Chapter 16
Using Oxygen-18 and Deuterium to Delineate Groundwater Recharge at Different Spatial and Temporal Scales

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16.1 Introduction

Over the past five decades, stable isotopes of oxygen (^{18}O) and hydrogen (^{2}H, or deuterium [D]) have been used to delineate sources and timing of precipitation, identify effects of evaporation, and apportion end-member contributions in streamflow and groundwater (Darling et al. 2005). Equilibrium and kinetic fractionations cause these isotopes to be preferentially enriched in liquid water and depleted in water vapour relative to the lighter, more common stable isotopes ^{16}O and ^{1}H. As condensation and precipitation occur, the remaining water vapour becomes isotopically lighter; this process is promoted by decreasing temperature. During a storm, rainout can result in progressive depletion in the ^{18}O and ^{2}H contents of precipitation. Similarly, rainfall becomes progressively depleted with distance from the coast

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in mid-latitude regions and with elevation as air masses move inland and upward (Darling et al. 2005). Isotopic analyses of precipitation from stations around the world show the following general relationship, known as the Global Meteoric Water Line (GMWL; Craig 1961):

$$\delta^2\mathrm{H} = 8\delta^{18}\mathrm{O} + 10 \quad (16.1)$$

where the relative abundance of stable isotopes is defined as

$$\delta = \left(\left(\frac{R_{\text{sample}}}{R_{\text{standard}}}\right) - 1\right) \times 1000 \quad (16.2)$$

and R refers to the isotopic ratio ($^{18}O/^{16}O$ or $^{2}H/^{1}H$). Both $\delta^{18}O$ and $\delta^{2}H$ are reported in per mil (‰) notation relative to Standard Mean Ocean Water (SMOW; Craig 1961) or the equivalent Vienna SMOW (VSMOW) (Kendall and Caldwell 1998). Local meteoric water lines (LMWLs), commonly with slopes <8, reflect seasonal variability in rainfall and moisture source areas. Partial evaporation can cause differential enrichment of ^{18}O relative to ^{2}H in residual soil moisture and surface water, resulting in $\delta^{2}H$ versus $\delta^{18}O$ trends sub-parallel to MWLs (Darling et al. 2005).

Variability in $\delta^{18}O$ and $\delta^{2}H$ over broad spatial and temporal scales facilitates the use of water isotopes in identifying sources and timing of groundwater recharge and flow. Recharge tends to be only slightly modified by evaporation (typically within ~0.5‰ in $\delta^{18}O$ relative to bulk rainfall), but different sources of recharge (e.g. partly evaporated surface water or intruded seawater in coastal regions) can impart distinctive isotopic compositions to groundwater (Darling et al. 2005). In regional aquifer systems, groundwater residence times can be as long as 10^6 years (Sturchio et al. 2004), although actively circulating groundwater is commonly much younger (Darling et al. 2005). Consequently, deep groundwater can serve as a paleoclimatic archive, preserving evidence of recharge during glacial periods as indicated by depleted values of $\delta^{18}O$ and $\delta^{2}H$ (Jasechko et al. 2015). Stable isotopes of younger groundwater ($\lesssim 10^4$ years) show seasonality of recharge (i.e. during winter in arid and temperate climates and during the wet season in tropical regions; Jasechko et al. 2014). Although dispersion during groundwater recharge and flow dampens variability in $\delta^{18}O$ and $\delta^{2}H$, storm event-scale (hourly to daily) fluctuations in stable isotopes and other hydrochemical parameters can be evident in surficial aquifers with relatively rapid circulation. This is pronounced in karstified limestone, where solution-enhanced permeability can result in integrated surface and subsurface drainage networks linking sinkholes to springs (Darling et al. 2005). The development of isotope-ratio infrared spectroscopy (IRIS), such as cavity ring-down spectroscopy, during the past 20 years has simplified measurements of $\delta^{18}O$ and $\delta^{2}H$ relative to gas-source isotope-ratio mass spectrometry (IRMS) (van Geldern and Barth 2012). As a result, large sample sets, such as high temporal-resolution storm hydrographs, are amenable to stable isotope analyses (Tweed et al. 2016).

Fig. 16.1 Locations of study sites. HP = Southern High Plains (USA); MA = Middle Atlas plateau (Morocco); WB = western Bengal basin (India); H = Houzhai karst basin (China). Modified from www.freeusandworldmaps.com/html/World_Projections/WorldPrint.html (Copyright J. Bruce Jones 2019)

This paper reviews the use of $\delta^{18}O$ and $\delta^{2}H$ to constrain sources and timing of recharge in two regional sedimentary aquifer systems and two mountainous karst terrains. The study sites are located between 21°N and 36°N (Fig. 16.1) and span a variety of climatic settings. The regional aquifer systems include the unconfined High Plains aquifer and underlying confined aquifers in the northern part of the Southern High Plains (Texas, USA; continental, temperate, semi-arid climate) and the semi-confined Holocene–Pleistocene aquifers of the western Bengal basin (West Bengal, India; monsoonal, tropical climate). The karst terrains include the Liassic aquifer of the Middle Atlas plateau (Morocco; Mediterranean [dry-summer, sub-tropical] climate) and the Houzhai basin of the Southeast Asian karst region (Guizhou, China; monsoonal, sub-tropical climate). We focus on using stable isotopes to delineate spatial variability in regional aquifers, including paleorecharge to deep aquifers, diffuse versus focused recharge to surficial aquifers and sources of salinization. For mountainous karst aquifers, which may be sensitive to climate change (Hartmann et al. 2014), we focus on temporal variability in individual spring basins and identify recharge at event to seasonal time scales.

16.2 Materials and Methodology

Water samples were collected from water and oil wells in the Southern High Plains (HP) in July–August 1997; from water wells in the western Bengal basin (WB) in May 2003–2005 and November 2007; from Zerouka spring in the Middle Atlas (MA) daily from 19 March 2014 to 28 March 2015; and from Maoshuikeng spring in the Houzhai basin (H) hourly to bihourly on 23–25 June 2018 (Table 16.1). Stable

Table 16.1 Study sites, numbers of samples collected and water bodies sampled

Study site	Location	No. of samples	Water body
Southern High Plains	Carson and Gray Counties, Texas, USA	9 3 3	High Plains (Ogallala) aquifer Whitehorse Group (Permian) Wolfcampian and Upper Permian petroleum reservoirs
Western Bengal basin	Murshidabad district, West Bengal, India	43 27	East-bank (Sonar Bangla) aquifer West-bank aquifer
Middle Atlas plateau	Ifrane, Morocco	375	Zerouka spring, Liassic aquifer
Houzhai karst basin	Puding County, Guizhou, China	36	Maoshuikeng spring, Guanling Formation

isotopes were analysed by IRMS for HP and WB (2003–2005) samples and by IRIS for WB (2007), MA and H samples. Details of monitoring, including sample collection and analyses, are given in Mehta et al. (2000a) for HP, in Mukherjee et al. (2007b, 2018) for WB, in Howell et al. (2019) for MA and in Barna (2019) for H.

16.3 Results and Discussion

Southern High Plains

The High Plains aquifer is the largest in the USA. In the Southern High Plains, this aquifer occurs within the Ogallala Formation (Upper Tertiary), which consists of clayey to gravelly sediments overlying Triassic sandstones and mudstones (Dockum Group) and Permian evaporites, carbonates and clastic redbeds. The High Plains aquifer is extensively exploited for agriculture as well as public and industrial uses. In the northern half of the region, High Plains groundwater typically has total dissolved solids (TDS) < 400 mg/L. However, two saline plumes (maximum Cl^- concentration >500 mg/L and maximum TDS >2000 mg/L) of combined areal extent >1000 km^2 occur in the aquifer near its northeastern edge (Mehta et al. 2000b). The southern plume overlies the Panhandle oil and gas field, which produces petroleum from Pennsylvanian and Permian carbonate and clastic reservoirs with TDS typically 140–290 g/L (Mehta et al. 2000a). Identifying the mechanism of salinization of the High Plains aquifer (natural vs. anthropogenic) is important for regional water resources management.

A plot of δ^2H versus δ^{18}O (Fig. 16.2), which includes data from the previous regional studies, shows that four of seven groundwater samples from the southern plume are isotopically depleted (δ^{18}O −8.8 to −6.9‰, δ^2H −88 to −70‰) relative to

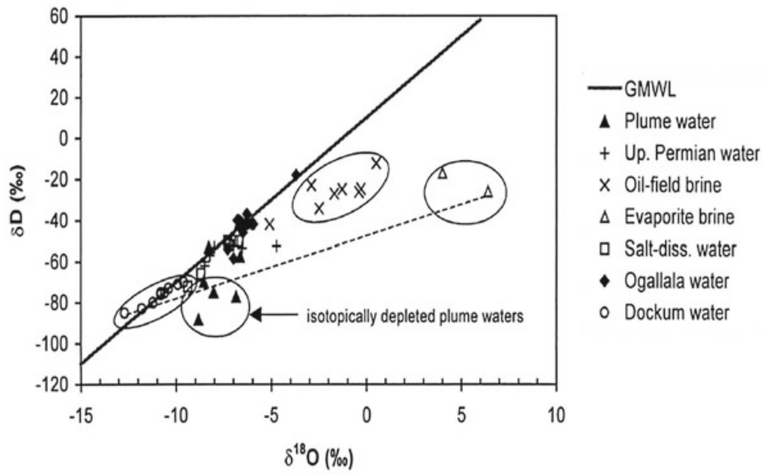

Fig. 16.2 δD (δ^2H) versus $\delta^{18}O$ relationship for end-member waters in the northern part of the Southern High Plains. Reprinted from *Applied Geochemistry*, Vol. 15, Mehta, S., Fryar, A. E., and Banner, J. L., Controls on the regional-scale salinization of the Ogallala aquifer, Southern High Plains, Texas, USA, pp. 849–864, Copyright 2000, with permission from Elsevier

upgradient High Plains groundwater, water from the salt-dissolution zone in Permian evaporites and oil-field brines. On the plot of $\delta^{18}O$ versus Cl^- (Fig. 16.3), the isotopic signatures of plume water can be explained by cross-formational mixing of depleted water from the confined Dockum aquifer with water from Permian evaporites and thence with High Plains groundwater. Consequently, petroleum production is not implicated in regional-scale salinization of the High Plains aquifer (Mehta et al.

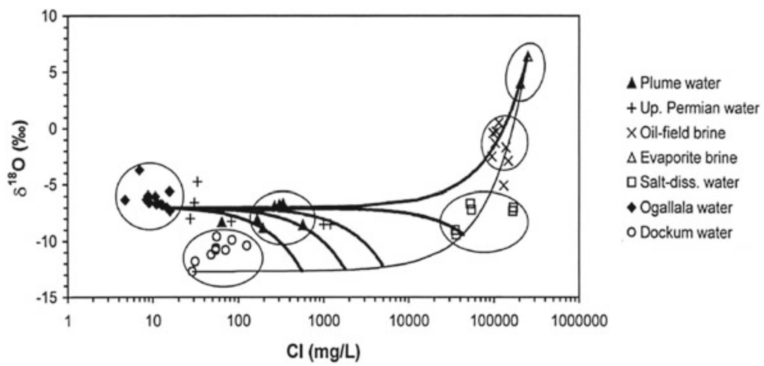

Fig. 16.3 $\delta^{18}O$ versus Cl^- relationship for end-member waters with selected mixing lines to explain the origin of salinity in the High Plains aquifer. Reprinted from *Applied Geochemistry*, Vol. 15, Mehta, S., Fryar, A. E., and Banner, J. L., Controls on the regional-scale salinization of the Ogallala aquifer, Southern High Plains, Texas, USA, pp. 849–864, Copyright 2000, with permission from Elsevier

2000a). Numerical modelling indicates that groundwater recharged during Pleistocene or earlier times flows laterally tens of km to >100 km within the Dockum and contiguous Upper Permian units. Salinization may result from relatively low rates (<1 L/day) of cross-formational discharge into the High Plains aquifer (Mehta et al. 2000b).

Western Bengal Basin

The Bengal (Ganges–Brahmaputra–Meghna) basin is the world's largest fluvio-deltaic basin. Its western margin is marked by the River Bhagirathi-Hooghly, the primary distributary of the River Ganges in India, which flows ~200 km south to the Bay of Bengal. East of the Bhagirathi-Hooghly, meandering and aggradation have created a sequence of channel sands that comprise the regional, semi-confined Sonar Bangla aquifer (Mukherjee et al. 2007a). This and other Holocene aquifers in the Bengal basin are marked by the widespread occurrence of As concentrations in groundwater >0.01 mg/L (the World Health Organization drinking-water guideline). Reductive dissolution of sedimentary Fe (oxyhydr) oxides appears to release adsorbed As to groundwater (Bhattacharya et al. 1997). Groundwater in surficial aquifers west of the Bhagirathi-Hooghly tends to have As concentrations <0.01 mg/L, even though total As in sediments does not systematically vary between areas with high and low As in groundwater (Mukherjee et al. 2018). Consequently, As mobilization from sediments into groundwater appears to depend upon local redox and groundwater flow conditions.

A plot of δ^2H versus δ^{18}O (Fig. 16.4) shows distinct differences between groundwater samples from east and west of the Bhagirathi-Hooghly in the northwest corner of the Bengal basin (Murshidabad district, West Bengal). With the exception of one sample that may have been affected by infiltration along the well casing, east-bank

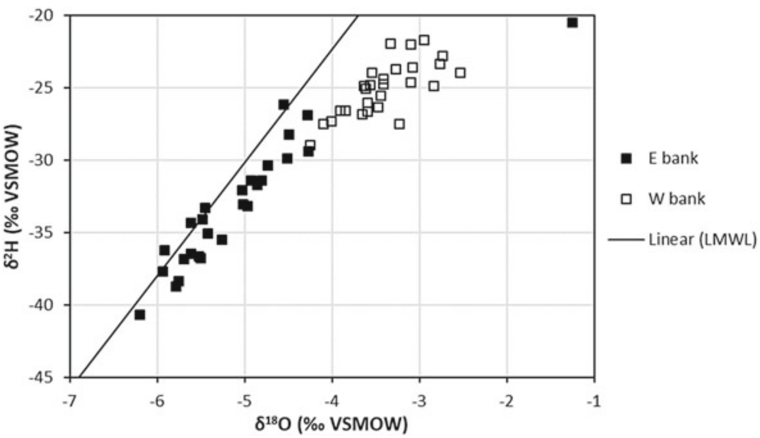

Fig. 16.4 δ^2H versus δ^{18}O relationship for east-bank (Sonar Bangla aquifer) and west-bank groundwater, Murshidabad district, West Bengal. Data from Mukherjee et al. (2007b, 2018); LMWL (δ^2H $= 7.83\delta^{18}$O $+ 9.01$) from Datta et al. (2011)

samples in the Sonar Bangla aquifer fell along the LMWL of Datta et al. (2011) and had lower $\delta^{18}O$ values than west-bank samples, which fell sub-parallel to the LMWL. Isotopically depleted east-bank values appear to reflect focused, minimally evaporated recharge through paleochannels that are incised through near-surface clays, whereas enriched west-bank values reflect diffuse recharge in upland areas (Mukherjee et al. 2018). Several previous studies in the area have noted a coincidence of paleochannels (as opposed to artificial ponds; Datta et al. 2011) with elevated As in underlying groundwater. We speculate that focused infiltration associated with monsoonal flooding introduces organic matter capable of mobilizing As.

Middle Atlas

Around the Middle Atlas plateau, springs in Jurassic (Liassic) dolomitic limestones and calcareous dolomites form the headwaters of Morocco's two largest rivers (the Sebou and Oum Er-Rbia). A series of SW–NE trending normal faults runs through the plateau and adjoining Saiss basin to the north. Development of preferential flowpaths and karst features is promoted by faulting and limited by the Mg content of the carbonate rocks. Recharge occurs at elevations $\gtrsim$800 m above mean sea level (amsl) and is associated primarily with cool-season (October–April) rainfall (Howell et al. 2019). Morocco is susceptible to droughts lasting years to decades, and the western Mediterranean region is projected to be a hotspot of climate change during the twenty-first century (Schilling et al. 2012). Understanding event scale to seasonal responses of springs to precipitation and air temperature is thus important for managing water supplies for municipal use, agriculture and environmental flows.

A 13-month time-series plot for Zerouka spring (Fig. 16.5) shows that hourly water temperature was nearly invariant (mean 12.54 °C, range 12.49–12.61 °C), in contrast to daily $\delta^{18}O$ fluctuations (mean −7.84‰, range −8.28 to −7.22‰). Temperature fluctuations appear to be dampened by flow circulating to depths >100 m below land

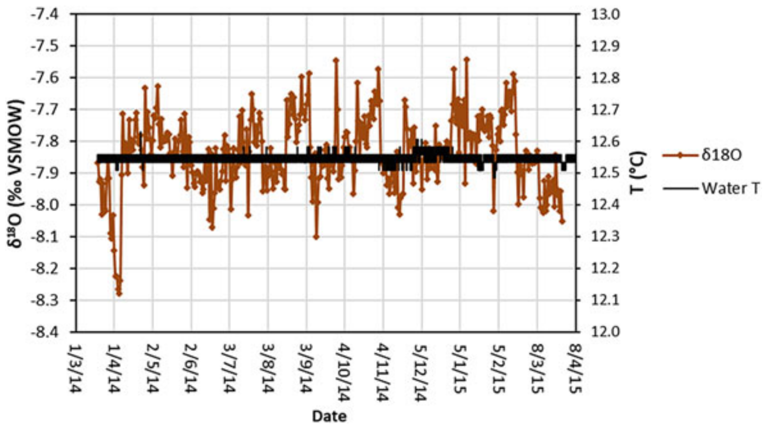

Fig. 16.5 Daily $\delta^{18}O$ and hourly water temperature for Zerouka spring, Middle Atlas plateau, March 2014–April 2015. Data from Howell et al. (2019)

surface at Zerouka (1664 m amsl). Howell et al. (2019) observed that Zerouka water samples from late winter–early spring tended to fall along the LMWL ($\delta^{18}O = 6.9\delta^{2}H + 6.9$; Benaabidate and Fryar 2010), whereas samples at other times were more scattered and sub-parallel to the LMWL. Similarly, 10-day moving averages of $\delta^{18}O$ and $\delta^{2}H$, which smoothed variability in daily signals, tracked together in March–April 2014 and February–March 2015 (Howell et al. 2019). The seasonal coincidence of smoothed $\delta^{18}O$ and $\delta^{2}H$ signals suggests that less-evaporated, focused recharge displaces more-evaporated, diffuse recharge as the aquifer refills. The insensitivity of water temperature to storm events indicates significant inertia and subsurface storage in the spring basin, perhaps because of limited karstification. Consequently, discharge may respond relatively slowly (over periods of years) to anticipated changes in recharge (Howell et al. 2019).

Houzhai Basin

The ~73.5-km^2 Houzhai basin is located on the Yunnan–Guizhou plateau near the centre of the South China karst region. The basin is marked by Neogene cockpit karst, comprised of conical hills and star-shaped valleys, developed in Triassic carbonates of the Guanling Formation. Elevation ranges from 1565 m amsl in the headwaters to 1218 m amsl at the basin outlet (Maoshuikeng spring; Zhang et al. 2017). The southern part of the basin is marked by a well-developed conduit network with multiple branches, whereas surface drainage is pronounced in the northern part of the basin, where dolomite and mudstones are more prevalent. Monsoon rains during summer cause the conduit network to fill and overflow passages to become active. As summarized by Zhang et al. (2017) and Barna (2019), numerous studies during the past three decades have investigated the hydrology and geochemistry of the Houzhai basin. However, the relative contributions of different branches of the conduit network to discharge at Maoshuikeng are still not completely understood.

A 46-h time-series plot (Fig. 16.6) shows responses of $\delta^{18}O$ and manually measured water temperature at Maoshuikeng following 60 mm of rainfall in the preceding 53 h. Sampling began 5 h after the stage peak. Temperature was marked by two distinct drops and an intervening rebound, each ~3 °C, which suggests the arrival of two successive storm pulses at the spring. In comparison, $\delta^{18}O$ data (and $\delta^{2}H$; Barna 2019) shows three drops, which may represent recharge from progressively farther up the watershed. This inference is consistent with relatively depleted values measured in the Chenqi sub-catchment near the headwaters of the Houzhai basin (Chen et al. 2018). The multiple pulses observed at Maoshuikeng could also represent fast- and slow-flow contributions from different branches of the conduit network, consistent with dye tracing (Barna 2019). The results of this study are useful for understanding the susceptibility of local water supplies to possible sources of contamination.

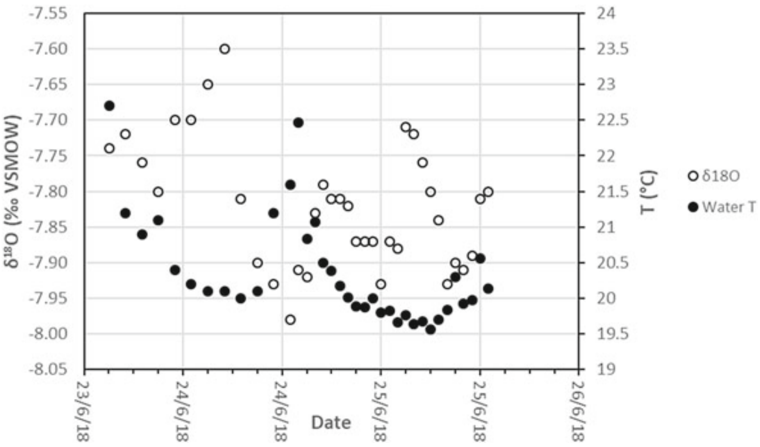

Fig. 16.6 Hourly to bihourly δ^{18}O and water temperature for Maoshuikeng spring, Houzhai Basin, 23–25 June 2018. Data from Barna (2019)

16.4 Conclusions

The case studies presented in this paper illustrate the utility of stable isotopes of water for constraining sources and timing of recharge over a range of spatial and temporal scales. In regional sedimentary aquifer systems, δ^{18}O and δ^{2}H values can indicate sources of paleorecharge and salinization (as in the High Plains aquifer) and differentiate between diffuse and focused recharge (as in the western Bengal basin). In karst terrains, where groundwater flow is relatively rapid, δ^{18}O and δ^{2}H values can indicate event scale to seasonal variability in recharge, as in the Houzhai basin and Middle Atlas plateau, respectively. In each of these cases, water isotopes complement other techniques, such as monitoring of other hydrochemical parameters (e.g. solutes and temperature), use of anthropogenic tracers and mathematical modelling of groundwater flow, in understanding the behaviour of groundwater flow systems in various settings. The development of IRIS, with its relatively low-cost, high-throughput analyses, should make the use of stable isotopes more routine in hydrologic studies.

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