations; (2) predicting water movement and responses of aquifer geochemistry to recharge; and (3) planning the monitoring of active plants. Optimally, the use of isotope methods would be initiated as a basic part of every AR project starting in the planning stage. In order to understand the response of a natural groundwater system to artificial recharge as well as the simple mixing of infiltrated water with local groundwater, the baseline geochemical and isotopic characteristics of an aquifer and involved waters should be monitored for a sufficiently long time period so that all normal variations of isotopes and geochemistry of groundwater are known.

The primary reason to use isotope methods is to provide information about the waters involved in an aquifer before and during active AR. The key isotopes used for this end are the traditional water isotopes, i.e. oxygen and hydrogen, which provide a geographically specific isotopic fingerprint through precipitation to groundwater. For best results, basic isotopic tools based on the isotopic composition of oxygen and hydrogen in atmospheric precipitation would provide background values in AR studies. This comprises defining the long term weighted mean annual isotopic composition of precipitation and the local meteoric water line (LMWL) (see Section 2.2). These will provide an idea of what proportion of modern precipitation is recharging a certain aquifers if any. Waters exposed to the atmosphere have distinctive isotopic labeling through surficial processes such as evaporation. It is essential to be aware of all potential isotopically distinct water bodies or separate aquifer units within a hydrological system which may interact. In the simplest situation, two end-member mixing systems exist.

A key issue in the successful use of oxygen and hydrogen isotope methods is whether sufficient isotopic difference exists between local groundwater and the infiltration water used. In practice, the difference should be at least 3–5 times the analytical uncertainty or more if strong seasonal variations exist. The bigger the isotopic difference the better the separation and the lower the statistical error in mixing calculations between analyzed waters ([86]. Besides oxygen and hydrogen isotopic ratios, certain conservative dissolved elements, such as chloride or other water quality parameters may be usable in mixing calculations [87]. The use of multiple isotopic and geochemical tracers is generally recommended and necessary when isotopic differences between end member waters are small. For more information on mixing models, see Sections 4 and 5. Infiltration water may be either enriched or depleted in respect to heavier isotopes and thereby distinct from local groundwater. Within shallow soil aquifers, there are seldom significant isotopic variations observed. However, some seasonality may exist, which can be applicable in separating subunits of an aquifer. It is essential to determine the natural seasonal variations in all end-member waters in order to have a reliable evaluation of the mixing ratios of involved waters. Infiltration water containing systematic isotopic variations related to seasons offers an additional tool for monitoring groundwater flow and estimating water retention times (see Section 4). In the planning stages of an AR project, a comprehensive monitoring network for isotopic composition of oxygen and hydrogen should be established. It should cover areas where the active AR is taking place but also the margins to keep eye on unwanted leaks from the operation area. It is generally undesirable for infiltrated water to flow into other groundwaters systems or private wells. The advantage of long term isotope monitoring is that one can learn the isotopic behavior of critical parts of a groundwater system and be able to recognize even the smallest deviations as AR starts. The time span involved from sampling to completed isotopic analyses can be an issue when there is a need to make rapid decisions during the artificial recharge process. For example, in cases where there is a plan to use isotopes of oxygen and hydrogen as a daily or weekly base monitoring method, quick turnaround of analyses is required. Fortunately, new analytical techniques such as laser absorption based spectroscopy for stable isotopes can be used when rapid, but high quality analyses are needed (e.g. [88, 89]).

Besides the stable isotopes of water, isotopes of constituents dissolved in water such as carbon and strontium can be isotopically distinct in groundwater and infiltration water and thus be useful for tracer studies. In contrast to oxygen and hydrogen isotopes in water itself, the isotopic differences in dissolved inorganic carbon (DIC) and Sr are inherited from distinctive inorganic and organic carbon sources and in case of Sr from Ca-bearing mineral sources and their interactions with waters (e.g. [90, 91]). Isotopic differences may exist even within an aquifer and thus these methods are an essential part of the initial hydrogeochemical picture of the groundwater system. Unlike water isotopes, both the isotope value and concentration of dissolved constituents varies in different water bodies and should be considered when studying the mixing of isotopically distinct water reservoirs. In practice this also means that basic groundwater geochemical parameters (e.g. pH, alkalinity, anions and cations) should also be determined. Similarly, underground weathering processes and possible anthropogenic sources can be evaluated using other isotopic tracers, such as nitrogen and sulfur, and trace elements like uranium, lead and lithium, for example (see Section 5 and Ref. [91]).

In planning an AR scheme, one main objective is to define flow distance in order to determine whether the retention time is long enough for natural purification processes to take place. The complicated structure of an aquifer, with varying groundwater retention times in existing sub-aquifer units, must be understood in order to define locations for either surficial infiltration areas or to determine whether a chosen aquifer should be artificially recharged using infiltration wells (e.g. [87]). The traditional qualitative methods based on activity amounts of radiocarbon and tritium in water can be applied in these cases. To achieve more accurate groundwater ages, helium-tritium, CFCs or noble gases can be used (see Sections 2 and 4). In smaller scale studies, the behavior of groundwater flow can be detected by adding a chemical compound, such as coloring agents or salts, into groundwater. Isotope tracers, such as enriched water, or ‘heavy water’, can also be considered. The ultimate tracer test is conducted when isotopically distinct infiltration water is introduced into the system for the first time.

3.2. CASE STUDY: VIRTTAANKANGAS AQUIFER, SW FINLAND

A common denominator for AR projects in Finland and in most northern countries is a lack of groundwater reservoirs productive enough to constitute a sufficient water supply which can meet the increasing demands of constantly growing cities. These regions have, however, abundant surface water resources and common glaciofluvial deposits. Such sedimentary deposits provide a medium for natural purification processes for surface waters, producing good quality drinking water requiring little chemical treatment. A residence time of a few weeks to a few months between an infiltration area and uptake wells is typically required in order to obtain the required purification level.

3.2.1. Study site

The Virttaankangas AR scheme has been operated by Turku Region Water Ltd. since 1999. The project aims to provide artificially recharged groundwater to the 285 000 inhabitants of the Turku region, living on the southwest coast of Finland (Fig. 3). Infiltration water will be taken from the Kokemäenjoki River and fed through a pipeline to the Virttaankangas area where the pretreated river water is recharged into the esker aquifer using the pond infiltration method (Fig. 4). Daily infiltration rates will reach about 70 000 m^3 maximum. Natural recharge and through flow in the system is about 25 000–30 000 m^3/d. The AR is engineered to allow great control over the infiltration and intake processes. This level of control is necessary because introduced recharge water must be kept within the operational area of the AR plant and hydraulic heads and flow in the areas surrounding the aquifer should be maintained at natural levels.

The Virttaankangas aquifer is located in a NW-SE esker chain composed of Quaternary deposits. The study area covers 80 km^2, and the total thickness of unconsolidated sediments above the bedrock is about 30–90 m [92]. The stratigraphical succession is composed of three main stages, creating a complex hydrological system. The esker core was deposited first, forming an unconfined, highly conductive aquifer. The majority of groundwater flow in the Virttaankangas aquifer takes place in the core and a three-dimensional geologic model of the site (Fig. 5; [93]) shows the stratigraphy of the Virttaankangas Formation. The first stage is followed by an interlobate glaciofluvial ridge and fine-grained glaciolacustrine deposits.

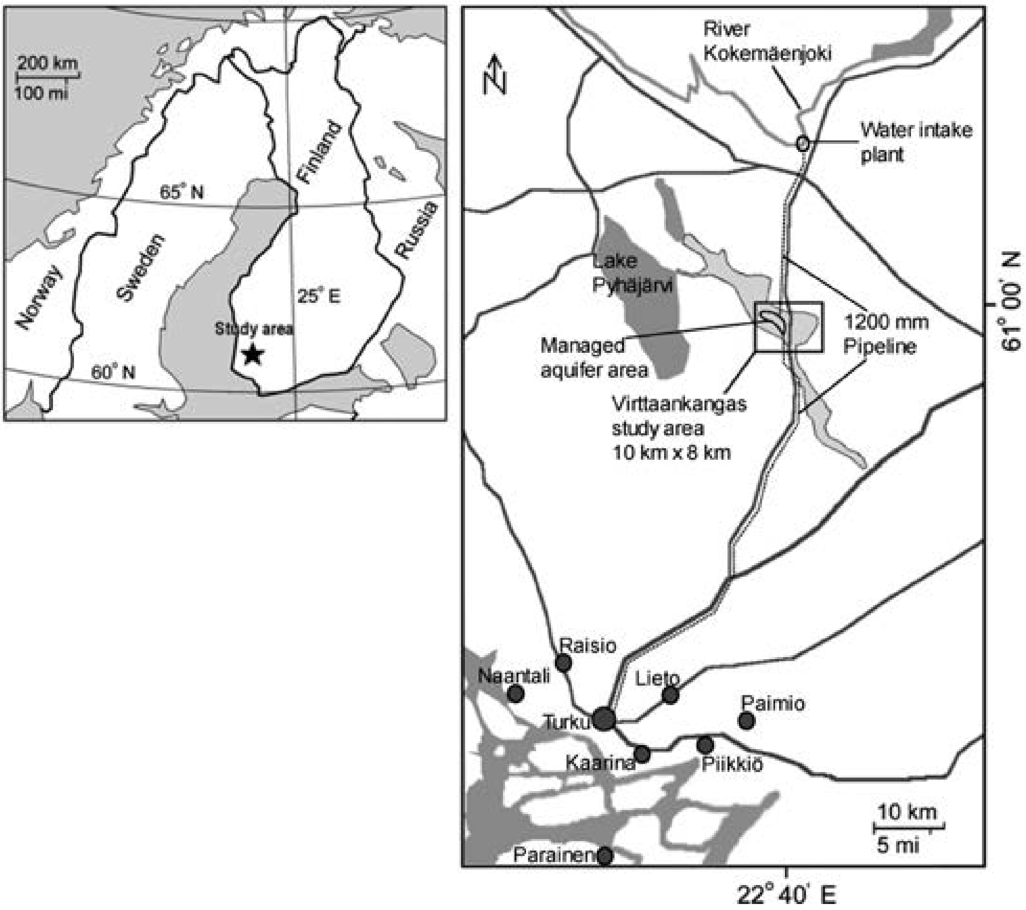


FIG. 3. Location of the Virttaankangas study area and the AR scheme. Modified from [92].

FIG. 4. Infiltration pond at the Virttaankangas area (picture Aki Artimo).

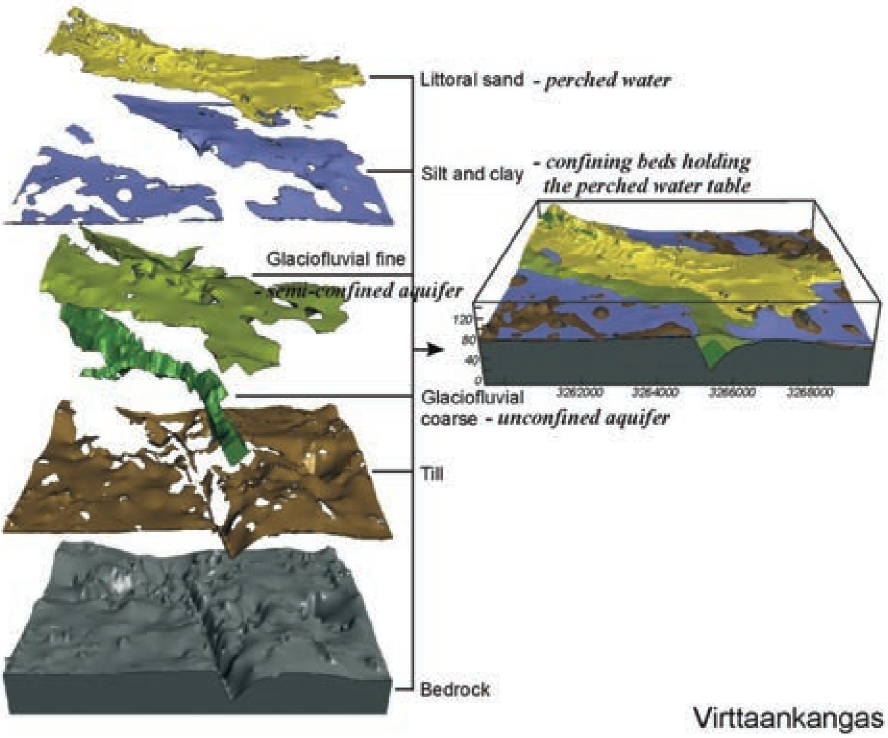


FIG. 5. The structure and the hydrogeologic units of the 3-D model describing the internal structure of the Virttaankangas complex. The model area covers 8 × 10 km^2 (modified from [93]). Exaggeration on the z-axis is 15 times compared to that on x- and y-axes. On the left side of glaciofluvial coarse unit (dark green) a tributary esker branches out from the main formation.

Locally, the glaciolacustrine deposits form a confining interlayer holding a perched water table in sorted littoral sands. This sand unit is the uppermost unit of the succession. A tributary esker is branched out from the main formation (Fig. 5).

3.2.2. Aims of the isotope studies

The desire to quantify the inputs of surface water into the subsurface from volumetric and spatial perspectives is one of the main reasons that measurement of oxygen and hydrogen isotopic ratios has been a key effort in planning for AR implementation in the Virttaankangas project. Isotope methods are used with the intention of monitoring the efficiency of the infiltration process, to calculate ratios of infiltration water and local groundwater and to control the flow paths of infiltrated water. The isotope geochemical study was undertaken to study the interaction of groundwater with solid carbonates and soil CO_2, and thereby to evaluate the origin of the exceptional geochemistry of the Virttaankangas groundwaters. The isotopic composition of carbon in DIC was applied as a key variable to study interaction of the groundwater system with solid carbonates and soil CO_2. The relative ages and characteristics of different hydrological units in the Virttaankangas aquifer were studied using chemical and isotopic (^{13}C, T, ^{14}C, $^{87}Sr/^{86}Sr$) compositional parameters [94]. The isotopic composition of carbon and strontium in water was used to evaluate the hydraulic connections between the carbonate bearing main aquifer and a tributary esker lacking carbonate minerals. The Virttaankangas project has collected comprehensive multi-isotopic and geochemical background data covering all groundwater types in the area. This will be essential as the actual AR using chemically and isotopically distinct river water begins. Monitoring of the changing geochemical conditions in

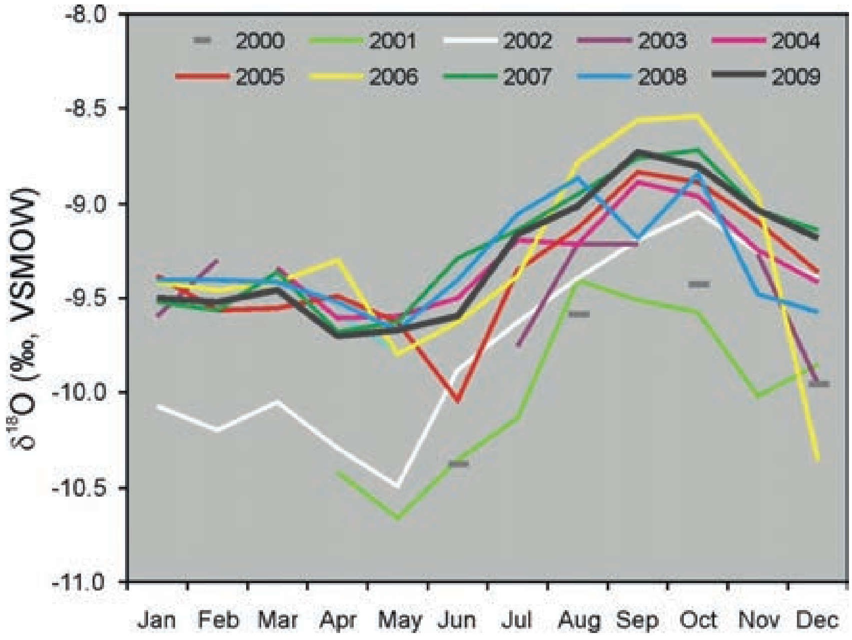


FIG. 6. Seasonal variations of $\delta^{18}O$ values in Kokemäenjoki river water.

the aquifer can be undertaken by using the isotopes of dissolved species as tracers for certain chemical reaction taking place in the aquifer.

3.2.3. Isotopic and geochemical characterization of the groundwater formation

The isotopic composition of oxygen and hydrogen in local groundwater and the infiltration water of the Kokemäenjoki River have been monitored since June 2000 in order to resolve the magnitude of isotopic differences between the two end members and to trace seasonal variations. A significant isotopic difference between local groundwater and river water has been recorded, and is approximately 3‰ for oxygen and 15‰ for hydrogen; thereby the isotope separation method is very applicable. The mean $\delta^{18}O$ and ^2H values for river water are −72.5 ± 4.3‰ and −9.30 ± 0.69‰ (2σ), respectively, with pronounced seasonal variations. Timing of seasonal isotopic maximums and minimums is similar year after year as illustrated in the $\delta^{18}O$ values of Fig. 6. The annual level has increased somewhat since the first years of monitoring. Groundwater in the main flow units has the mean isotopic values of −12.29‰ for oxygen and −87.8‰ for hydrogen with fairly low seasonal variations of 0.30‰ and 2.2‰ (2σ), respectively. High contrast in seasonal isotopic variation between groundwater and infiltration water enables the use of isotope time series for constant retention time monitoring in the recharge area.

Isotope values for groundwater inherited from modern precipitation are typical in this area of Finland [95]. The isotopic compositions of deeper groundwater and perched waters plot on the Finnish local meteoric water (LMWL), which has fairly similar equation to that of the global meteoric water line (GMWL). The $\delta^{18}O$ and δ^2H values for water bodies related to the Virttaankangas AR system are illustrated in Fig. 7. In the Virttaankangas formation there is a kettle pond lake with water clearly enriched in ^{18}O and ^2H compared to the groundwater. The $\delta^{18}O$ vs. δ^2H-graph, however, reveals the original source of lake water as the lake evaporation line crosses the LMWL has precisely the mean composition of that

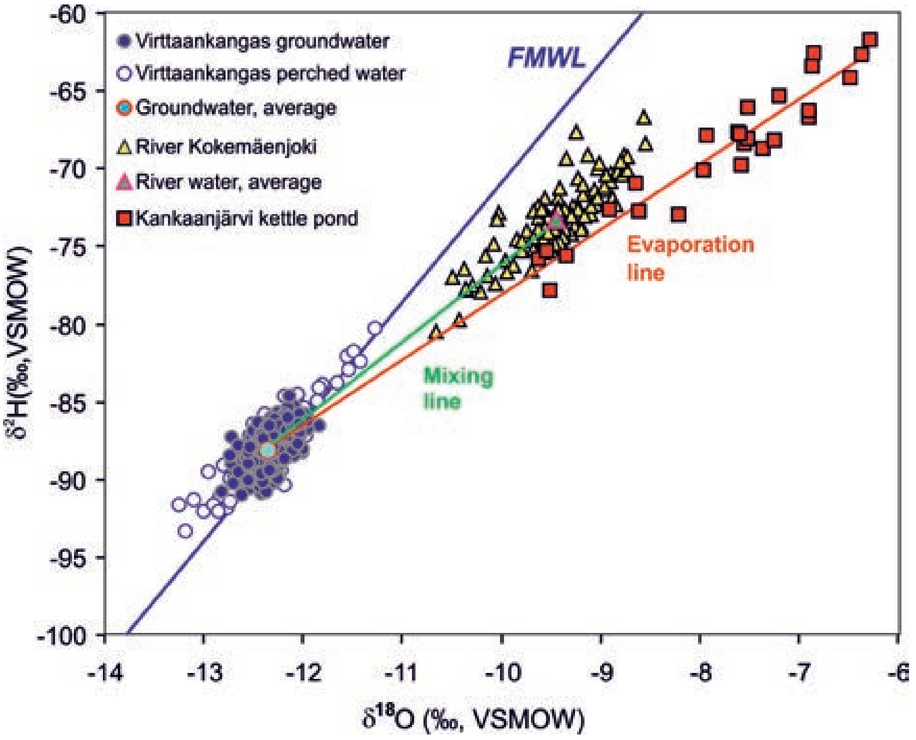


FIG. 7. Isotopic composition of oxygen and hydrogen in Virttaankangas groundwater, Kankaanjärvi Lake and in the Kokemäenjoki River. The groundwater is located on the Finnish meteoric water line (FMWL; blue line; [96]. The FMWL illustrates the linear correlation between the δ^{18}O and ^{2}H values recorded from precipitation in Finland. The river water (yellow triangles) and lake water (red squares) are dislocated from the FMWL. Lake water follows the local evaporation line (red line), which crosses the FMWL exactly at the mean isotopic composition of the Virttaankangas groundwater, indicating that Kankaanjärvi lake water originates completely from the local precipitation and groundwater. The isotopic composition of Virttaankangas groundwater differs significantly from that of illustrated surface waters, thus their mixing would be easily detected by their isotope rations. The green line is a mixing line between the long term mean isotope values of groundwater and river water. Mixture of these two waters would create isotope values along the green line.

of local groundwater. No evidence for leaks of lake water has been observed in the oxygen and hydrogen isotope ratios of groundwaters. The monitoring network has been engineered to cover both the main groundwater flow and discharge areas of the aquifer system. Infiltration experiments using river water for infiltration began in September 2010, providing a unique possibility for an isotopic tracer test.

The mean geochemical and isotopic composition of groundwater in the Virttaankangas aquifer units is summarized in Table 1. Groundwaters in the aquifer system show a considerable range in water pH — from 6.4 to 9.5. The chemical composition, ^{14}C and ^{3}H activities, $\delta^{13}C_{DIC}$ values, as well as $^{87}Sr/^{86}Sr$ ratios of groundwater in separate aquifer units vary according to aquifer mineralogy, the residence time of groundwater and the openness of the system to CO_2 exchange. This is clearly illustrated in Fig. 8 which shows the distribution of the $^{87}Sr/^{86}Sr$ ratios and Sr concentrations in four aquifer subunits.

TABLE 1. CHEMICAL AND ISOTOPIC COMPOSITION OF VIRTTAANKANGAS GROUNDWATER IN FOUR SUBREGIONS OF THE AQUIFER

Aquifer Unit	O_2 mg/L	EC µS/cm	K mg/L	Ca mg/L	Mg mg/L	Na mg/L	Si mg/L	Cl mg/L	Sr µg/L	NO_3 mg/L	SO_4 mg/L
Unconfined aquifer											
Mean (n=10)	11.2	81	0.69	11.25	0.99	2.11	4.71	1.24	15.50	0.40	5.67
Semi-confined aquifer											
Mean (n=5)	11.0	65	0.64	8.95	0.50	1.70	4.20	1.03	22.00	3.04	5.41
Perched water											
Mean (n=4)	12.7	42	0.45	4.69	0.78	1.59	4.12	0.92	11.00	0.23	5.78
Tributary esker											
Mean	6.8	92	0.8	8.5	2.8	3.1	9.3	6.7	28.6	0.7	4.3
± stdev (n=5)	±4.4	±54	±0.3	±5.6	±2	±1.6	±6	±9.6	±10.8	±0.4	±1.8

Aquifer **unit**	T °C	pH	Alk.[a)] mol/L	DIC	mCO_3^{2-} mmol/L	$mHCO_3^-$ calculated	$mCO_{2(aq)}$	$\log SI_{Cal}$	$\delta^{13}C$ ‰, VPDB	$^{87}Sr/^{86}Sr$	^{14}C pmC [b)]	^3H TU
Unconfined aquifer												
Mean (n=10)	6.1	8.9	0.58	0.56	1.35E−02	0.53	2.42E−03	−0.18	−15.55	0.73866	83.3	13.6
Semi-confined aquifer												
Mean (n=5)	6.1	9.3	0.38	0.33	2.16E−02	0.30	4.28E−04	−0.06	−15.26	0.74951	75.0	20.2
Perched water												
Mean (n=4)	6.2	6.9	0.22	0.29	1.02E−04	0.22	0.08	−3.01	−18.75	0.71891	110	11.0
Tributary esker												
Mean	5.6	6.6	0.6	0.8	2.18E−04	0.6	0.3	−2.8	−22.3	0.72640	–	–
± stdev (n=5)	±0.5	±0.4	±0.6	±0.6	±3.34E−04	±0.6	±0.1	±1.2	±1.5	±0.00669		

a) Alkalinity is expressed in HCO_3 mmol/L

b) ^{14}C is corrected for fractionation to −25‰

The oldest groundwater in the semi-confined aquifer unit is characterized by high pH values of > 9 (Table 1). These values are exceptional for shallow aquifers on glaciated crystalline bedrock. The high pH values are related to dissolution of calcite into groundwater under closed or nearly closed system conditions relative to soil CO_2. Groundwater in the unconfined main aquifer flow unit records pH values of close to 9 as well. The rise in pH is paralleled by increases in the contents of Ca and DIC and in the values of $\delta^{13}C_{DIC}$. Saturation with respect to calcite and diluted $^{14}C_{DIC}$ activities is compatible with calcite dissolution. Mineralogical studies of the sediments in the Virttaankangas Formation confirmed that very small quantities (0.5% at most) of clastic, fine-grained (ca. 0.1 mm in diameter) calcite is present in the unconfined and semi-confined aquifer units [97]. However, the uppermost littoral sands as well as the tributary esker system are lacking carbonate minerals. The distinct chemical and isotopic composition of groundwater into separate hydrogeologic units enabled use of these parameters as tracers in verifying groundwater flow paths for the groundwater flow model. Interaction of groundwater in the main unconfined aquifer unit and the tributary esker — which runs along the west side of the Virttaankangas main formation — was primarily determined using isotopic ratios of radiogenic Sr and carbon in DIC.

The highest DIC content and alkalinity, and thus the strongest buffering capacity of water, was recorded in the main groundwater flow unit of esker core. Depending on whether soil CO_2 levels will increase or decrease within the future artificial recharge vertical flow regime, the dissolution of calcite may be enhanced or limited, respectively, which has a significant effect on the composition of the artificially recharged groundwater. Thus, understanding the natural efficiency of sediment to buffer pH in infiltrated water is of high priority among the constructors of a new artificial groundwater recharge plant. It is essential in planning the location of infiltration sites in order to have all the benefits this natural alkalization system can provide. In Finland, the pH in groundwaters is often too low, and has to be upgraded towards higher values. Here, the isotopic composition of DIC may be used to trace the changes taking place in the carbonate equilibrium of groundwater systems.

3.2.4. Summary

The difference between the mean isotopic composition of oxygen and hydrogen in Kokemäenjoki river water and Virttaankangas groundwater is notable and enables a reliable mixing calculation between the two end-members, even in low mixing ratios. Monitoring has also shown that no other waters are mixed into groundwater system and thus a two component mixing system prevails. Long term monitoring of oxygen and hydrogen isotopic ratios of local groundwater and river water has provided a thorough understanding of natural seasonal variations in these waters. The groundwater shows very little variation in $\delta^{18}O$ and $\delta^{2}H$ values, whereas those of the river water express systematic seasonal cycles with the annual amplitude rising up to 3‰ in $\delta^{18}O$ values for instance (Fig. 6). This is essential, as the time series of $\delta^{18}O$ and $\delta^{2}H$ enable us to evaluate water retention times in the operation area throughout the year. One of the most significant moments for this AR scheme will be the first time river water is led to the infiltration ponds, launching a unique isotope tracer test.

Preliminary geochemical and isotopic studies in the Virttaankangas aquifer enabled specification of the initial isotope geochemical baseline in the formation, which appeared to close resemble the mineralogy and hydrogeological properties of the aquifer. Separate parts of the aquifers became identifiable on the basis of their geochemical and isotopic compositions (Table 1; Fig. 8), especially in relation to the occurrence of trace calcite in certain units of the formation. Due

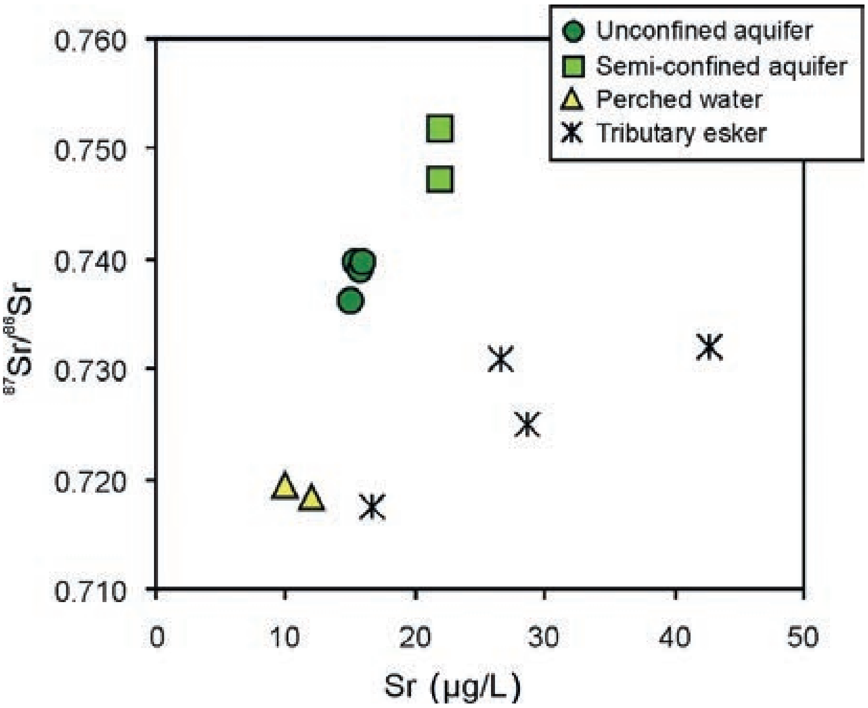


FIG. 8. Strontium and strontium isotope relationships in the four Virttaankangas aquifer subunits showing clear separation between the subunits.

to closed system conditions prevailing locally in the aquifer, calcite dissolution has the ability to raise water pH in the aquifer. For this reason, the natural efficiency of sediments to buffer pH in infiltrated water has been a high priority in the AR scheme. Variations in sediment lithology have also provided useful isotopic fingerprints, such as Sr and DIC, used for assisting flow modeling in discharge areas of the aquifer.

4. MONITORING ARTIFICIAL RECHARGE AND AQUIFER STORAGE AND RECOVERY SYSTEMS

This section describes two case studies which help illustrate how isotopes can be used to monitor hydrological conditions during the ASR process and to evaluate the efficiency of the recharge process. The first example from Santa Clara, USA, describes how stable isotopes, tritium, helium, and noble gases (neon) can be used to track artificial recharge via surface water infiltration. The second example, from Damascus, Syrian Arab Republic, describes how stable isotopes, tritium, and geochemical data can be used to evaluate artificial recharge through an injection well system. Both of these examples demonstrate the value of isotopic methods in monitoring artificial recharge schemes and reinforce the importance of a multi-tracer approach.

4.1. MONITORING ASR WITH ISOTOPES IN SANTA CLARA, USA

Here we show the utility of oxygen-18, tritium, helium isotopes, and neon concentrations to determine groundwater flow dynamics and tracking managed recharge (ASR) in the Santa Clara Valley, California, USA. Included in this study are data from groundwater samples collected in 2007 [98–100], combined with data collected in 2001 [99], both as part of the Groundwater Ambient Monitoring and Assessment (GAMA) Programme, sponsored by the California State Water Resources Control Board (SWRCB). Results of isotopic studies demark the extent, timing, and subsurface flow of ASR water in the Santa Clara Valley.

4.1.1. Methods used in the Santa Clara Valley, California

Groundwater samples for deuterium and oxygen-18 were collected at the well head in 60 mL glass bottles, ~35 cm long by ~1cm OD copper tubes were used for noble gas samples, and 1-L glass bottles for tritium samples. Tritium, deuterium, and oxygen-18 were analyzed at the USGS [3], and deuterium, oxygen-18, and noble gas samples were sent to the Lawrence Livermore National Laboratory (LLNL) and examined using in-growth of ^{3}He with an isotope dilution protocol and VG–5400 mass spectrometer [101]. The excess air component (ΔNe) for each sample was calculated using the NOBLEGAS programme [102]. Additional details of sampling and analyses methods, as well as calculations are provided in Refs [98, 99].

4.1.2. Description of the Santa Clara Valley study area

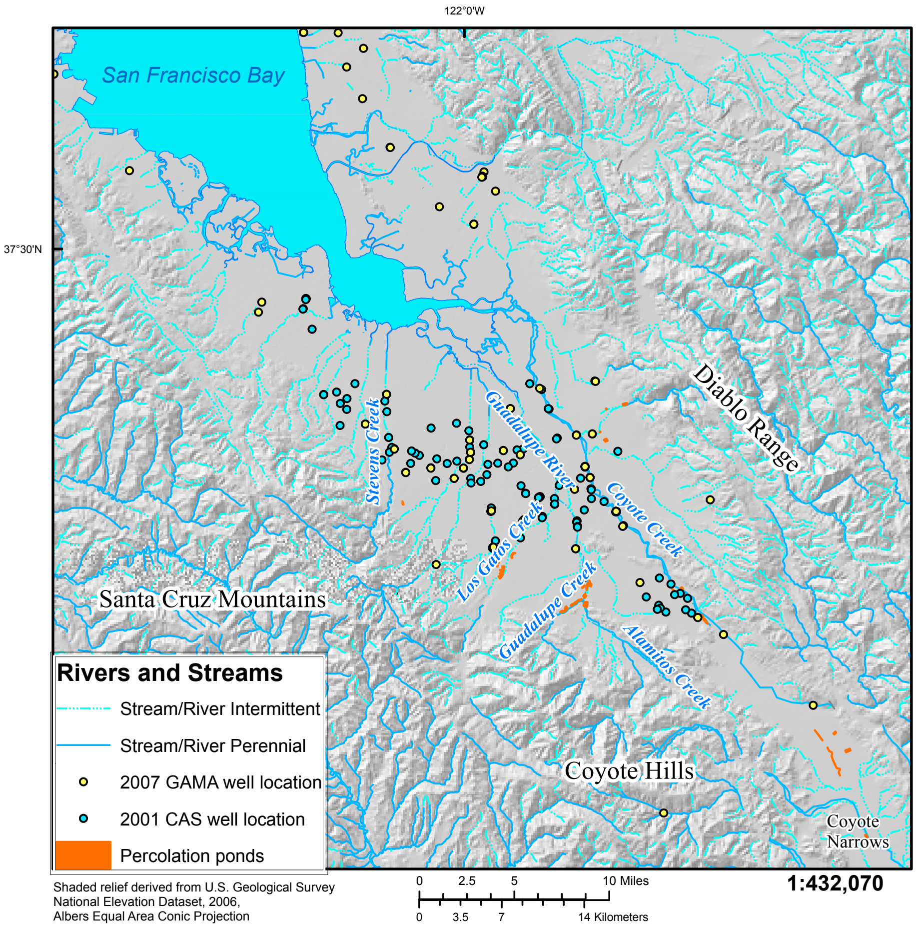
The Santa Clara Valley occupies the southern end of the structural trough containing San Francisco Bay in California, USA. The valley topography is characterized by gently sloping and coalescing alluvial fans composed of fluvial and estuarine deposits of gravel, sand, silt and clay [98]. The onshore groundwater basin is bound on the west by the Santa Cruz Mountains (up to 1100 m), to the east by the Diablo Range (up to 1500 m), and to the south by the Coyote Hills and Coyote narrows, which is the Santa Clara basin groundwater divide (Fig. 9).

The Santa Clara Valley includes the Santa Clara and Coyote groundwater sub-basins, which extend from San Francisco Bay south and along Coyote Creek to Coyote narrows, respectively. The Santa Clara sub-basin is confined in the northern part of the basin, and unconfined in the southern forebay, where recharge occurs. Surface water systems in the Santa Clara Valley include the natural stream network, seven reservoirs, and a system of aqueducts, pipelines, and storm drains. Coyote Creek and Guadalupe River are the major streams that discharge directly into southern San Francisco Bay. The reservoirs discharge directly into the surface stream network along Stevens, Los Gatos, Guadalupe, Alamitos, and Coyote Creeks. The aqueducts and pipelines are used to transport imported water directly to water purveyors and managed recharge facilities. The storm drain channels drain runoff from the valley floor to San Francisco Bay. Recharge to the aquifer system includes stream infiltration, irrigation return, rainfall, and managed recharge (ASR) of surface water imported from northern California, which now represents about half the annual recharge to the groundwater system [103].

The Santa Clara Valley Water District, which manages the water basin, operates 18 recharge sites with a total average capacity of ~157 000 acre-ft [104]. Nearly half of the total recharge is in-stream (behind dams), 20% is direct stream channel infiltration, and 35% is off-stream recharge from ponds [104]. Natural recharge from rainfall and runoff also occurs throughout the basin, which has an average annual rainfall in San Jose of 36.8 cm. Irrigation return flow and leakage from pipes represent additional sources of non-natural recharge.

4.1.3. Oxygen-18 ($\delta^{18}O$) distributions in the Santa Clara Valley, California

The distribution of $\delta^{18}O$ measured in groundwater samples in the Santa Clara basin is shown in Fig. 10. Of interest is that in the center of the basin $\delta^{18}O$ values increase from the south, near the recharge facilities, northward towards San Francisco Bay, while on the western side



Shaded relief derived from U.S. Geological Survey National Elevation Dataset, 2006, Albers Equal Area Conic Projection

FIG. 9. Hydrogeology of Santa Clara Valley, California.

of the basin, where natural recharge occurs, values are consistently higher than values in the southern part of the basin.

In order to interpret the $\delta^{18}O$ distribution in Santa Clara basin groundwater, initial $\delta^{18}O$ values for water introduced as recharge to the basin must be identified. Sources of groundwater recharge water include local precipitation and stream flow, imported municipal water, and imported water for ASR. Recharge from precipitation and stream flow infiltration results in native groundwater with an average, time-integrated range in $\delta^{18}O$ of −5‰ to −6.5‰ [105]. Municipal water is imported to the Santa Clara basin from the Hetch-Hetchy reservoir system, and this water has an average $\delta^{18}O$ of −13.0‰ to −14.0‰ [99]. Although municipal water is not used for managed recharge, it is a component of groundwater recharge due to leaking pipes and irrigation return flow. Imported managed recharge water in the Santa Clara basin has two sources, the California State Water Project and California Central Valley Project. These two water projects both divert their water from the Sacramento and San Joaquin river systems, and they have average $\delta^{18}O$ values ranging from −9‰ to −12‰ [99].

Based on the contrast in $\delta^{18}O$ values between ambient, native groundwater (−5‰ to −6.5‰) and imported water (−9‰ to −14‰), $\delta^{18}O$ groundwater values provide an indicator of areas impacted by imported water. However, it must be noted that when imported water is introduced at managed recharge sites, it is subject to evaporation (which may increase $\delta^{18}O$ values), and to mixing with locally derived water. Upon recharge, imported water mixes with ambient, native groundwater and the resulting groundwater mixture has $\delta^{18}O$ values that are an average of

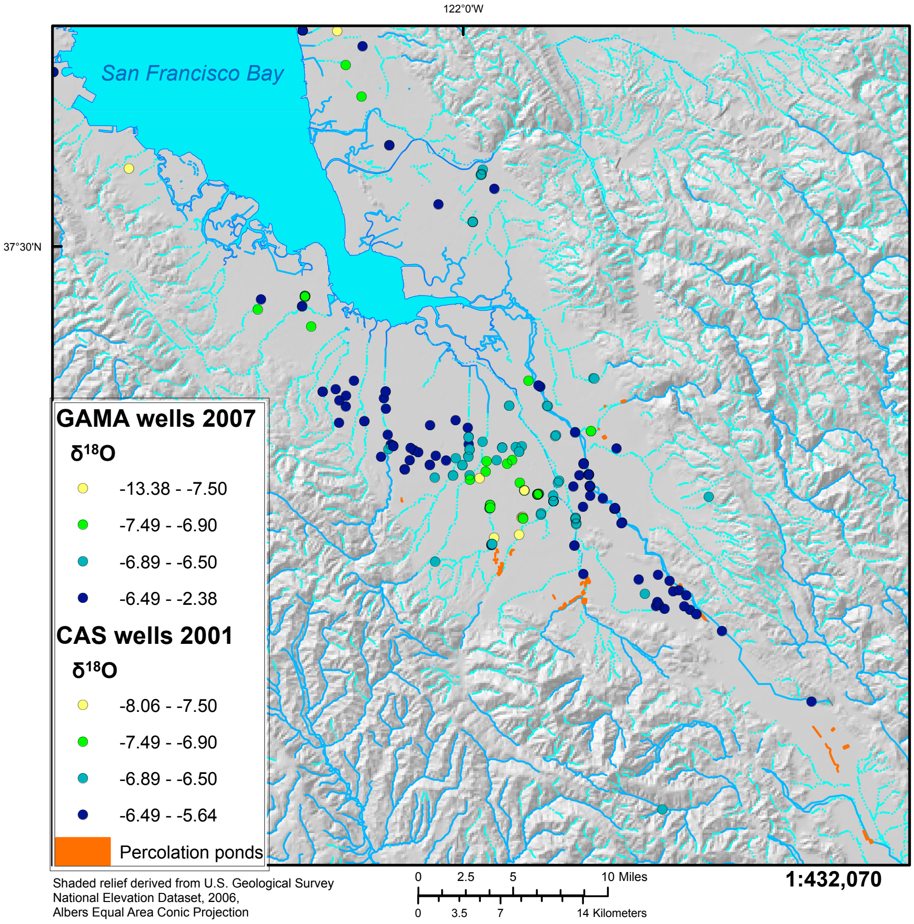


FIG. 10. Oxygen-18 ($\delta^{18}O$ in ‰ vs. VSMOW) distribution in the Santa Clara Valley, California.

the mixing components. However, the difference in $\delta^{18}O$ values between locally derived native groundwater and imported water, even after mixing, is sufficient to identify areas impacted by imported water.

It is reasonable to conclude that the lower $\delta^{18}O$ values extending from the southern part of the basin near the managed recharge sites down gradient to San Francisco Bay result from the introduction, mixing, and subsurface flow of imported water. The $\delta^{18}O$ groundwater values are a useful tracer, providing valuable information on the influence of managed recharge groundwater, even though different sources of imported water exist.

Groundwater from wells along the west side of the basin have $\delta^{18}O$ values that reflect locally derived groundwater recharge which has not been impacted by imported water. Also of note is that groundwater down gradient of the Coyote Creek managed recharge site (Fig. 10) has $\delta^{18}O$ values similar to ambient, native groundwater from local precipitation and streamflow. This is due to the fact that excess water from local storm events is captured and used as managed recharge in this facility.

4.1.4. Tritium (^3H) distributions in the Santa Clara Valley, California

The distribution of ^3H measured in groundwater samples from the Santa Clara Basin is shown in Fig. 11. Of note is that the higher values of ^3H come from wells in the southern part of

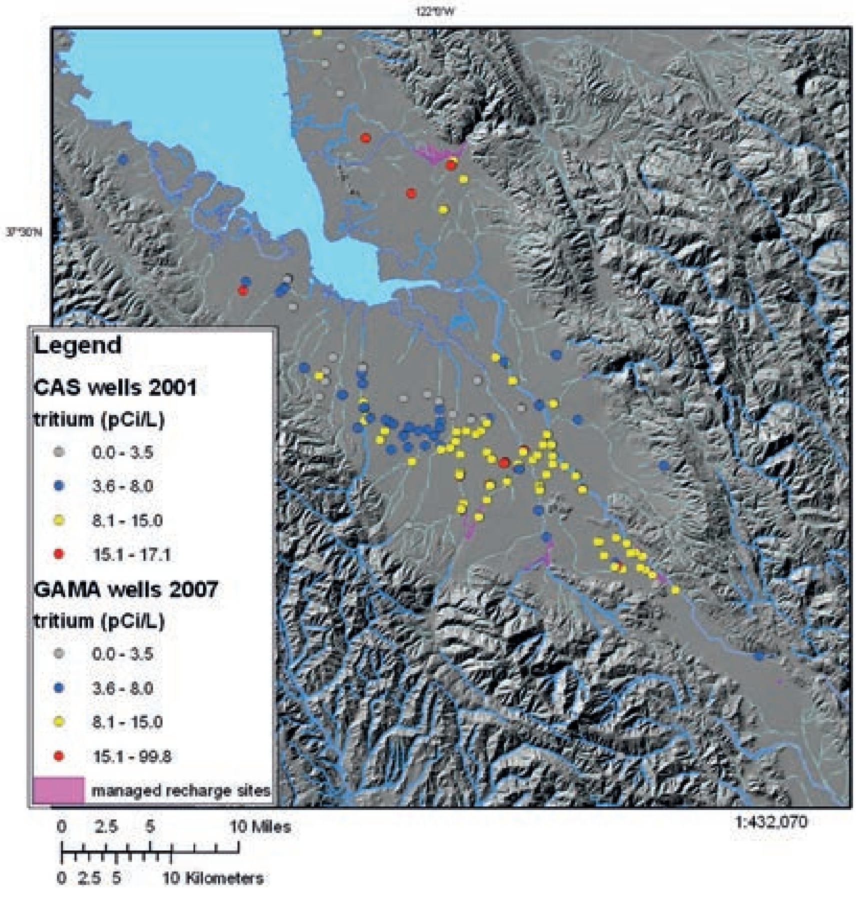


FIG. 11. *Tritium (^3H in pCi/L) distribution in the Santa Clara Valley, California.*

the basin, along the mountain front in the west of the basin, and along the river and stream channels. Tritium values range from 99.8 to < 1 pCi/L, where 1 TU = 3.19 pCi/L.

The spatial distribution of ^{3}H identifies the locations of recent recharge and indicates the direction of groundwater flow. The gradient of high ^{3}H values at wells in the forebay (south) to wells that are ^{3}H dead (<1 pCi/L) in the confined areas near San Francisco Bay (north) reveals the northward groundwater flow direction. The highest tritium values are observed in wells directly downgradient from managed recharge sites, and near the streams that they feed. The managed recharge sites include Coyote Creek, Los Alamitos, Las Gatos Creek, and Alameda Creek (Fig. 11).

Tritium and $\delta^{18}O$ have similar spatial distributions suggesting that high tritium concentrations, like low $\delta^{18}O$ values, are associated with imported water recharged at ASR facilities. Another reason that tritium is a useful tracer is because managed recharge water re-equilibrates with the atmosphere when it is spread for infiltration, resetting the tritium clock. Any groundwater with measurable tritium has recharged in the past 50 years. However, the use of tritium alone does not enable a distinction between managed recharge and natural recharge; it merely confirms that groundwater has been recharged relatively recently. Establishing a tritium concentration gradient identifies the direction of groundwater flow, and provides an estimate of groundwater flow velocity, based on the distance between recharge site and wells with tritium concentrations of < 1pCi/L.

4.1.5. ^{3}H–^{3}He groundwater age distributions in the Santa Clara Valley, California

The distribution of ^{3}H–^{3}He ages of groundwater sampled in Santa Clara Basin is shown in Fig. 12. The ^{3}H–^{3}He ages of groundwater samples were calculated using Eq. 3. Groundwater ages show a coherent pattern similar to ^{3}H distribution in the basin, with younger groundwater in the southern part of the basin, increasing in age as one moves northward towards San Francisco Bay. The ^{3}H–^{3}He ages provide a quantitative description of groundwater residence times for that part of the groundwater recharged after 1955. The ages also provide a more detailed assessment of groundwater movement than ^{3}H alone. Wells near the managed recharge facilities have groundwater ages between 0 and 21 a. Further north down gradient, groundwater ages range 22–32 a, and further north from 33 to more than 50 a.

The horizontal groundwater flow rate for the portion of the water dateable using the tritium–helium method was estimated at 150 m/a, based on transit time from the recharge areas (near managed recharge facilities) northward to a band of wells with ages of more than 50 a. This value agrees with previous estimates of 152 m/a [99], and represents the groundwater flow rate for the portion of water recharged since 1955.

4.1.6. ΔNe — entrained air — distribution in the Santa Clara Valley, California

The amount of entrained air, or ΔNe, was calculated for each sample (see section. 2.5) from the concentration of noble gases He, Ne, Ar, Kr, and Xe measured in groundwater samples from the Santa Clara Valley. The distribution of ΔNe measured in groundwater samples in the Santa Clara Basin is shown in Fig. 13. Of note is that the higher values of ΔNe are from wells in the southern part of the basin, along the mountain front in the west of the basin, and along the river and stream channels. Values of ΔNe range from 0% to 1200%. Areas with higher ΔNe

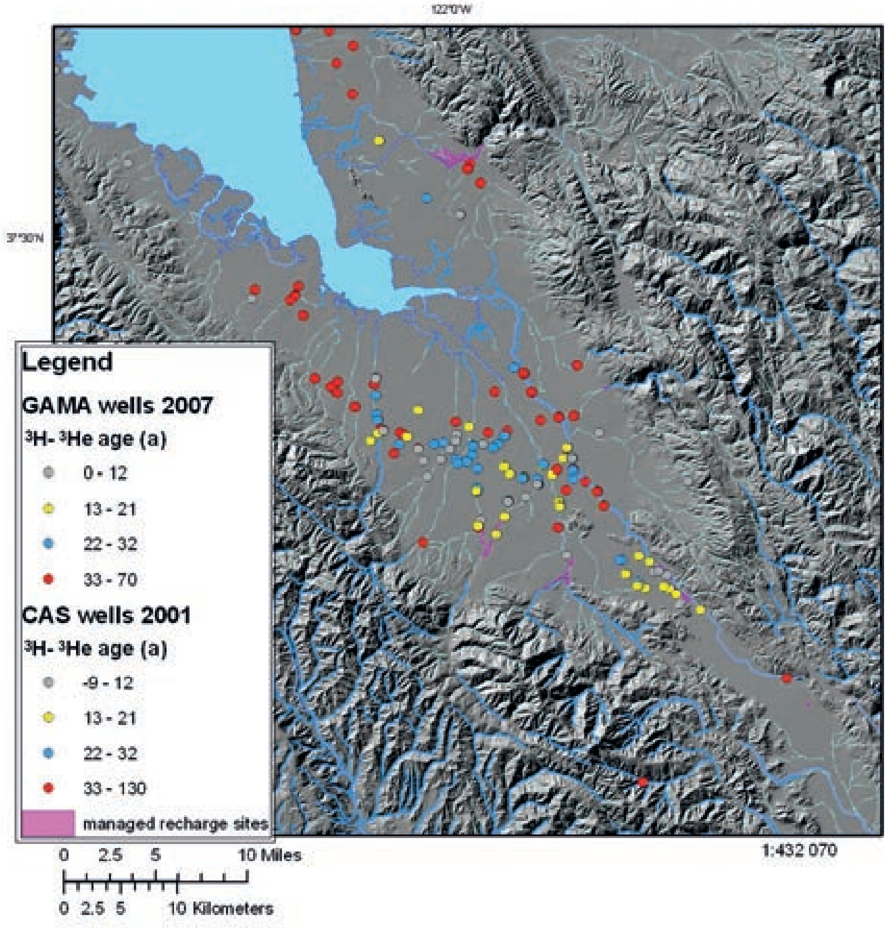


FIG. 12. ^{3}H –^{3}He groundwater age distribution in the Santa Clara Valley, California (in years).

correspond to areas with higher tritium activity, higher $\delta^{18}O$, and younger water. These areas are most impacted by ASR water.

The tritium dead groundwater had lower air-entrained water than the tritium live groundwater. The recently recharged groundwater, particularly the water with lower $\delta^{18}O$ values, indicative of imported water, also had higher concentrations of air-entrained water. Rapid recharge processes have been shown to result in the entrapment of air bubbles, resulting in concentrations of noble gases (neon) which are greater than the concentrations expected for air saturated water.

4.1.7. Summary of findings in Santa Clara Valley, California

Results from a study of groundwater in the Santa Clara Valley, California, USA, demonstrate the utility of oxygen-18, tritium, helium isotopes, and ΔNe in identifying groundwater flow dynamics and tracking managed recharge (ASR) water in the Santa Clara Valley. Results of isotopic studies demark the extent, timing, and subsurface flow of ASR water in the Santa Clara Valley; these are distinguished by high $\delta^{18}O$, tritium activity, entrained air (ΔNe), and young groundwater age. Individually, these techniques provide a means to identify and track ASR water, and when used together, provide strong evidence to demark the extent, movement, and timing of groundwater flow in the Santa Clara Valley.

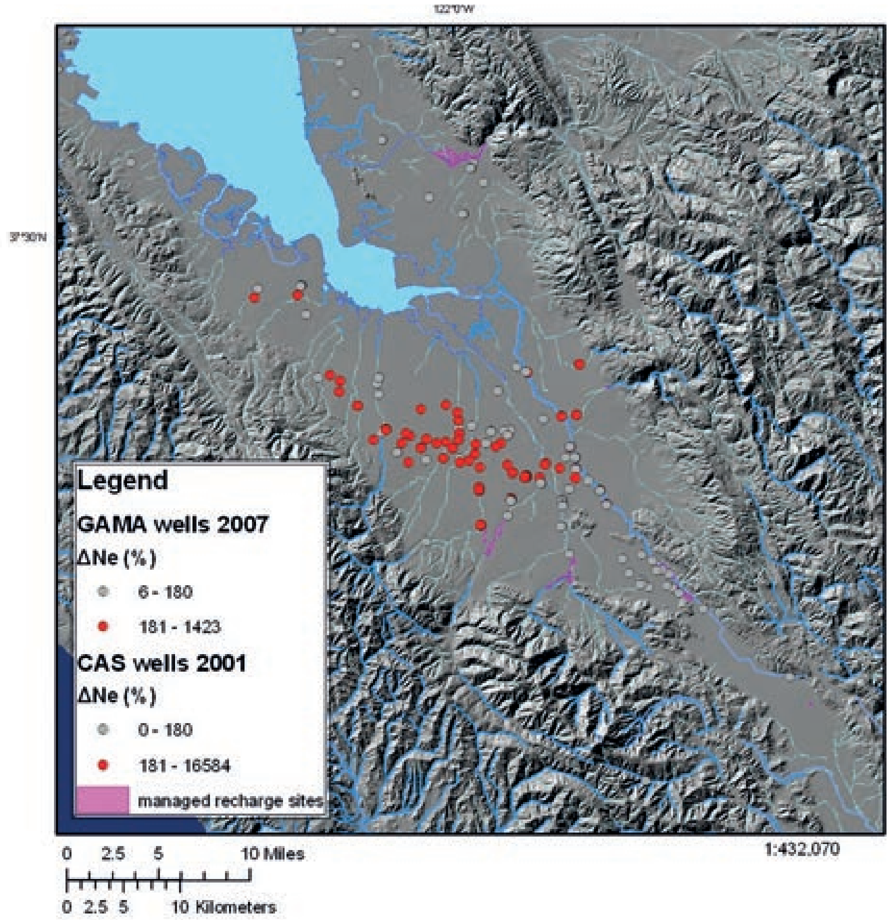


FIG. 13. ΔNe — entrained air — distribution in the Santa Clara Valley, California (in %).

4.2. ISOTOPE MONITORING OF MANAGED AQUIFER RECHARGE USING DIRECT PUMPING

An alternative approach to promoting recharge via surface water infiltration into aquifers is to directly inject water into an aquifer using a pumping well (often referred to as aquifer storage and recovery, ASR). This type of artificial recharge scheme requires injection wells, as well as pumping and piping equipment not typically required when using more passive surface water infiltration schemes. The benefits include significantly reduced or minimal evaporation losses, minimal lag time for infiltration through the vadose zone, better protection of recharge water from surface contamination sources, and no need for large infiltration ponds or reservoirs on the land surface. In the case study described below, isotopes and geochemical tracers were used to evaluate a series of aquifer injections from a borehole in Damascus, Syrian Arab Republic as part of an IAEA regional technical cooperation project [106, 107].

4.2.1. Background of the Damascus study area, Syrian Arab Republic

Water resources in the city of Damascus, Syrian Arab Republic and the Damascus basin in general are under extreme pressure because of dry climate conditions (the average annual precipitation is 212 mm) and increasing demands for water [106, 107]. To potentially alleviate some of the water demands, artificial recharge using injection was examined using an injection well and a series of monitoring wells at the Damascus University campus. Water captured during high flow periods in springtime from the Figeh springs outside of Damascus was piped into the Damascus subsurface water supply system to a specially designed injection well. This approach has the advantage of storing high flow spring water to supplement the Damascus aquifer. The spring water is of high quality and would normally evaporate during its surface water journey into the desert. A variety of environmental tracers were used to monitor the water injection process. The main objectives of the study were to: (1) assess the feasibility of using the injection approach in the Damascus basin and (2) to evaluate which isotope and geochemical tracers were best for monitoring the movement of injected water and mixing within the aquifer system.

4.2.2. Methods used in Damascus, Syrian Arab Republic

Water from Figeh springs was injected during three spring time (2006, 2007, 2008) high flow events into the Damascus University campus injection well. The 80 cm diameter well is complete within the shallow Quaternary alluvial aquifer, reaching a total depth of 45 m. The injection process was monitored at the injection well and at four monitoring wells. Deuterium, oxygen-18, tritium, and chloride were used to monitor mixing of the injection water and ambient groundwater. A few samples of chlorofluorocarbons (CFCs) were also collected in order to examine the feasibility of CFCs in monitoring the injection process. Samples for isotopes and geochemical analyses were generally collected weekly during the injection period and on a semi-monthly to monthly basis during non-injection periods. Injections took place during the March to May period and the rate of injection was in the range of 20–90 m^3/h, depending on the amount of high flow from the Figeh springs. Additional details on sampling, analyses, and the injection process can be found in Ref. [107].

4.2.3. Results and discussion, Damascus, Syrian Arab Republic

As noted above, tritium samples were analyzed to see if they could be used to monitor mixing of injection water in the aquifer. However, analyses conducted early in the project showed that the injection water and the groundwater had similar tritium values. Thus, tritium was not suitable for monitoring artificial recharge at the Damascus site [106]. An artificial recharge study in the United Arab Emirates conducted as part of an IAEA regional project also determined that tritium was not that useful for monitoring artificial recharge [106]. However, in cases where young water (containing tritium) is being used to recharge old tritium free groundwater, tritium can be a useful tracer as discussed in the Santa Clara example in Section 4.1. Analysis of a few groundwater recharge samples should be sufficient to determine the suitability of tritium for monitoring artificial recharge.

CFCs presented the same problems as tritium during the Damascus study in that injection water and groundwater values were too similar. However, CFCs may work well in other artificial recharge studies where young water containing CFC is being injected into old, CFC free groundwater. As was done in this case, a small pilot study to test the suitability of CFCs as an artificial recharge tracer is recommended before establishing a full monitoring programme. Additional information on the use of CFCs in hydrology can be found in [108].

Despite the ineffectiveness of tritium and CFCs in the Damascus study, the other tracers proved to be quite useful in monitoring how and where the injection water was moving into the alluvial aquifer system. The injection water values of both deuterium and oxygen-18 from the Figeh springs were distinct from groundwater values in the vicinity of the injection well.

The advantage of stable isotopes for artificial recharge studies is that values in groundwater are typically constant or vary over a limited range. Thus, if injection water stable isotope values are different from those of groundwater, then stable isotopes can be used to understand where the injection water is moving to and monitor the injection water/groundwater mixing ratio. Because the areas in which the springs are recharged are at least partly at a high altitude and not subject to as much of an evaporation effect as that of Damascus City groundwater, the injection water has more negative stable isotope values than the groundwater. The impact of injections on the aquifer can be seen in Fig. 14 for the three injection periods. Monitoring wells W13 and W14 both show clear shifts to more negative δ^{18}O values due to mixing with injected water. Well W13 is closest to the injection well (~30 m away) and thus shows a bigger response than W14. Wells W15 and WHz are over 100 m from the injection well and do not show a response to the injections, which indicates they are outside the injection water mixing zone. The variability of wells W15 and WHz appears to be related to the effects of seasonal and climate variations of local recharge rather than the injection water [107].

Using the stable isotope values of injection water and groundwater for wells W13 and W14, the percent of injection water in the vicinity of the monitoring wells can be estimated using the equation:

$$x = \frac{\delta_{\mathrm{Well}} - \delta_{\mathrm{GW}}}{\delta_{\mathrm{SW}} - \delta_{\mathrm{GW}}} \tag{5}$$

where δ_{Well} is the δ value of the well water (mixed); δ_{SW} is the δ value of the source water; and δ_{GW} is the δ value of native groundwater (additional discussion and mixing model examples are provided in Section 5.4). Using this approach, Kattan et al. [107] calculated values for the three injection periods and found the maximum percentage of injected water was 74% to 84% in wells W13 and 29, respectively, and to 53% in well W14 (ranges varied depending on

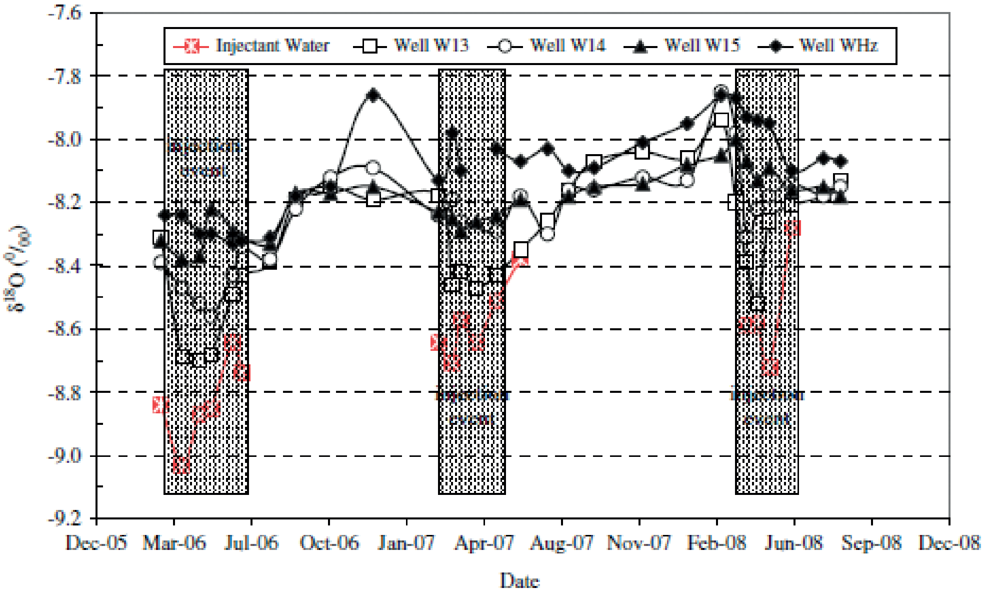


FIG. 14. Temporal variations in δ^{18}O values in injection water and monitoring well samples for three injections carried out during 2006–2008. The red symbols indicate the injection water, the open symbols indicate monitoring wells that responded to the injections and the closed symbols indicate wells that did not respond to injections.

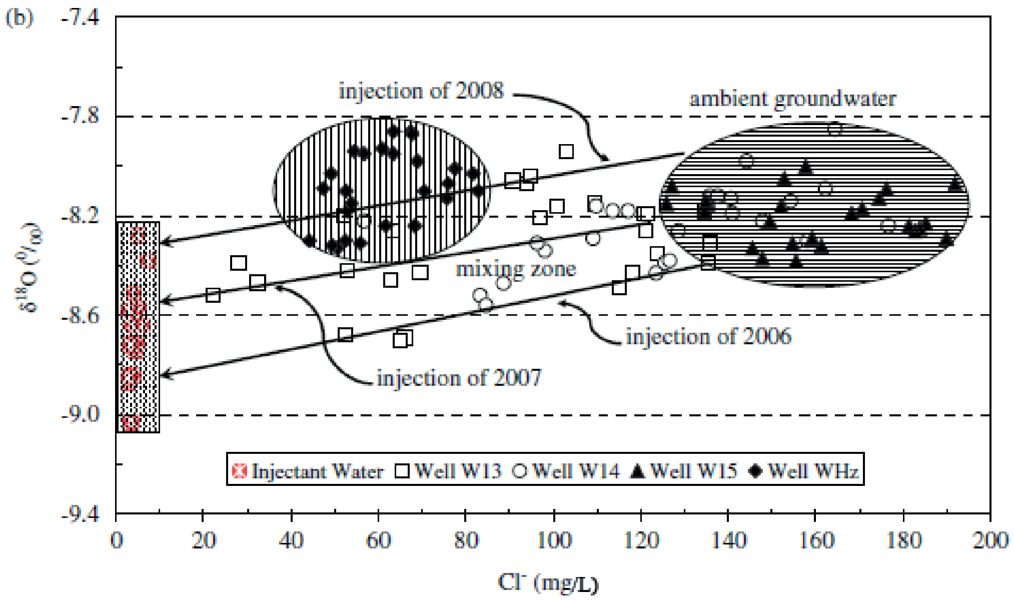


FIG. 15. Mixing relationships for oxygen-18 and chloride between ambient groundwater and injected water for the three injection periods in the Damascus University Campus study.

conditions during the three injection periods). Values typically increased quickly once injections started and returned to background (0%) by July after injections were stopped in May. Chloride was also used as a tracer because the groundwater contained much higher concentrations of it than the injected spring water. Mixing model results for chloride were similar to stable isotope based estimates, which supports the theory that mixing estimates are realistic and that stable isotopes can be used effectively in artificial recharge studies. The mixing process in the aquifer based on injections and monitoring values is illustrated by Fig. 15, which shows the mixing line responses of wells W13 and W14 between injection water and ambient groundwater during the three injection periods.

In summary, the Damascus study showed that isotopes can be used effectively to monitor artificial recharge schemes which use active injection of water into an aquifer. A multi-tracer approach is recommended because, as demonstrated here, some tracers may not be effective in discriminating ambient groundwater from injected water. Once the usefulness of a set of tracers is established at a particular artificial recharge site, a robust monitoring programme can then be established. Based on the success of this study, springtime injections of Figeh water are planned in the future to supplement the Damascus aquifer. An additional example of the use of isotopes to understand processes during aquifer storage and recovery operations using well injection can be found in Ref. [109].

5. USE OF STABLE ISOTOPES AS A BASIS FOR WATER QUALITY ASSESSMENTS IN ARTIFICIAL RECHARGE AND AQUIFER STORAGE AND RECOVERY SYSTEMS

5.1. INTRODUCTION

This section shows how isotopes can be used indirectly and directly to understand the fate and transport of water constituents, most importantly contaminants at AR sites. A central objective of artificial groundwater recharge can be to improve the quality of infiltrating water. Artificial recharge (AR) acts as a purification step due to physical, chemical and biological processes which remove or partly remove suspended solids, pathogens, heavy metals, nutrients etc. from source water through filtration, adsorption and/or biodegradation. At some sites, the recharge process serves as the final treatment step for some compounds [110]. Other implications for water quality may include the dilution of low quality groundwater or the reverse, the contamination of good quality groundwater [111]. The latter is of particular concern in AR systems recycling wastewater, where pollutants such as disinfection by-products, infective micro-organisms, and organic compounds with unknown health risks may be introduced into aquifers used for potable water supplies [112]. Recently, the growing interest and need to research the occurrence and fate of pharmaceuticals and personal care products (PPCPs) and their residues in the aquatic environment has been acknowledged by various authors (e.g. [113, 114]). These and other polar pollutants are of particular concern in partly closed water cycles, where wastewater is recycled via, for example, AR [115].

AR systems vary largely in design, size and characteristics, ranging from aquifer storage and recovery (ASR) wells to infiltration ponds or large soil aquifer treatment (SAT) sites, among others (e.g. [116–118]). The quality of the source water is also strongly variable, starting with good quality surface water to stormwater or treated wastewater. Regardless of the type of system and source water quality, before water quality changes can be properly assessed, it is essential to understand where the recharge water is going, how fast it is flowing and to what extent it mixes with ambient groundwater (e.g. see discussion in Section 4). When attempting to interpret the behaviour of — mostly reactive — organic and inorganic pollutants during infiltration, these hydrogeological basics form a fundamental prerequisite necessary to avoid data misinterpretation. For example, mixing proportions are required in order to differentiate between real contaminant removal and pure dilution. The evaluation of time scales is important first because the threat of contamination by bacteria, viruses and parasites decreases with increasing residence time within the subsurface and second because only with sufficient knowledge of time scales is an estimate of degradation rates of biodegradable compounds possible.

Moreover, water quality problems may be assessed directly with the help of compound specific isotope methods. The fate and degradation of organic pollutants and dissolved organic components (DOC) may be assessed using $\delta^{13}C$ and $\delta^{2}H$, while $\delta^{15}N$ and $\delta^{18}O$ are potentially useful to investigate nitrogen elimination processes, for example denitrification. The consumption of oxygen, an important electron acceptor in many microbially mediated processes (e.g. [119]), can be studied using $\delta^{18}O$. With $\delta^{34}S$, the oxidation of and reaction with pyrite and sulfate reduction may be evaluated. In the following, we provide briefly introduced

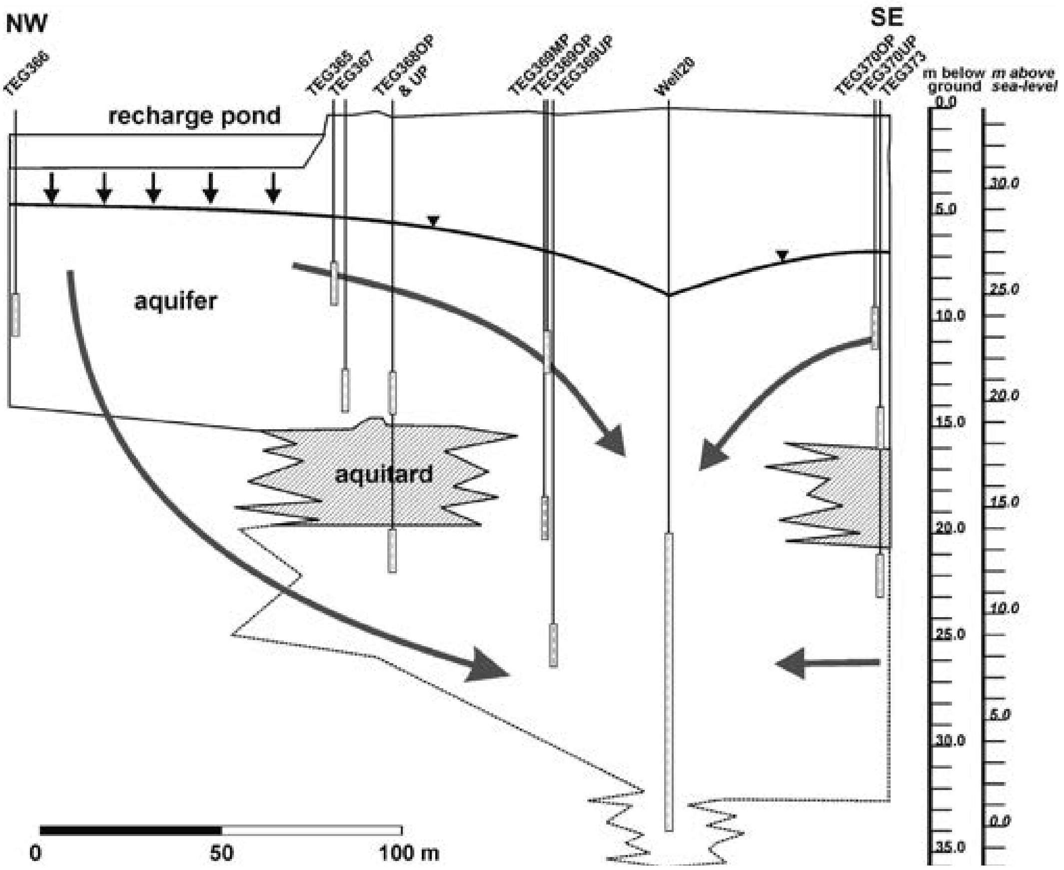


FIG. 16. Schematic cross-section of a research transect between a recharge pond and a production well (well 20) in Berlin. Filter screens of monitoring wells above and below a local discontinuous glacial till layer are shown as rectangles. The general flow direction is indicated (modified from [117]).

examples on the use of carbon, sulphur and nitrogen isotopes. One reason that these compound specific isotope analyses are potentially useful is that artificial recharge is often undertaken as a strategy for wastewater reuse and recharge water can therefore contain high concentrations of DOC, NH_4^+ and/or NO_3^- as well as organic pollutants.

It is important to note that in order to fully understand the hydrochemical changes which occur during AR, it is not sufficient to sample and investigate source water and abstracted well water, as the abstracted water is generally a mixture of native groundwater and recharge water. A more suitable approach is to install a transect of monitoring wells (preferably multi-level wells) in the flow direction between the infiltration pond (or injection well etc.) to be able to monitor changes that take place during the water's passage through the aquifer. In addition, the transect should include at least one well inland of the respective production well in order to investigate the surrounding unaffected groundwater. An example of a transect at a recharge pond in Berlin is provided in Fig. 16.

5.2. TRAVEL TIME ESTIMATIONS USING ISOTOPE TIME SERIES

When the elimination of water compounds, most importantly pollutants, is examined during AR, concentrations are often plotted (or documented) versus distance, rather than travel time. When the factor time is ignored, it is impossible to quantify elimination, for example to derive degradation rate constants for water constituents. Due to large variations in site specific characteristics (especially with regard to hydraulic conductivities), this practise also does not allow for transfer of results between sites. It is more reasonable to account for travel (or residence) times in the subsurface as done, for example, by Dillon et al. [118] in a project comparing ten ASR sites in order to determine the fate of natural organics, disinfection by-products, selected endocrine disruptors and pathogens during subsurface storage.

With regard to pathogens, maximum velocity, measured by the first arrival of a tracer in a tracer experiment, is of great interest. Such velocity can only be derived from tracer tests when a tracer is added to recharge water in a controlled manner and tracer breakthroughs are monitored at wells. For example, Clark et al. [112] reported on gas tracer experiments near an AR site in northern Orange County, California. They used sulfur hexafluoride (SF_6) and xenon isotopes (^{124}Xe, ^{129}Xe, ^{136}Xe) as tracer substances. However, it is difficult to conduct an economical tracer test at an AR site, since large volumes of recharge water have to be spiked with the tracer substance. It is also possible that regulations do not allow for the addition of substances to the recharge water. Mean travel times can also be derived from tracer tests or with the help of environmental isotopes already present in temporally variable concentrations in the recharge water. The stable isotopes of oxygen ($\delta^{18}O$) and hydrogen (δ^2H) have proven to be effective tools to assess travel times and pathways as well as the extent of mixing with ambient groundwater. Because they are part of the water molecule itself, they act as ideal conservative tracers.

It is common practise to assess travel times near a losing stream or river with time series analysis, because temperature dependent fractionation processes in clouds, precipitation and surface water generally lead to seasonal patterns in surface water, which is depleted in ^{18}O and ^2H in winter and enriched in ^{18}O and ^2H in summer [120]. The time difference between a marked isotopic or likewise physicochemical change in surface water and a subsequent change in well water (‘lag time’), can be obtained from continuous time series analysis (e.g. [121–124]). For ideal tracers like ^{18}O and ^2H, these lag times are equivalent to mean travel times from surface water to a well. This method is similarly suitable for artificial recharge systems as long as the source water displays a seasonal isotopic signature, which is generally the case where surface water acts as the source water for AR. Depending on local dispersion, a seasonal signal cannot be resolved after more than a few years and for longer residence times in an aquifer, other methods like the tritium-helium dating method first developed by Tolstikhin and Kamenskiy [125] have to be used (see Section 4.1 and also Ref. [112]). Once travel times are known, average flow velocities can be calculated based on respective distances to the wells.

5.3. EXAMPLE FROM BERLIN, GERMANY

In Berlin, the potable water supply relies on induced bank filtration and AR. Surface water infiltration of the naturally gaining surface water courses is induced by several hundred production wells placed alongside rivers and lakes. Though induced bank filtration (BF) may not be strictly artificial recharge, it is certainly a form of managed aquifer recharge and the principle of isotope time series analysis is similar to that of AR sites recharging surface water. Ratios of $\delta^{18}O$ and δ^2H in the surface water of Berlin display a typical seasonality with more negative values in winter (Fig. 17). Approximate mean travel times were obtained from phase shifts of stable isotopes shown for a selection of monitoring sites near Lake Tegel [126].

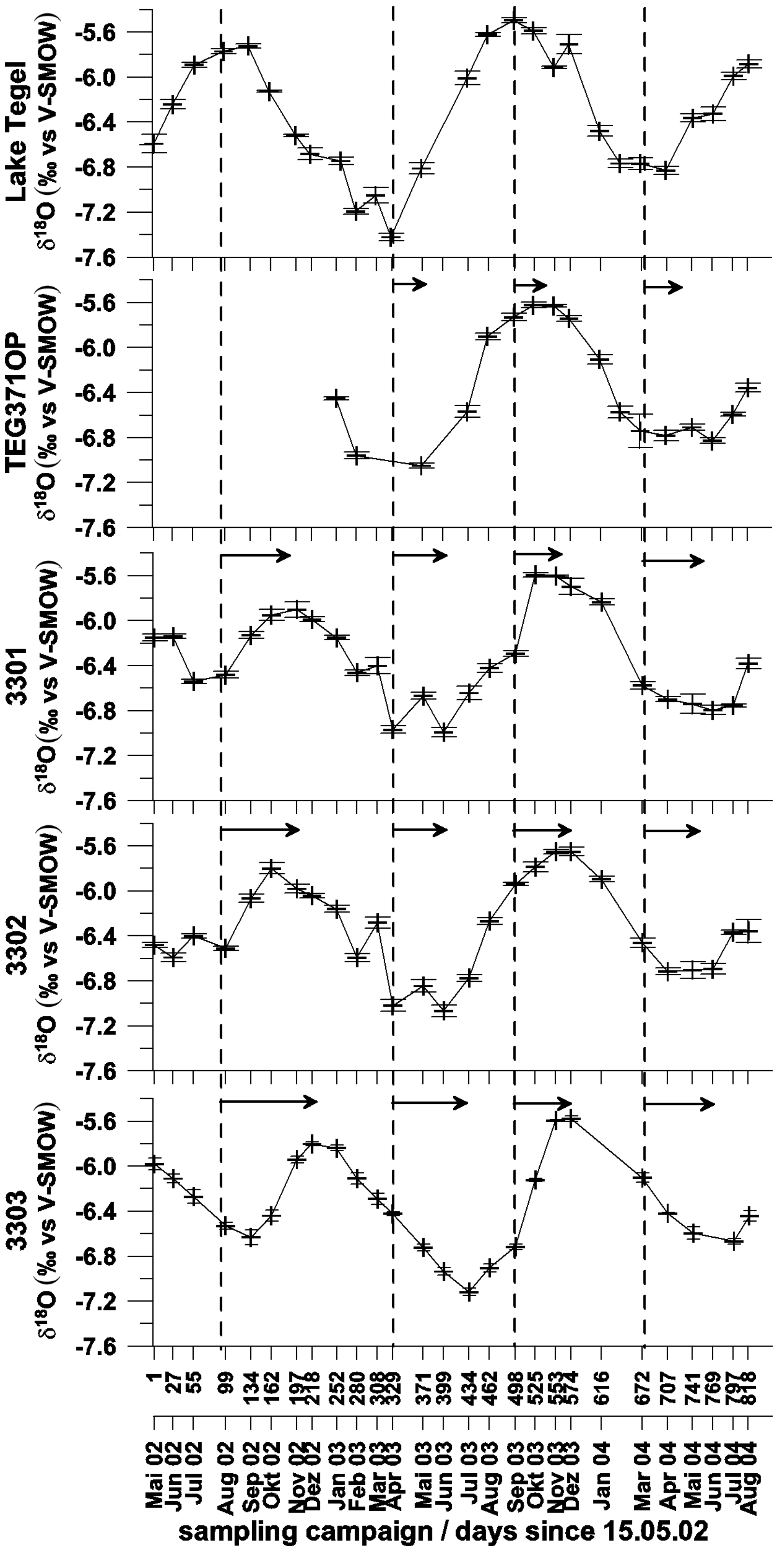


FIG. 17. Time series of $\delta^{18}O$ in samples from groundwater observation wells along an approximate pathway between surface water (uppermost graph) and the nearest production well (not shown) at an induced bank filtration site in Berlin [126]. The surface water maxima and minima are marked with a dashed line, while arrows indicate the phase shift to individual monitoring wells and vertical error bars display the analytical error (1σ).

Clearly, all shallow groundwater wells shown reflect the surface water signal with a phase lag of ~1 to more than 4 months at maximum. For travel times of less than one month, resolution of the method is governed mainly by sampling frequency. In the present example, the phase lag was smaller (i.e. travel times were shorter) in 2004 compared to 2002/2003. Travel times can be computed more accurately on the basis of stable isotope analysis using finite difference transport model software.

Based on travel time evaluation of monitoring wells at two BF and one AR site in Berlin, hydrochemical processes and the behaviour of a large range of organic trace compounds from an extensive two year sampling campaign were evaluated (NASRI project). Parameters monitored included various pharmaceuticals and their residues, which originate from the fraction of treated wastewater in the surface water (in a partly closed water cycle). Publications on organic trace compounds from the project include Refs [117, 127–131], as well as others.

Grünheid et al. [127], for example, investigated bulk DOC and adsorbable organic halogens. Grünheid et al. [127] used travel times to compare removal efficiencies from the AR and a BF site and to define relevant travel times and distances to realize degradation.

Massmann et al. [117] investigated redox conditions and the redox dependant removal of Phenazone-type pharmaceuticals at the AR site. By plotting O_2 and NO_3^- concentrations at the research transect shown in Fig. 16 versus travel times estimated from tracer results for three summer and winter months, seasonal differences caused by the temperature dependency of O_2 and NO_3^- reduction became visible (Fig. 18). First order reaction rate constants and half-lives were calculated. In summer, O_2 was consumed within the first metres of infiltration and denitrification occurred along the transect. In winter, O_2 reduction proceeded much more slowly and O_2 was the major electron acceptor along the transect (Fig. 18).

Accounting for retardation and mixing, Wiese et al. [131] quantified absolute and relative removals of 38 organic trace compounds by subtracting well concentrations from surface water concentrations at the time of infiltration (corrected for travel time). Removals were then investigated with respect to travel time, redox conditions, surface water concentration and field site, using a combination of graphic plotting and statistical parameters.

Surprisingly, samples from several deeper observation wells screened at the bottom of the aquifer used for BF abstraction in Berlin displayed no significant isotopic seasonality, but nevertheless contained organic trace substances originating from the surface water. Lack of seasonality suggested a travel time of several years, which was confirmed by tritium–helium dating [130]. As an example, the time series of $\delta^{18}O$ for one of the monitoring wells is shown in Fig. 19. Despite a distance of less than 30 meters to the lake in a sandy aquifer, the observation well does not reflect the transient tracer signals of the lake. Even though such a time series does not allow for the estimation of travel times, it nevertheless provides valuable information. The combined tracer approach by Massmann et al. [126] revealed a strong age stratification of the infiltrate, which was explained by site specific hydraulics and different infiltration zones. The older, deeper bank filtrate contained some very persistent residues of phenazone-type pharmaceuticals in concentrations exceeding those of present day surface water, reflecting changes in historical surface water concentrations.

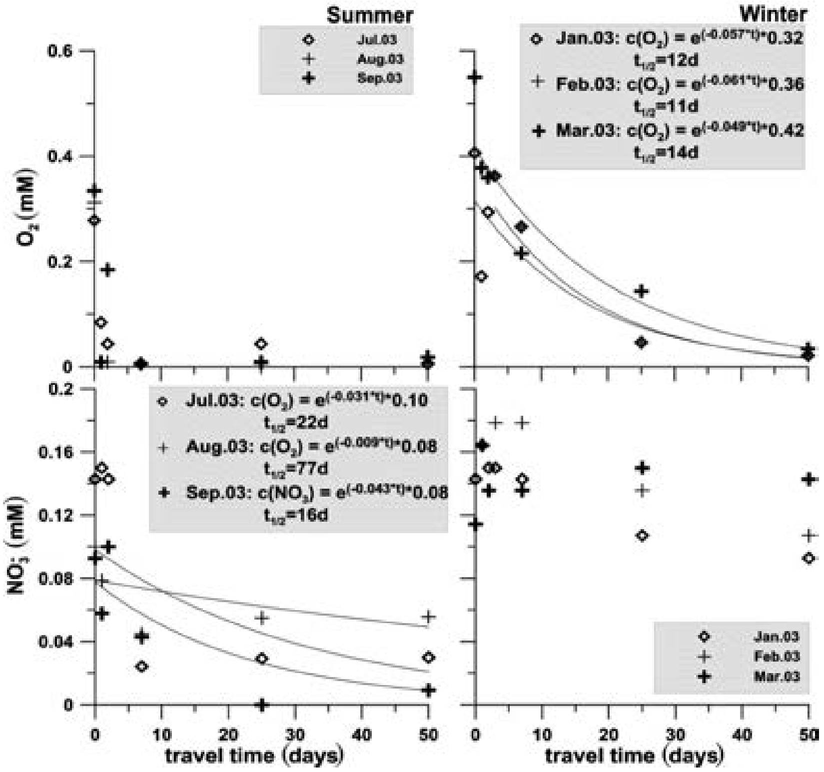


FIG. 18. O_2 and NO_3 concentrations (mM) plotted versus travel times estimated from tracer results for three summer and winter months [117]. Samples taken in the flow direction along a transect of monitoring wells between a recharge pond and a production well (Fig. 16). In summer, O_2 was rapidly consumed in the infiltration zone and denitrification occurred along the transect, while in winter, O_2 reduction continued along the entire transect and little NO_3^- reduction occurred. Degradation rate constants and half-lives were calculated where possible (assuming first order degradation).

5.4. MIXING EVALUATION USING ISOTOPE MASS BALANCE

It is essential to understand the fraction of recharge water in a well in order to differentiate between dilution and real contaminant removal. For example, if the nitrate concentration in a production well is only 10% of what the surface water concentration during infiltration (corrected for travel time) was, without further investigation, operators might assign this to efficient denitrification occurring in the aquifer during AR. However, if the fraction of AR water in the well was only 10% in total, then this conclusion would be completely wrong, and could lead to misinterpretation and mismanagement of a site. Hence, a substantial basis for hydrochemical site investigations is to account for mixing. For example, in the assessment of pollutant removal during AR and BF in the Berlin example given above, mixing was always accounted for.

As explained in Ref. [132], the isotopic composition of water formed by mixing two or more waters with different isotopic signatures is additive and shown by isotope mass balance using

$$\delta_1 n_1 + \delta_2 n_2 + \delta_3 n_3 ... = \delta_f (n_1 + n_2 + n_3 ...) \tag{6}$$

where δ_1 is the value of component 1; n_1 is the amount of substance (atoms) in component 1; and δ_f is the δ value of the product.

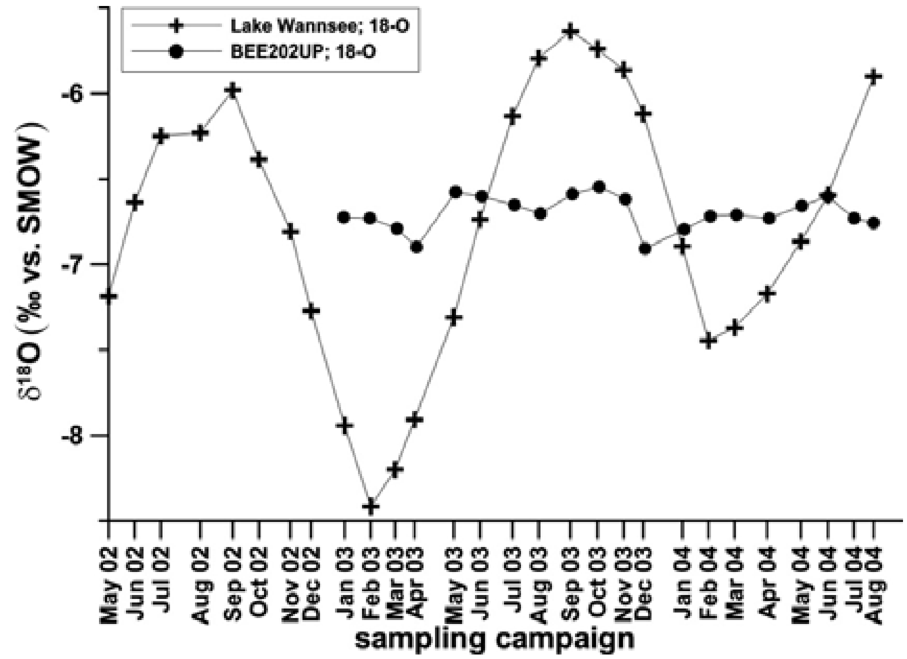


FIG. 19. Time series of $\delta^{18}O$ values in surface water (at Lake Wannsee) showing distinct seasonality and BEE202UP, screened at the bottom of the aquifer at the Wannsee transect 2. Clearly, the observation well does not reflect the seasonal variations of the lake (modified from [126]).

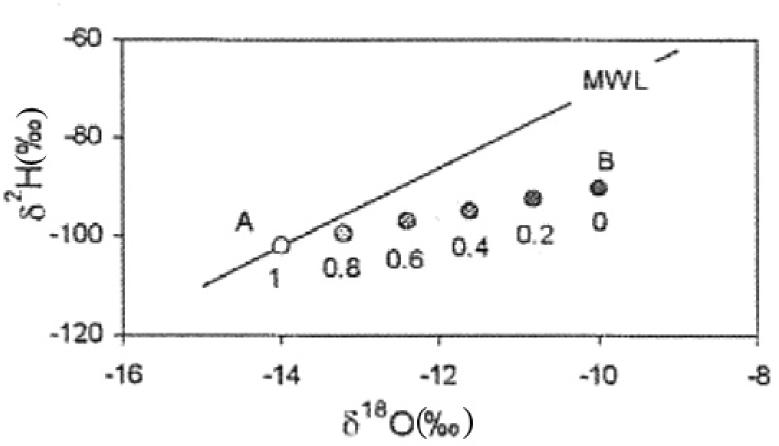


FIG. 20. Mixing proportions between two waters (A and B) calculated by isotope mass balancing using $\delta^{18}O$ and $\delta^{2}H$ [120].

For example, the addition of 75% of water A with $\delta^{2}H = -20$‰ and 25% of water B with $\delta^{2}H = -60$‰ yields a water sample of $\delta^{2}H = -30$‰ [132].

A consequence of this fact is that on a linear scatter plot of $\delta^{2}H$ versus $\delta^{18}O$, mixed samples of two waters (for example source water and surrounding native groundwater) will lie on a straight line connecting the δ values of the two waters, and percentages of each component can be estimated visually (Fig. 20).

In the case of two end members (for example source water and native groundwater) whose mole fractions add up to 1, the proportion of artificially recharged water or source water, x, can simply be calculated using Eq. (5) (which is reproduced below for convenience):

$$x = \frac{\delta_{\mathrm{Well}} - \delta_{\mathrm{GW}}}{\delta_{\mathrm{SW}} - \delta_{\mathrm{GW}}} \tag{7}$$

where δ_{Well} is the δ value of the well water (mixed); δ_{SW} is the δ value of the source water; and δ_{GW} is the δ value of native groundwater.

Such a mixing calculation likewise works with concentrations of other conservative tracers. An important precondition is that the isotopic signatures (or concentrations) in source water and native groundwater differ substantially from one another. At AR sites, this precondition is often valid. For example in Berlin, the groundwater generally displays a more negative isotopic signature than the artificially recharged surface water. In more arid climate zones, recharge waters are often imported over greater distances and tend to be isotopically different and distinguishable from local surface water and/or groundwater. These isotopic differences are caused by geographical variations of precipitation; precipitation with lower isotopic signatures (i.e. isotopically light) falls inland, at cooler temperatures, and at higher elevations [112]. Examples of studies in which imported waters at AR sites were traced in the subsurface include the Damascus case study described in section 4.2 as well as Muir and Coplen [112, 133, 134]. When more than two end members mix in a well, isotope mass balance is further complicated, although mixing models can be made for more than two end-members.

5.5. EXAMPLE FROM SANTA CLARA VALLEY IN CALIFORNIA

An early study for isotope mass balancing was conducted by Muir and Coplen [133] in the Santa Clara Valley, California, USA. Muir and Coplen [133] used $\delta^{18}O$ and δ^2H signatures of imported water from northern California and local groundwater to calculate the fractions of AR water in abstraction wells. These two end members differed strongly from one another. Fig. 21 displays a map of δ^2H values of some sampled wells. The δ^2H value of the groundwater and water imported between May 1974 and April 1977 were found to be −41‰ and −74‰

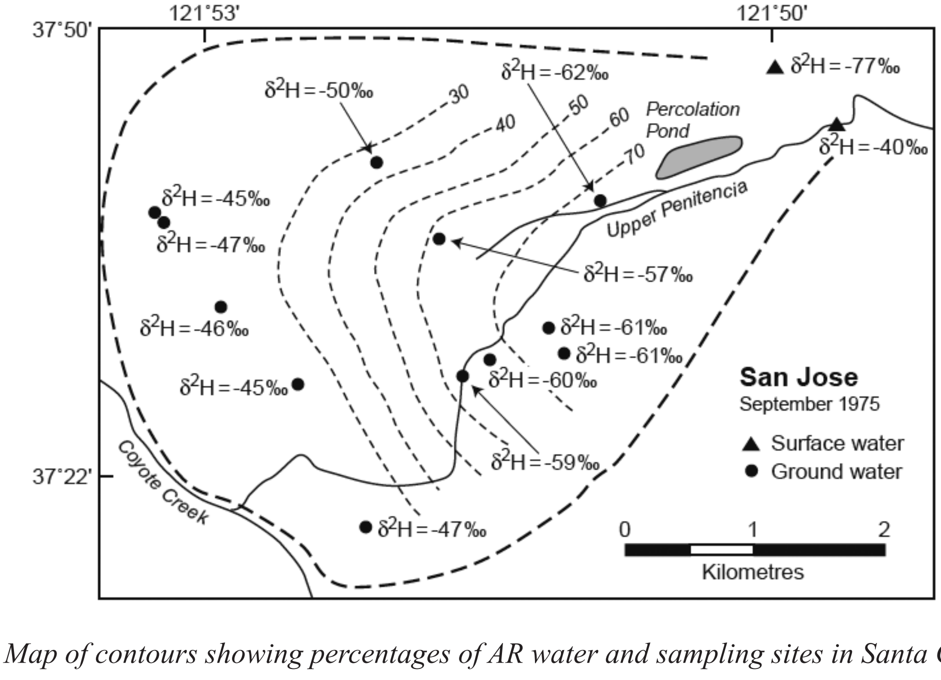


FIG. 21. Map of contours showing percentages of AR water and sampling sites in Santa Clara Valley, California [132, 133].

respectively, while mixing proportions for individual wells were calculated using isotope mass balancing. In addition to calculated percentages of imported AR water, contours of similar percentages of AR water are shown in the map, also allowing for identification of AR water flow direction.

5.6. APPLICATION OF CARBON ISOTOPES

Though the use of carbon isotopes is relatively common in hydrogeological investigations, its potential for AR studies is still largely underutilized. Carbon isotopes (^{13}C, ^{14}C) are used to date relatively old groundwater and to trace the carbon cycle. Dissolved species of organic and inorganic carbon take part in microbial reactions, degrading organic compounds, and interaction with carbonates dominate the geochemical evolution of shallow groundwater [120]. Section 2.6 describes carbon isotope systematics and the typical isotopic signatures of carbon species from various sources and fractionation processes.

In many cases, the source water for AR is treated wastewater containing high concentrations of organic carbon. Biodegradation is the most important process eliminating bulk organic carbon and organic trace compounds during AR [135]. Regarding water quality of the end water, reduced DOC concentrations are an advantage, while potential contamination of groundwater with high DOC waters may raise concerns.

Two examples showing the use of carbon isotopes in ASR schemes near Adelaide in South Australia were provided by Herczeg et al. [136] and Le Gal La Salle et al. [137]. Herczeg et al. [136] reported on an ASR scheme at Andrews Farm, where storm water was injected into a karstic, confined, brackish carbonate aquifer. Using carbon isotopes and geochemical data Herczeg et al. [136] could show that injected organic matter is oxidized, producing substantial $CO_{2(aq)}$ and resulting in more negative $\delta^{13}C_{DIC}$ values. Le Gal La Salle et al. [137] used $\delta^{13}C_{DIC}$ and ^{14}C activities to complement traditional geochemical tracers in the interpretation of geochemical reactions during injection at the Bolivar site. The injected treated effluent was distinct from native groundwater with regard to $\delta^{13}C_{DIC}$ and ^{14}C activities. Organic matter oxidation and calcite dissolution altered the $\delta^{13}C_{DIC}$ value of the injectant at the beginning of subsurface migration. At a greater distance from the injection well, both ^{13}C and ^{14}C signatures were dominated by isotopic exchange with the matrix surface and minimal overall dissolution. The following, more detailed example provided by Kortelainen and Karhu [138] is one of the few recent examples describing use of carbon isotopes in AR schemes with pond infiltration. Kortelainen and Karhu [138] used the isotopic composition of dissolved inorganic C ($\delta^{13}C_{DIC}$) in recharged water as a tracer for redox reactions. Determinations of DIC isotope ratios in experimental AR simulation systems have also agreed with the results on quantification of organic matter removal from infiltrated water [139, 140].

5.7. EXAMPLE FROM THE TUUSULA AR PLANT, FINLAND

At the Tuusula artificial groundwater plant, surface water derived from Lake Päijänne, about 100 km NNE of the plant, is recharged into a glaciofluvial esker aquifer using a pond infiltration method. The volume of artificially recharged water accounts for 70% of water intake from the groundwater system. The distance between the farthest intake well and the infiltration ponds is 700 m. The time span from infiltration to intake of water is approximately 36–51 days. Precipitation and artificial infiltration are the only notable sources of recharge into these aquifers. To prevent leakage from other surface water sources, the groundwater table is controlled by infiltration and pumping. The isotopic composition ($\delta^{18}O$, $\delta^{2}H$) of the groundwater directly below the sprinkling or basin recharge sites was almost equal to that of infiltrated lake water. In production wells, the infiltrated water fraction ranged from 70% to 90%, depending on distance from the recharge sites.

The isotopic composition of DIC in the infiltration water was used to trace the reduction of DOC in subsurface processes. Reducing the concentration of DOC in surface water to a recommended level is the main challenge for managers of groundwater recharge in Finland. A general observation is that the infiltration of surface water through mineral soil leads to a significant decrease in the DOC content, and thus the early stage of subsurface flow is critical. Two distinct processes are suggested for the reduction of the DOC content in infiltrated water during artificial recharge: (1) DOC may be adsorbed as organic matter on the surface of soil particles, and; (2) DOC could be oxidized and decomposed through bacterially mediated processes. In earlier attempts to quantify the removal of DOC, O_2 consumption measurements and the production of CO_2 have been the only methods applicable for reaction rate calculations.

Water samples were collected from 10 sites outside and within the artificial recharge system, and analysed for the isotopic composition of oxygen, hydrogen and DIC, as well as for DOC and TOC contents and basic hydrochemical parameters. The total DIC content was calculated from the chemical composition of the water.

Based on $\delta^{13}C_{DIC}$ determinations and the content of DIC and DOC, the hydrogeochemical evolution of infiltrated water could be divided into three successive stages, in which different processes dominate in the removal of DOC:

(1) The initial DOC content decreased by 44% during the first 330 m of groundwater flow. At the same time, the content of total dissolved carbon (DIC + DOC) remained constant, indicating that the system was closed to external carbon sources. The sources of DIC include atmospheric and soil CO_2, the admixture of local groundwater with a high DIC content, and carbonate dissolution. The recharge water recorded a considerable decrease in $\delta^{13}C_{DIC}$ from −10.7‰ to −16.3‰ at the first observation well next to the infiltration ponds. The change in $\delta^{13}C_{DIC}$ is attributed to the mixing of carbon from two isotopically distinct sources; from the oxidation of DOC in the infiltrated water with terrestrial carbon ($\delta^{13}C = -27‰$, e.g. [141]) and from DIC initially present in the infiltration water ($\delta^{13}C_{DIC} = -10.7‰$). A mean $\delta^{13}C_{DIC}$ value of −20.8‰ was measured for local groundwater. The measured $\delta^{13}C_{DIC}$ values in the water agree with the modelled change in $\delta^{13}C$ values as a function of increasing DIC content. It can be concluded that oxidative decomposition is the main process reducing the content of DOC and producing DIC in the first stage of groundwater flow to a distance of 330 m from the infiltration ponds.

(2) Between 330 m and 450 m from the infiltration ponds, the concentration of DOC decreased by 23% relative to the initial value. DIC content simultaneously decreased. As a result, total dissolved carbon was removed from the system, suggesting that organic carbon was adsorbed on mineral surfaces. Oxygen isotope ratios indicated no significant mixing with local groundwater.

(3) A final decrease of 14% in DOC content was observed between a distance of 450 m and 700 m from the ponds. At the furthest intake well (700 m) the proportion of local groundwater had increased to 52%, adding an additional carbon source to the system. This

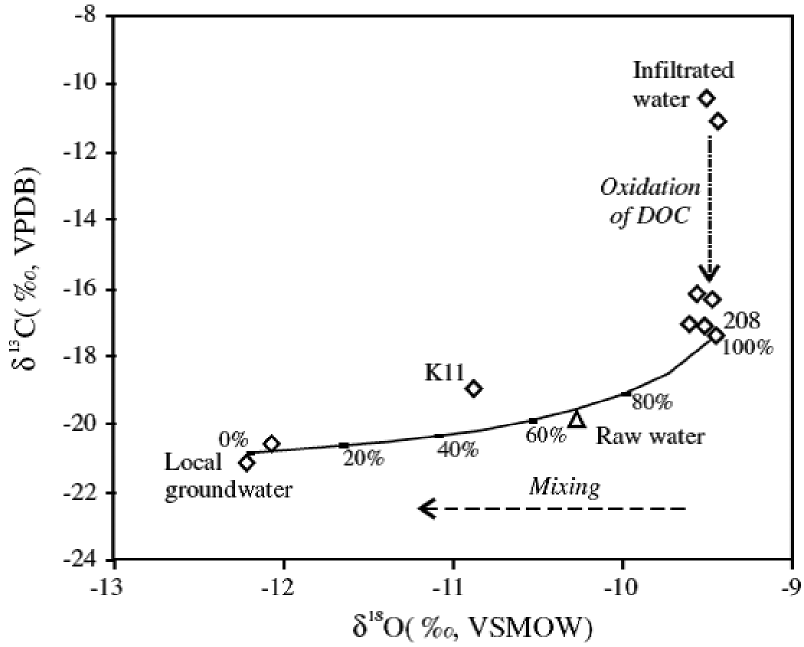


FIG. 22. Variations in $\delta^{18}O$ and $\delta^{13}C_{DIC}$ in infiltrated surface water, artificial groundwater and local groundwater. Oxidative decomposition of DOC is shown as a decrease in $\delta^{13}C_{DIC}$ without any change in $\delta^{18}O$. Mixing of recharged water with local groundwater defines a mixing hyperbola (solid line). The percentages refer to the proportion of infiltrated water in the mixture (from [138]).

> shows up as a significant rise in the concentration of DIC and a decrease in the $\delta^{13}C_{DIC}$ value in water. The $\delta^{13}C_{DIC}$ and $\delta^{18}O_{water}$ values were consistent with a modelled change in $\delta^{13}C$ and $\delta^{18}O$ values, when two end member waters with different DIC contents and isotope ratios were mixed in varying proportions. The results suggested that the shift in $\delta^{13}C_{DIC}$ and in dissolved carbon contents observed at the final stage can be mostly attributed to mixing between infiltrated water and local groundwater.

The total drop in DOC observed at the artificial recharge plant was 0.35 mmol/L or 81% relative to the level in infiltrated water. Fig. 22 illustrates changes in $\delta^{13}C_{DIC}$ and $\delta^{18}O$ during subsurface passage due to oxidative decomposition of DOC and mixing of local groundwater with the water at well 208.

5.8. APPLICATION OF SULFUR AND NITROGEN ISOTOPES

Besides use of stable water molecule isotopes ($\delta^{18}O$, $\delta^{2}H$) and $\delta^{13}C$, other compound specific isotope analyses are potentially of use in AR investigations and monitoring, though examples are still rare.

Sulfur isotopes ($^{34}S/^{32}S$) can be used to identify different sources and sinks of SO_4^{2-} and to quantify bacterial reduction and oxidation of sulfur species during AR, as in any other hydrogeological investigation. Both SO_4^{2-} reduction and sulfide mineral oxidation have impacts on water quality. The dissolution of sulfides (e.g. pyrite) is disadvantageous, as it can generate large amounts of dissolved sulfate (SO_4^{2-}) and iron (Fe^{2+}) and generates acidity. In a carbonate aquifer, the acidity produced in turn induces dissolution of the aquifer matrix as, for example, observed by Herczeg et al. [136] at the Andrews Farm ASR site. It has long been recognised that SO_4^{2-} reduction is isotopically competitive due to the preferential consumption of the lighter ^{32}S isotope (and also ^{16}O), leading to the formation of H_2S and HCO_3^- depleted in ^{34}S and ^{18}O relative to the original SO_4^{2-}. Consequently, the residual SO_4^{2-} fraction will become heavier, or enriched in ^{34}S and ^{18}O (e.g. [142–146]). The reduced sulfide is isotopically light and minerals such as pyrite consequently have relatively negative $\delta^{34}S$. Most studies dealing with isotope fractionation during pyrite oxidation showed that little or no fractionation occurs, and $\delta^{34}S$ values of the SO_4^{2-} produced resembled that of the sulfur source (e.g. [136, 147–151]) used sulfur isotopes and dissolved SO_4^{2-} data for the above mentioned ASR study at Andrews Farm. Following injection, $\delta^{34}S$ values initially shifted towards more negative values, due to the oxidation of light sulfide minerals. The process was also reflected in an increase of Ca^{2+} and Mg^{2+} as a result of dissolution of carbonate minerals in the aquifer matrix. After the first two injection cycles, sulfide oxidation tapered off, probably due to a lack of readily oxidizable sulfide minerals. In storage phases, SO_4^{2-} reduction occurred, resulting in a decrease of net SO_4^{2-} and an increase in $\delta^{34}S_{SO4}$ (Fig. 23).

Stable isotope ratios of $\delta^{15}N$ and $\delta^{18}O$ in nitrate are used in hydrogeological studies to identify processes and sources that affect the concentration of nitrogen species in groundwater. High levels of nitrate in groundwater are undesirable, mainly because it can cause methemoglobinemia in infants [152]. The World Health Organisation and many national environmental agencies allow maximum permissible limits of 10 ppm nitrate-N (equal to 50 ppm as NO_3^-) in drinking water. Hence, understanding the effectiveness of nitrification and/or denitrification during AR is important, especially since AR is often used as a method for wastewater recycling (wastewater tends to have high concentrations of different N species).

Because the $\delta^{15}N_{NO3}$ of different sources (such as fertilizers, soil, manure or domestic waste) can often be differentiated (Fig. 24; [152]), $\delta^{15}N_{NO3}$ has the potential to trace NO_3^- derived from AR if wastewater is the source water. As in other isotope fractionation processes, the lighter isotope (^{14}N) reacts faster than the heavier isotope (^{15}N), resulting in reaction products which are isotopically lighter than the reactants. For example, during nitrification, when ammonium is turned into nitrate, the reaction product (nitrate) is isotopically lighter (with a lower $\delta^{15}N$ value) than the ammonium left behind (e.g. [152]). Therefore, $\delta^{15}N$ can be used to identify processes like nitrification and denitrification occurring in the subsurface following injection (or recharge) in AR systems. Also, because denitrification alters the $\delta^{15}N_{NO3}$, it can potentially be used as a tracer to differentiate between nitrate dilution and denitrification in groundwater.

5.9. SUMMARY AND CONCLUSIONS

An important objective of artificial recharge can be to improve the quality of source water, which can range from various surface water sources to treated wastewater. Stable isotopes can be used indirectly and directly to help understand the fate and transport of water constituents, most importantly contaminants at AR sites. As a prerequisite for water quality assessments, stable isotopes of the water molecule ($\delta^{18}O$, δ^2H) are essential tools to identify residence times and mixing between native groundwater and AR water through time series analysis and isotope mass balancing. Knowledge of these hydrogeological basics allows for calculation of degradation rate constants and half-lives of pollutants, and enables differentiation between contaminant removal and dilution. Stable isotopes are still largely underutilized for direct water quality applications at AR sites. Stable isotopes of carbon, sulfur and nitrogen in particular can support hydrochemical investigations to identify geochemical processes such as organic matter oxidation, calcite dissolution, sulfide mineral oxidation, sulfate reduction, nitrification and denitrification occurring during subsurface flow.

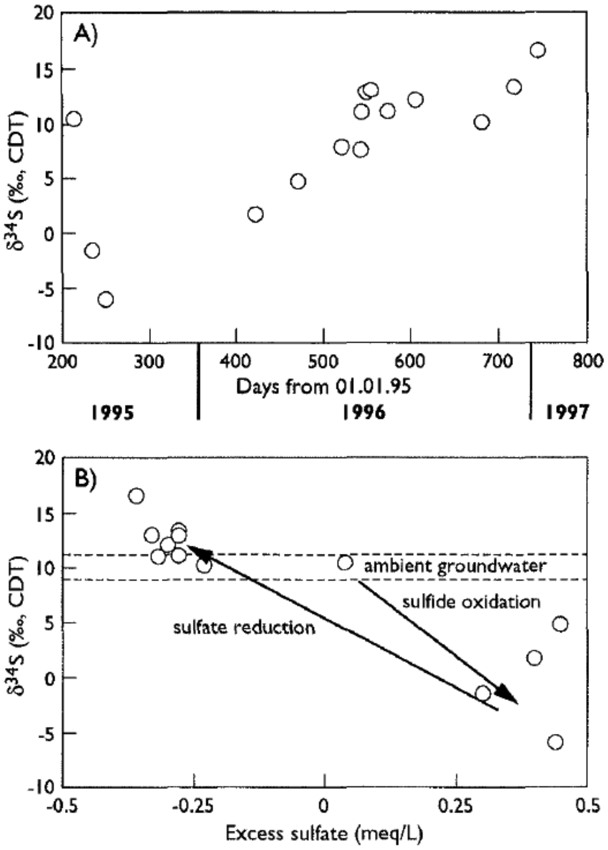


FIG. 23.(a) Changes in $\delta^{34}S_{SO4}$ over a one year period following the third injection of storm water to the aquifer at the Andrews Farm ASR site in South Australia; (b) $\delta^{34}S_{SO4}$ versus excess SO_4^{2-} following injection and storage at Andrews Farm [136].

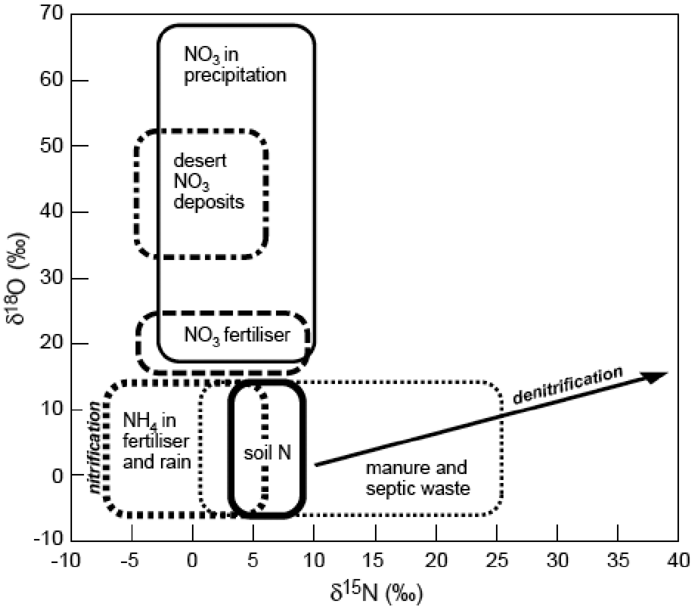


FIG. 24. Typical ranges of $\delta^{18}O$ and $\delta^{15}N$ signatures of nitrate. The large range in δ values is due to nitrification of ammonium and/or organic-N in fertiliser, precipitation, and organic waste. From Ref. [153] in [152].

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ABBREVIATIONS

AR	Artificial recharge
ASR	Aquifer storage and recovery
CFCs	Chloroflurocarbons
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
GINP	Global Network of Isotopes in Precipitation
GMWL	Global Meteoric Water Line
HDPE	High-density polyethylene
LMWL	Local Meteoric Water Line
PPCPs	Pharmaceuticals and personal care products
TOC	Total organic carbon
VPDB	Vienna Pee Dee Belemnite
VSMOW	Vienna-Standard Mean Ocean Water
ΔNe	Ne supersaturation with regard to the noble gas temperature. The term is proxy to ‘excess air’ or ‘entrained air’.

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