

ISOTOPE METHODS IN WATER RESOURCES MANAGEMENT

© M. Ragheb
11/23/2015

INTRODUCTION

The rational management of water resources requires the human interaction and natural processes in the hydrologic cycle to be fully understood. This requires an interdisciplinary, holistic approach with a long term outlook. Without knowledge of age, recharge, and mixing, investments in water supply and quality are at risk.

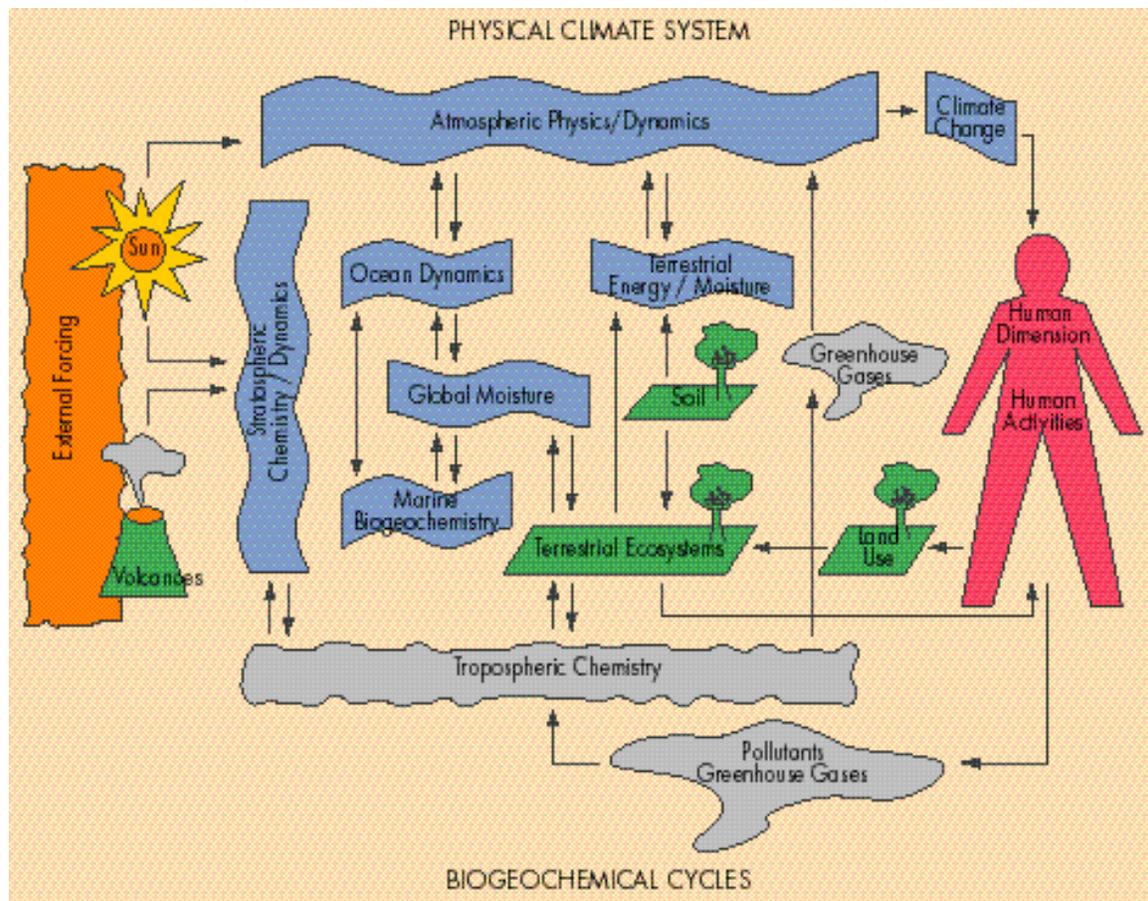


Figure 1. The biogeochemical cycles in the physical climate system. Source: IAEA.

In aquifer studies, the uncertainty about recharges sources and processes and the recharge rate are major considerations. Groundwater does not exist in isolation, but is an integral link in the predominant hydrological cycle at a given location. The most important determinant of available water for extraction in an aquifer system is the rate of

replenishment or recharge from precipitation. Another factor is surface water percolation into the aquifer.

WATER SOURCES AGE DETERMINATION

Age determination is used as a guide for the classification of the susceptibility of ground water to near surface contamination. Environmental isotopes and tracers are used to determine the age of ground water.

The radioactive isotope Carbon¹⁴ is used to date ground water that is older than 1,000 years. Chlorofluorocarbons or Freon and tritium as a product of above ground nuclear weapons testing in the 1960s techniques are used to date ground water that is less than 50 years old. The analysis of dissolved gas samples can estimate the temperature of ground water at the time of recharge. This is used in the age determination techniques.

Table 1. Time span for the environmental isotopes and tracers used to assess the age of water sources.

Methodology	Average time span [years]
Radiocarbon C ¹⁴ dating	1,000 – 30,000
Tritium ¹ T ³ dating	0 - 50
Tritium to helium ³ , ¹ T ³ / ² He ³ isotopic ratio	0 - 30
Chlorofluorocarbons dating, CFC-11, CFC-12, CFC-113	0 - 50

Over-exploitation due to human population pressure result in problems of reduction in yields from water wells; which ultimately increases the cost of pumping and thus the price of urban water supplies, drying up of shallow wells which are subsequently abandoned because of falling water levels, land subsidence due to over exploitation; a major problem in many large cities, intrusion of salt water in coastal sites and rising of saline water from deep or adjacent groundwater in response to pumping at inland sites.

A major concern is the unsustainable depletion of non renewable ground water reserves, particularly of extremely old ground water derived from rainfall that fell over the last 30,000 years. The present extraction from these reserves is considered as “mining” the existing “fossil water” and is unsustainable due to the non replacement of this resource.

Table 2. Radioactive and stable isotopes of potential interest in water hydrology studies.

Isotope	Half life T _{1/2}	Natural Abundance a/0
¹ H ¹	-	99.985
¹ D ²	-	0.015
¹ T ³	12.33 a	10 ⁻¹⁵
² He ³	-	0.00014
² He ⁴	-	99.99986

${}^6\text{C}^{12}$	-	98.89
${}^6\text{C}^{13}$	-	1.11
${}^6\text{C}^{14}$	5,730 a	1.2×10^{-9}
${}^7\text{N}^{14}$	-	99.63
${}^7\text{N}^{15}$	-	0.37
${}^8\text{O}^{16}$	-	99.758
${}^8\text{O}^{17}$	-	0.038
${}^8\text{O}^{18}$	-	0.204
${}^{16}\text{S}^{32}$	-	95.02
${}^{16}\text{S}^{33}$	-	0.75
${}^{16}\text{S}^{34}$	-	4.21
${}^{16}\text{Cl}^{35}$	-	75.77
${}^{16}\text{Cl}^{36}$	3.01×10^5 a	-
${}^{16}\text{Cl}^{37}$	-	24.23
${}^{53}\text{I}^{131}$	8.041 d	-
${}^{60}\text{Nd}^{142}$	-	27.2
${}^{60}\text{Nd}^{143}$	-	12.2
${}^{60}\text{Nd}^{144}$	2.1×10^{15} a	23.8
${}^{60}\text{Nd}^{145}$	$> 10^{17}$ a	8.3
${}^{60}\text{Nd}^{146}$	-	17.2
${}^{60}\text{Nd}^{148}$	-	5.7
${}^{60}\text{Nd}^{150}$	-	5.6

GROUNWATER ANALYSIS

During the process of age determination, ground water samples are also analyzed for major dissolved constituents such as Radon²²² a radiological health hazard during bathing and through air inhalation in homes.

Nitrates and dissolved organic carbon also aid in age determinations and in the assessment of natural susceptibility.

Field properties such the pH value, alkalinity, temperature, specific conductance, and dissolved oxygen are also monitored during sample collection. The time to collect a sample is 2 - 3 hours.

Table 3. Sampled dissolved constituents of ground water.

Component	Constituent
Radionuclides	Radon ²²²
Organic carbon	Dissolved Organic Carbon (DOC)
Nutrients	NO ₂ and NO ₃ as N
Major ions	Ca, Mg, Na, K, Cl, SO ₄ , SiO ₂ , Fe, Mn, Sn

RADIOCARBON, CARBON¹⁴ DATING

The production of Carbon¹⁴, also referred to as radiocarbon with a half-life of 5,730 years, is an ongoing nuclear transformation from the cosmic rays bombardment of nitrogen¹⁴ in the Earth's atmosphere. Neutrons produced in cosmic ray showers are captured by the nitrogen nuclei forming radioactive C¹⁴, according to the (n, p) reaction:



Its concentration in the Earth's atmosphere increased by about a factor of 2 during the mid 1960's as a result of the atmospheric testing of thermonuclear weapons.

The atmospheric radiocarbon exists as C¹⁴O₂ and is inhaled or ingested by all fauna and flora. Because only living plants continue to incorporate C¹⁴, and stop incorporating it after death, it is possible to determine the age of organic matter. This is the basis of the Carbon Dating methodology.

The specific activity or activity per unit mass, of the carbon present in a sample A'(t) can be determined. Upon measuring the activity of the archaeological sample, A(t), and determining its weight g, one can calculate its specific activity as:

$$A'(t) = \frac{A(t)}{g} \left[\frac{\text{Becquerel}}{\text{min.gm}} \right] \quad (2)$$

The equilibrium specific activity A'_∞ of C¹⁴ in carbon has been constant, except for fluctuations at the times of solar flare events, at about 15 [disintegrations / (minute.gram)].

In the radioactive decay law:

$$\begin{aligned} A'(t) &= A'_{\infty} e^{-\lambda.t} \\ &= A'_{\infty} e^{-\frac{\ln 2}{T_{1/2}}.t} \end{aligned} \quad (3)$$

taking the natural logarithm of both sides, and solving for the time t, we get:

$$t = -T_{1/2} \ln \frac{A'(t)}{A'_{\infty}} \quad (4)$$

Substituting for the known value of the half-life of Carbon¹⁴ and the equilibrium specific activity, we get:

$$t = -5,730 \ln \frac{A'(t)}{15} [\text{years}] \quad (5)$$

By substitution of the measured value of the sample's specific activity from Eqn. 2 into Eqn. 5, one can then determine the organic sample's age t in years.

EXAMPLE

Two grams of carbon in an organic sample are analyzed and found to have an activity of 20 disintegrations per minute (dpm) or Becquerel / min.

The specific activity would be:

$$A'(t) = \frac{A(t)}{g} = \frac{20}{2} = 10 \left[\frac{\text{Bq}}{\text{min.gm}} \right]$$

An estimate of the approximate age of the sample becomes:

$$\begin{aligned} t &= -5,730 \ln \frac{A'(t)}{15} \\ &= -5,730 \ln \frac{10}{15} \\ &= 2,323 \text{ [years]} \end{aligned}$$

The ${}^{14}\text{C}$ activities are also expressed as a percent of modern carbon (pmC) where:

$$pmC = \frac{A'(t)}{A'_{\infty}} \times 100 \quad (6)$$

This leads to an alternate form of Eqn. 5 as:

$$t = -5,730 \ln \frac{pmC}{100} \text{ [years]} \quad (5)'$$

With a half-life of 5,730 years, ${}^{14}\text{C}$ is useful for dating ground water that is between 1,000 and 30,000 years old.

Diffusion and geochemical reactions within an aquifer can alter the ${}^{14}\text{C}$ activity. A geochemical reaction path model is usually used to account for the dilution and the addition of carbon along ground water flow paths.

TRITIUM, DEUTERIUM AND He^3 DATING

Tritium ${}^3\text{T}$ is the radioactive isotope of hydrogen with a half life of 12.33 years and is an excellent indicator of ground water recharge since 1952. The production of tritium in the atmosphere occurs naturally by cosmic ray spallation. The produced neutrons are captured by deuterium nuclei to form tritium, according to the reaction:



However, its main source was the atmospheric testing of thermonuclear weapons in the 1960s, which peaked around 1963 and is commonly referred to as the “tritium peak,” or “bomb peak.”

The standard unit of measure is the tritium unit (TU) for which one TU is equivalent to one tritium atom per 10^{18} atoms of hydrogen or in terms of radioactivity 3.2 picocuries per liter.

The atmospheric concentration of tritium has gradually declined since 1963 and present day ground water typically contains < 1 - 10 TU, and rarely exceeding 50 TU.

The tritium/helium³ or ${}^1D^2/{}^1T^3$ isotopic ratio method is based on the radioactive decay of tritium into He³, a beta particle and an antineutrino according to the equation:



Tritium and helium are relatively inert gases. Multiple sources of He³ are present in the environment such as the Earth's mantle and atmosphere, fluid inclusions within rocks, and excess air entrained in ground water during recharge. This method separates the ${}^2He^3$ derived from ${}^1T^3$ or tritogenic ${}^2He^3$ from that is derived from natural sources.

The apparent age estimates from the ${}^1D^2/{}^1T^3$ method can be extremely accurate to within months for ground water recharged since 1963 containing high concentrations. The ${}^1D^2/{}^1T^3$ method is a useful technique for sites that are contaminated with organic compounds.

Table 4. Some Radioactive Isotopes produced in the atmosphere by neutrons from cosmic rays.

Isotope	Half life	Activity density in the lower troposphere, [dis/(min.m ³)]
Tritium, ${}^1T^3$	12.3 years	10
Beryllium ⁷	53 days	1
Beryllium ¹⁰	2.7 million years	10^{-7}
Carbon ¹⁴	5760 years	4
Sodium ²²	2.6 years	10^{-4}
Silicon ³²	700 years	2.0×10^{-6}
Phosphorous ³²	14.3 days	2.0×10^{-2}
Phosphorous ³³	25 days	1.5×10^{-2}
Sulfur ³⁵	87 days	1.5×10^{-2}
Chlorine ³⁶	0.3 million years	3.0×10^{-6}

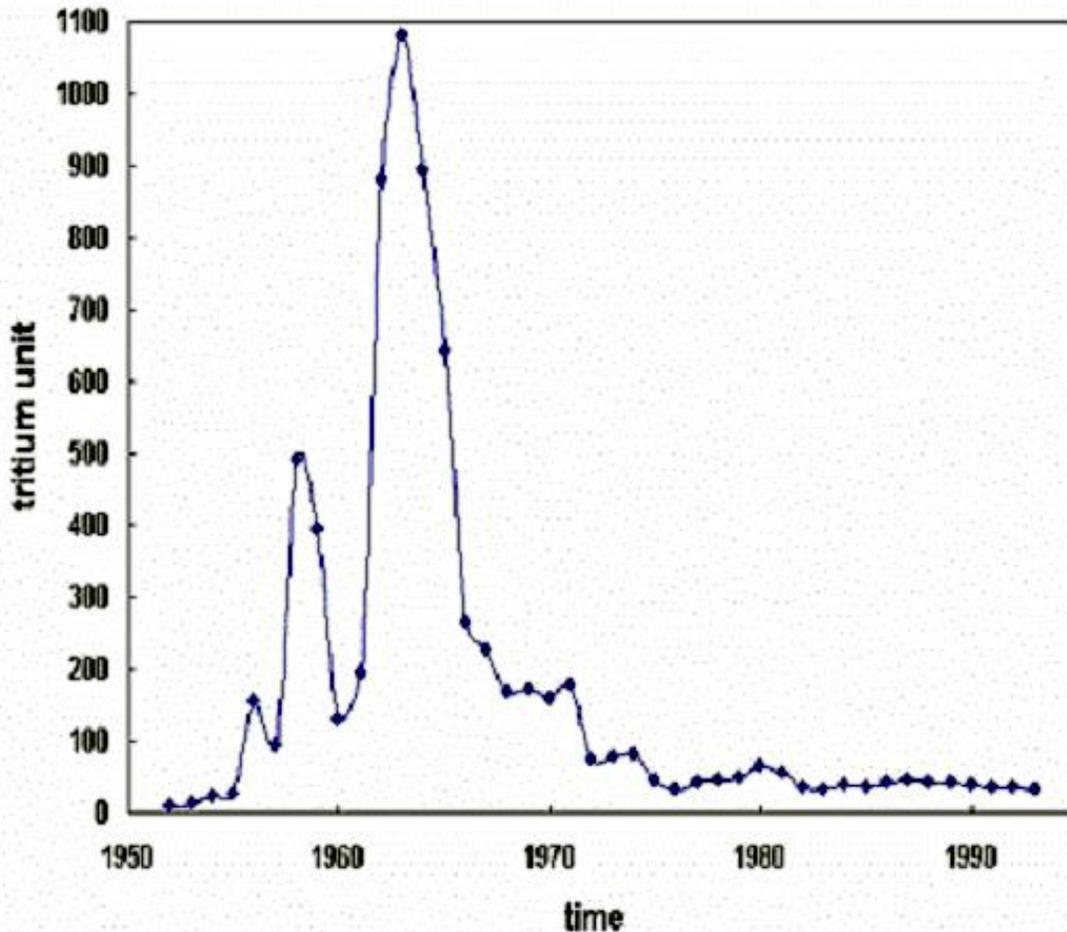


Figure 2. The tritium peak occurred around 1963 from the thermonuclear devices testing in the atmosphere.

CHLOROFLUOROCARBONS, CFCs DATING

Chlorofluorocarbons or CFCs are stable synthetic organic compounds that were first manufactured in the 1930's and used as refrigerants, aerosol propellants, cleaning agents, solvents, and blowing agents in the production of foam rubber and plastics. They were eventually released to the atmosphere and hydrosphere. A depletion of the Earth's ozone layer has been attributed to the rapid atmospheric accumulation of these compounds.

They can be used as dating tools and be classified into three main components with CFC-11 and CFC-12 making up 77 percent of the total global production of CFCs:

1. Trichlorofluoromethane, CCl_3F , CFC-11, or Freon 11,
2. Dichlorodifluoromethane, CCl_2F_2 , CFC-12, or Freon 12,
3. Trichlorotrifluoroethane, $\text{C}_2\text{Cl}_3\text{F}_3$, or CFC-113.

The atmospheric partial pressures of CFCs are determined by Henry's law from the recharge temperature estimated from dissolved gases in the sample or the N_2/Ar ratio and measured concentrations of CFCs in the ground-water samples. These calculated partial pressures are compared with the atmospheric mixing ratios of CFCs to determine the CFC modeled recharge date, which equates to the time that the water was isolated from air in the unsaturated zone.

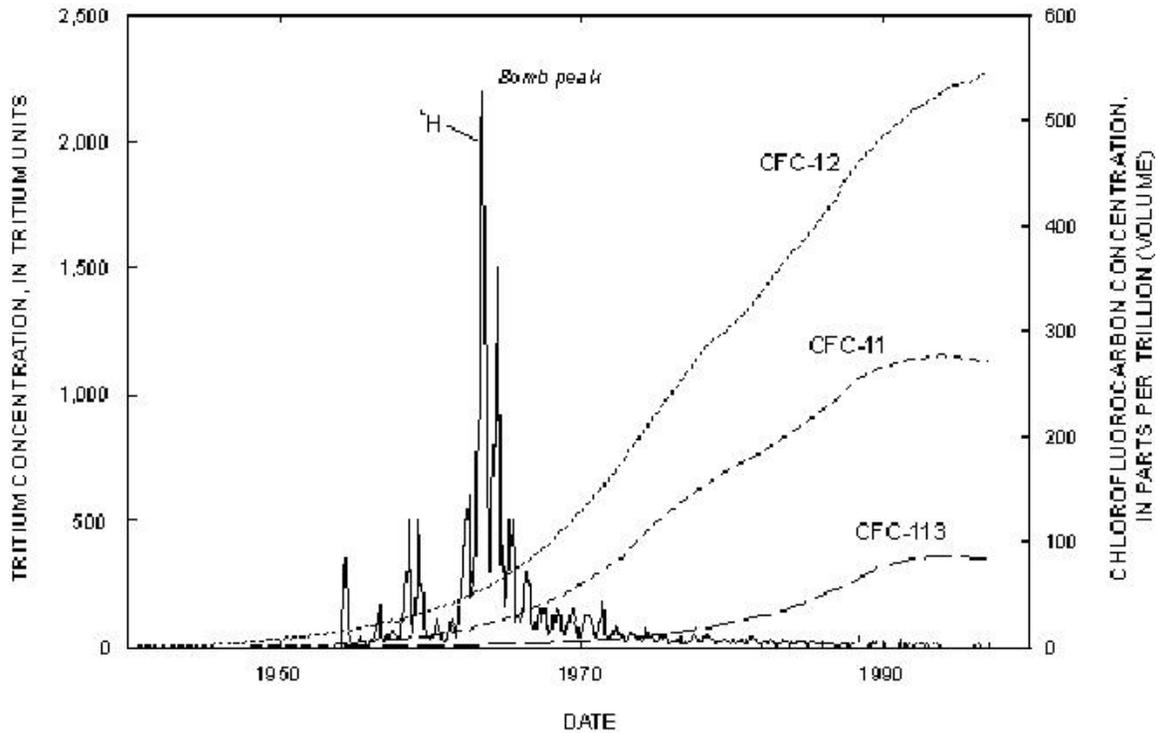


Figure 3. Chlorofluorocarbons CFCs and tritium concentrations as a function of time.
From Busenberg and Plummer [8].

GROUNWATER CONTAMINATION

Groundwater contamination and pollution is a major public health issue throughout the world. It is increasing due to agricultural practices as well as domestic and industrial wastewater releases, while rapid urbanization contributes pollutants in complex ways.

Wastewater is artificially recharging aquifer systems. Shallow aquifers are inadvertently recharged due to infiltration of wastewater as a consequence of agricultural practices as well as the use of hydraulic fracturing (fracking) for hydrocarbons extraction.

The phosphate fertilizer added to agricultural crops adds a level of radium and uranium isotopes to the treated soil. The levels are significant to necessitate health physics protection measures to the workers handling them.

The ashes left from burning coal in electrical energy production contain uranium and radium isotopes that could lead to subsurface water contamination if used in road construction or as fertilizer.

The provision of safe drinking water from deep tube wells is an important strategy being considered for the mitigation of arsenic contamination in many locations.

USE OF ISOTOPIC RATIOS

The linear correlations among the isotopic and meteorological variables are used in hydro geological studies to define the input function in time and amplitude that allows the determination of the groundwater recharge characteristics in terms of rate, season, and area.

The correlation of the stable isotopes with ambient temperature and amount of precipitation are useful in monitoring and recording changes in the temperature and meteorological regimes.

The first precise determinations of stable isotope ratios in meteoric waters performed in the early 1950s revealed a large variability in the isotopic composition of precipitation, both in time and space. The need for world wide tritium measurements was brought about by the nuclear weapon tests, which vastly exceeded the natural levels.

In 1961, the International Atomic Energy Agency (IAEA) in cooperation with the World Meteorological Organization (WMO) started a world-wide survey of the isotopic composition of monthly precipitation. During the initial phases, tritium monitoring was the central activity. The network has provided a detailed and complete picture of the increase of tritium levels in precipitation and its decrease to nearly natural levels at the present day.

The program was launched with the primary objective of collecting systematic data on the isotope content of precipitation on a global scale and, consequently, to provide basic isotope data for the use of environmental isotopes on hydrological investigations.

It became apparent soon that the collected data was also useful in other water-related fields such as oceanography, hydrometeorology, and climatology.

The stable isotope ratios of deuterium/hydrogen D/H and $^{18}\text{O}/^{16}\text{O}$ of water are measured in a mass spectrometer and expressed by convention as parts per thousand deviation from the Vienna Standard Mean Ocean Water.

To guarantee quality control and to support member states, the IAEA set up an isotope laboratory in Vienna. Inter-comparison tests and expert meetings are organized regularly to distribute information on advanced technology and applications.

Tracing the transient behavior of peak tritium has provided a unique opportunity to study short term processes in the hydrosphere. In particular the knowledge of the input concentration allows us to calculate model-based residence times of ground water.

RADIOACTIVE AND STABLE ISOTOPIC CONCENTRATIONS

Tritium concentration

The tritium concentration is measured by its radioactive decay.

The tritium to hydrogen ratio T/H in water is expressed in terms of the Tritium Unit (TU). One TU is defined as:

$$1 \text{ TU} \triangleq \frac{T}{H} = 10^{-18} \quad (9)$$

which is equivalent to 0.118 Becquerel (Bq) or 3.189 pico Curie (pCi) per liter of water:

$$\begin{aligned} 1 \text{ TU} &= 0.118 \frac{\text{Bq}}{\text{liter}} \\ &= 0.118 \frac{\text{Bq}}{\text{liter}} \frac{1}{3.7 \times 10^{10} \frac{\text{Ci}}{\text{Bq}}} 10^{12} \frac{\text{pCi}}{\text{Ci}} \\ &= 3.189 \frac{\text{pCi}}{\text{liter}} \end{aligned} \quad (10)$$

The tritium half-life is usually considered as 12.32 years for data from 2000. The tritium content in a water sample is corrected to the middle of the month. The analytical error for tritium analysis is given in TU when known.

Deuterium D² and O¹⁸ isotope ratios

The deuterium D to hydrogen H isotope ratio: D/H, as well as the O¹⁸ isotope to O¹⁶ isotope ratio O¹⁸/O¹⁶ are usually expressed as the dimensionless δ values, which is the “per thousand” or “per mille” (mille in French is thousand) deviation of the isotope ratio from an internationally accepted standard:

$$\delta(\text{‰}) = \frac{(R_{\text{sample}} - R_{\text{V-SMOW}})}{R_{\text{V-SMOW}}} \times 10^3 \quad (11)$$

where: R = D²/H¹ or O¹⁸/O¹⁶.

The reference standard used is called the Vienna Standard Mean Ocean Water (V-SMOW).

The Deuterium and Oxygen¹⁸ contents of the samples are measured on a mass spectrometer as ratios of D²/H¹ and O¹⁸/O¹⁶. They are expressed in terms of the per mille deviation of the isotope ratio from a standard. Usually the long term precision is about \pm 0.1 per mil for Oxygen¹⁸ and \pm 1per mil for deuterium, at the one standard deviation level.

Vienna Standard Mean Ocean Water (V-SMOW) Standard

The Vienna Standard Mean Ocean Water, V-SMOW has an isotope standard for the deuterium to hydrogen ratio as:

$$\frac{D^2}{H^1} = 156 \times 10^{-6} = 156 \text{ ppm} \quad (12)$$

and for the oxygen ratio:

$$\frac{O^{18}}{O^{16}} = 2,005 \times 10^{-6} = 2,005 \text{ ppm} \quad (13)$$

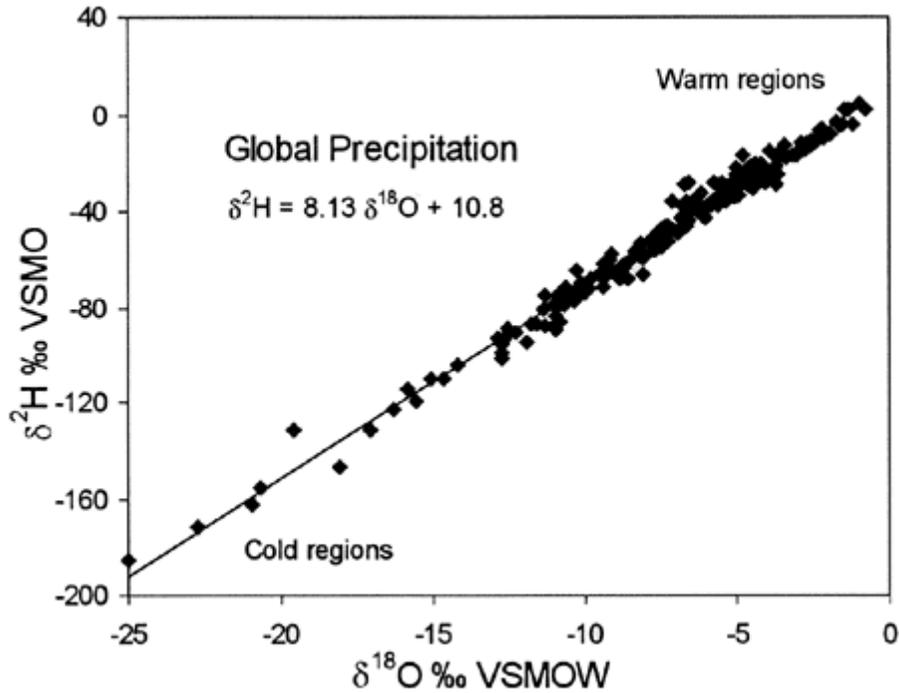


Figure 4. Global precipitation line fit of deuterium versus O^{18} concentration. Source: IAEA.

Deuterium Excess

The deuterium excess, d , is calculated on the basis of the relationship between deuterium and O^{18} content in fresh water on a global scale:

$$d = \delta D - 8\delta O^{18} \quad (14)$$

STATISTICAL ANALYSIS

The numerical treatment of a given isotope and the corresponding meteorological data involves the use of statistical linear regression methodologies to determine the existing correlations.

Linear correlations that can be determined include:

1. Monthly deuterium vs. monthly O^{18} content using a Least Squares Fit (LSF).
2. Monthly deuterium v. monthly O^{18} content using orthogonal regression, also referred to as the Reduced Major Axis (RMA) line approach,

3. Monthly values of O¹⁸ content vs. monthly temperature,
4. Monthly values of O¹⁸ content vs. the amount of monthly precipitation.
5. Logarithms of the monthly tritium concentrations at a given station versus those for Vienna, Austria for northern hemisphere data and Kaitoke, New Zealand for southern hemisphere data.

LEAST-SQUARE FIT APPROACH

The objective is to calculate the parameters a and b in the best fit line:

$$y = ax + b \quad (15)$$

The slope a, and its standard deviation are given by:

$$a = \frac{\sum_{i=1}^n x_i y_i - \frac{\sum_{i=1}^n x_i \cdot \sum_{i=1}^n y_i}{n}}{\sum_{i=1}^n x_i^2 - \frac{(\sum_{i=1}^n x_i)^2}{n}} \quad (16)$$

$$\sigma_a = \frac{S_{y,x}}{\left[\sum_{i=1}^n x_i^2 - \frac{(\sum_{i=1}^n x_i)^2}{n} \right]^{1/2}} \quad (17)$$

where $S_{y,x}$ is the Standard Error of the Estimate (SEE) of y on x, and is given by:

$$S_{y,x} = \left[\frac{\sum_{i=1}^n y_i^2 - b \sum_{i=1}^n y_i - a \sum_{i=1}^n x_i y_i}{n-2} \right]^{1/2} \quad (18)$$

The interception with the y axis b and its standard deviation are calculated from:

$$\begin{aligned} b &= \frac{\sum_{i=1}^n y_i}{n} - a \frac{\sum_{i=1}^n x_i}{n} \\ &= \bar{y} - a\bar{x} \end{aligned} \quad (19)$$

$$\sigma_b = S_{y,x} \left[\frac{\sum_{i=1}^n x_i^2}{n \sum_{i=1}^n x_i^2 - \frac{\left(\sum_{i=1}^n x_i\right)^2}{n}} \right]^{1/2} \quad (20)$$

The correlation coefficient ρ is defined as:

$$\rho^2 = \frac{\left(\sum_{i=1}^n x_i y_i - \frac{\sum_{i=1}^n x_i \sum_{i=1}^n y_i}{n} \right)^2}{\left[\sum_{i=1}^n x_i^2 - \frac{\left(\sum_{i=1}^n x_i\right)^2}{n} \right] \left[\sum_{i=1}^n y_i^2 - \frac{\left(\sum_{i=1}^n y_i\right)^2}{n} \right]} \quad (21)$$

ORTHOGONAL REGRESSION, REDUCED MAJOR AXIS (RMA) LINE APPROACH

In this methodology orthogonal regression, also referred to as the Reduced Major Axis (RMA) line approach, the slope a and its standard deviation are given as:

$$a = \frac{S_x}{S_y} = \left[\frac{\sum_{i=1}^n y_i^2 - \frac{\left(\sum_{i=1}^n y_i\right)^2}{n}}{\sum_{i=1}^n x_i^2 - \frac{\left(\sum_{i=1}^n x_i\right)^2}{n}} \right]^{1/2} \quad (22)$$

$$\sigma_a = a \left(\frac{1 - \rho^2}{n} \right)^{1/2} \quad (23)$$

where S_y and S_x are the standard deviations for y and x .

The interception with y axis, b and its standard deviation can be calculated from:

$$b = \bar{y} - a\bar{x}$$

$$= \frac{\sum_{i=1}^n y_i}{n} - a \frac{\sum_{i=1}^n x_i}{n} \quad (24)$$

$$\sigma_b = S_y \left[\frac{1-\rho}{n} \left(2 + \left(\frac{\sum_{i=1}^n x_i}{n} \right)^2 \frac{1+\rho}{S_x^2} \right) \right]^{1/2} \quad (25)$$

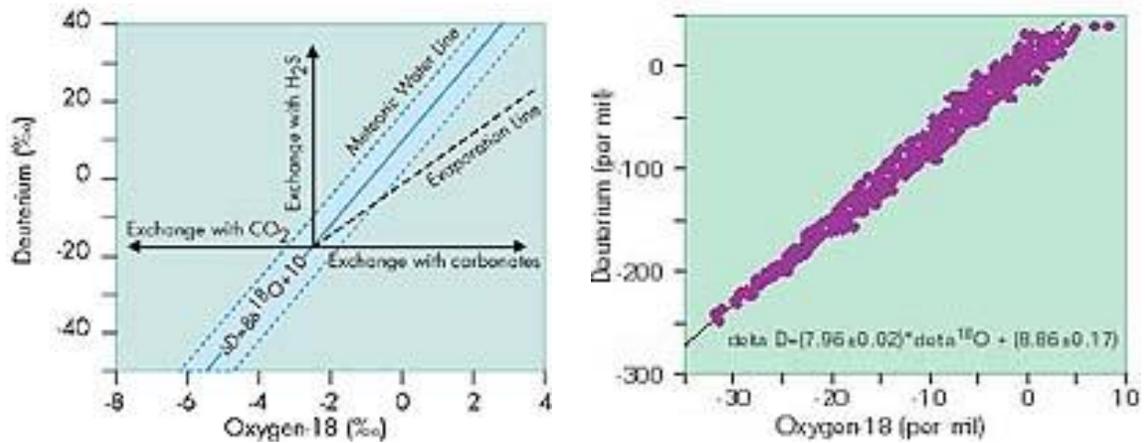


Figure 5. Oxygen¹⁸/Deuterium relationship for monthly precipitation. Deviations from the Global Meteoric Water Line indicate specific atmospheric conditions at the source region of precipitation and/or at the site of its collection. Source: IAEA.

ISOTOPES IN THE GLOBAL WATER CYCLE

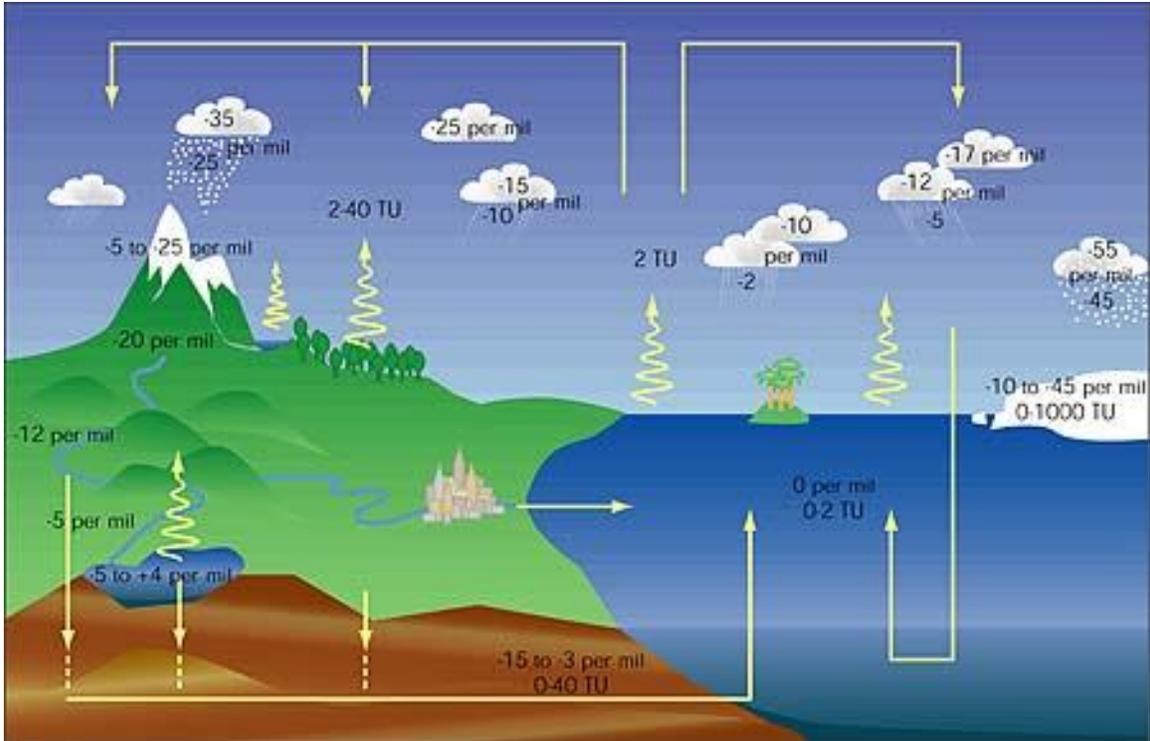


Figure 6. Tritium and isotopic ratios in the water cycle. Source: IAEA.

The radioactive isotope tritium ${}^3_1\text{T}$ and the stable isotopes deuterium ${}^2_1\text{D}$ and ${}^{18}_8\text{O}$ are rare components of the water molecule H_2O . They offer a broad range of possibilities for studying processes within the water cycle.

Tritium was released to the atmosphere during the atmospheric test phase for thermonuclear weapons. The very low natural levels were overwhelmed by concentrations several orders of magnitude higher. Since then, tritium levels have been progressively decreasing due to washout processes and the admixture of moisture from the oceans. Due to the long residence time of ocean water at 2,000 years as compared to the half-life of tritium at 12.4 years, the oceans act as a sink for tritium.

Tritium in precipitation has been monitored since the beginning of the atmospheric weapons tests in late 1952. The data enabled the establishment of timescales for the transport of water through different compartments of the hydrological cycle.

For instance, groundwater, which does not contain tritium, must have infiltrated as rain before 1952 because the natural concentrations have already decayed below the detection limit. If one measures 1,000 tritium units (TU) in glacier ice, this layer must originate from snowfalls in 1963, the time period when tritium injections to the atmosphere reached a maximum.

The stable isotopes label in a different way: since a water molecule containing ${}^2_1\text{D}$ or ${}^{18}_8\text{O}$ is heavier than a normal ${}^1_1\text{H}{}^1_1\text{H}{}^{16}_8\text{O}$ molecule. Water vapor forming precipitation will be depleted in the heavy isotopes relative to the ocean water. Condensation forming raindrops from a cloud reverses this process. The heavier molecule condenses first, with the rain isotopically enriched, and the cloud moisture is subsequently depleted as the rain continues.

The isotopic fractionation during phase transitions of vapor-liquid-solid is temperature dependent. A water sample is thus labeled depending on the environmental conditions it has experienced. Heavy rains are more depleted than light rains; summer precipitation is less depleted than winter precipitation. Precipitation in Polar Regions is isotopically lighter than in low latitudes. Ground waters originating from infiltration at high altitudes are lighter than those formed in lowlands. Surface waters preferentially lose the lighter water molecules due to evaporation. They are often enriched in heavy isotopes as compared to the isotopic composition of rainwater from which they were formed.

Nearly all the water molecules forming precipitation originate from the oceans and return after their individual and often comparable travel through the water cycle to the ocean again. The mean residence time ranges from days to months in the atmosphere, to years, centuries, and millennia on the continents and in the oceans, to several hundred thousand years in Antarctica. The history of a molecule is strongly influenced by the differences in ocean-continent distribution. It follows that the isotopic composition of water covers a broad spectrum in space and time.

Phase changes of water from solid-liquid-vapor lead to isotopic fractionation, because the saturation vapor pressures of ${}^1\text{H}^1\text{H}^1{}_8\text{O}^{18}$ and ${}^1\text{D}^2{}_1\text{H}^1{}_8\text{O}^{16}$ are slightly lower than that of ${}^1\text{H}^1\text{H}^1{}_8\text{O}^{16}$. A Rayleigh model considers the isotopic fractionation occurring in an isolated air parcel. Condensation is assumed to take place under equilibrium conditions with the surrounding water vapor followed by immediate or progressive rainout.

The major sources of water vapor are the tropical oceans. Transport of this water toward the poles results in gradual rainout and thus in a depletion of the remaining moisture in ${}^1\text{D}^2$ and ${}_8\text{O}^{18}$.

RELATIONSHIP TO ENVIRONMENTAL PARAMETERS

The observed isotope distribution in space and time can be related to a number of environmental parameters which characterize the source region and the sampling site.

Seasonality, amount of precipitation, altitude dependence, continentality, the role of local temperature, together with the source specific fractionation between ${}_8\text{O}^{18}$ and ${}^1\text{D}^2$. These effects can contribute to the isotope content of a sample of precipitation.

The attraction to use stable isotopes in paleoclimate studies has mainly derived from their relation to atmospheric temperature.

Depending on the latitude, rainfall intensity or temperature may dominate the seasonal distribution of isotopes in precipitation. In mid and high latitudes, the isotopes in monthly precipitation are correlated with temperature. Seasonally changing temperatures lead to variations in the total precipitable water in the atmosphere, due to the varying degrees of rainout from air masses as they are transported toward the poles.

Low latitudes show a different response. Isotopic content is modulated by the seasonal variations in the volume of precipitation instead. During the rainy season, precipitation is isotopically depleted.

The long-term monthly and annual mean values for ${}_8\text{O}^{18}$ correlate well with the average monthly amount of precipitation, whereas the correlation with temperature is virtually non-existent.

CONTINENTAL EFFECT

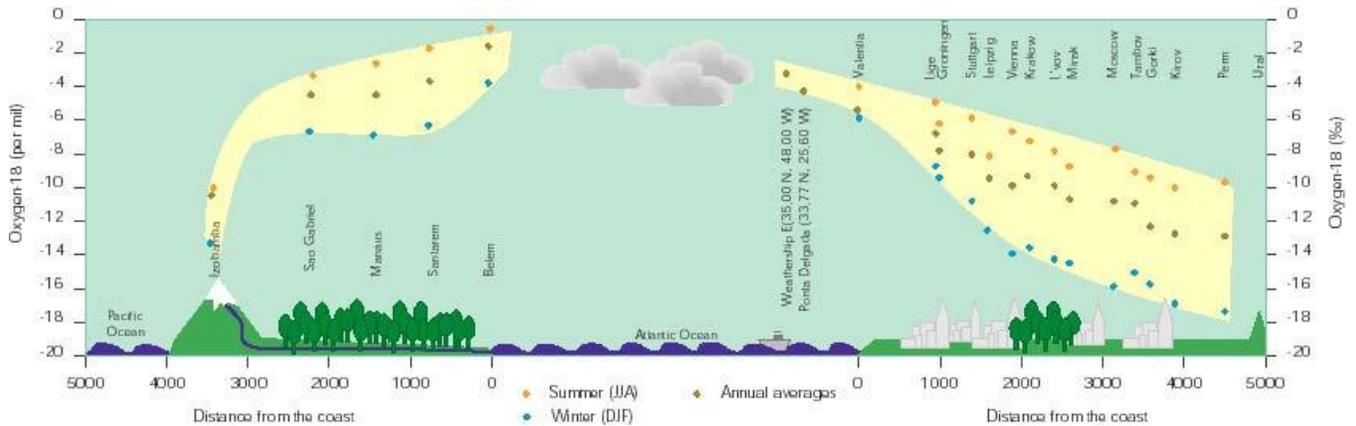


Figure 7. When clouds move inland from the coast, they become isotopically depleted progressively, as a result of their loss of moisture. Source: IAEA.

When clouds move inland from the coast, they become isotopically depleted progressively, as a result of their loss of moisture. In addition, the isotopic signatures reflect the topography of the continent. Mountain chains deplete the clouds too, because of the orographically forced rainout. The degree of continentality, as defined by the isotopes, is a function of the effect of the steep temperature gradient between the ocean and the interior especially in winter. This leads to progressive isotopic depletion, as precipitable water is lost with the passage of air inland.

The process prevails for as long as the ocean is the dominant moisture source and re-evaporated moisture does not play a major role.

The transect across the South American Continent at low latitudes differs remarkably from the European example. Variations in the seasonal isotopic composition are less and the gradient from the coast inland is small, except in the Andean region, where the altitude effect dominates. One reason for the difference is the reduced temperature gradient in the lower latitudes; another is the greater importance of recycled moisture over the Amazon and Orinoco basins.

ALTITUDE EFFECT

When air masses are orographically uplifted they cool and precipitate preferentially the heavier isotopes. Depending on the precipitation history, the topographic situation, the degree of cooling and the precipitable moisture left, the altitude effect on $\delta^{18}\text{O}$ in mid latitudes generally ranges between 0.15 and 0.30 per mil for each 100 m of altitude gained. In applied isotope hydrology, this effect is used to estimate the altitude of groundwater recharge areas.

DEUTERIUM EXCESS

The close relationship between ${}^1\text{D}^2$ and ${}^8\text{O}^{18}$ in freshwaters, including precipitation, gives rise to the best fit line:

$$\delta D = 8\delta O^{18} + 10$$

The concept of the deuterium excess is defined as:

$$d = \delta D - 8\delta O^{18}$$

This relationship is also well understood and can be reproduced by models based on the Raleigh approach. In addition to the phase changes under equilibrium conditions a kinetic effect results from a different diffusivity for the isotopically different water molecules in air.

The higher diffusivity for ${}^1\text{D}^2{}^1\text{H}^1{}^8\text{O}^{16}$ relative to ${}^1\text{H}^1{}^1\text{H}^1{}^8\text{O}^{18}$ results in an additional separation, and a higher deuterium excess. Humidity relative to saturation at sea surface temperature and wind speed is the major controlling factors. Within-cloud processes do not modify significantly the excess as long as only the formation of precipitation is considered.

The deuterium excess can be used to identify vapor source regions. Winter precipitation originating from the Mediterranean Sea is characterized by distinctly higher excess values, reflecting the specific source conditions during water vapor formation.

Increased deuterium excess in precipitation can also arise from significant addition of re-evaporated moisture from continental basins to the water vapor travelling inland. If moisture from precipitation with an average excess of 10 per mil is re-evaporated, the lighter ${}^1\text{D}^2{}^1\text{H}^1{}^8\text{O}^{16}$ molecule may again contribute preferentially to the isotopic composition of the water vapor and this leads to an enhanced deuterium excess in precipitation. Examples of deuterium enriched precipitation derived in this way are known from the Amazon Basin, the Great Lakes Region in North America, or from the Mongolian glacier data.

Stable isotope records from Greenland ice cores have revealed great variability in past climates, also on decadal time scales. From European climate records, a major source of inter-annual variability is the North Atlantic Oscillation (NAO), which is related to changes in SST and atmospheric moisture. The oscillating pressure patterns around Iceland and the Azores steer the system of zonal and meridional winds, which, in turn, influence European precipitation patterns.

ISOTOPIC TEMPERATURE EFFECT

The link between long-term changes in the isotopic composition of precipitation and surface air temperature at a given location is probably the most important relationship as far as paleoclimatic applications are concerned. A semi-empirical temperature/stable isotope relationship was established for coastal stations in the mid and high northern latitudes. The slope of 0.69 per mil per $^{\circ}\text{C}$ has been used in numerous climate studies to reconstruct past temperatures.

Modeling the present day behavior of stable isotopes in precipitation also reveals the basis for reconstructing past isotope distributions in order to assist in the

interpretation of paleo-data. Global Circulation Models generally reproduce well the main characteristics of isotopes on a global scale. Differences show up on regional and local scales, for instance in the tropics, where convective processes are involved. Paleo-data derived from empirical reconstruction at specific sites provide part of the ground truth for model testing.

FRESH WATER STATISTICS

The rising struggle for fresh water has the potential to escalate to a magnitude similar to the current geopolitical conflicts over energy supplies.

There is currently an ongoing war for the control of fresh water going on all over the world at the corporate level hashing out strategies at treatment facilities and offices. For instance, subsidiaries of European companies have been involved in fresh water supplies and treatment facilities management. The Illinois American Water Company, a subsidiary of a German company, manages the water supply and treatment facilities of the Mahomet Aquifer in Central Illinois in the USA around the twin cities of Champaign-Urbana.

The 3,000-10,000 years old fossil water dating back to the last glaciations period, is pumped out, dumped into the Kaskaskia drainage ditch which becomes the Kaskaskia River, and is conveyed downstream south to the water-short cities of Tuscola and Arcola to feed their chemical plants.

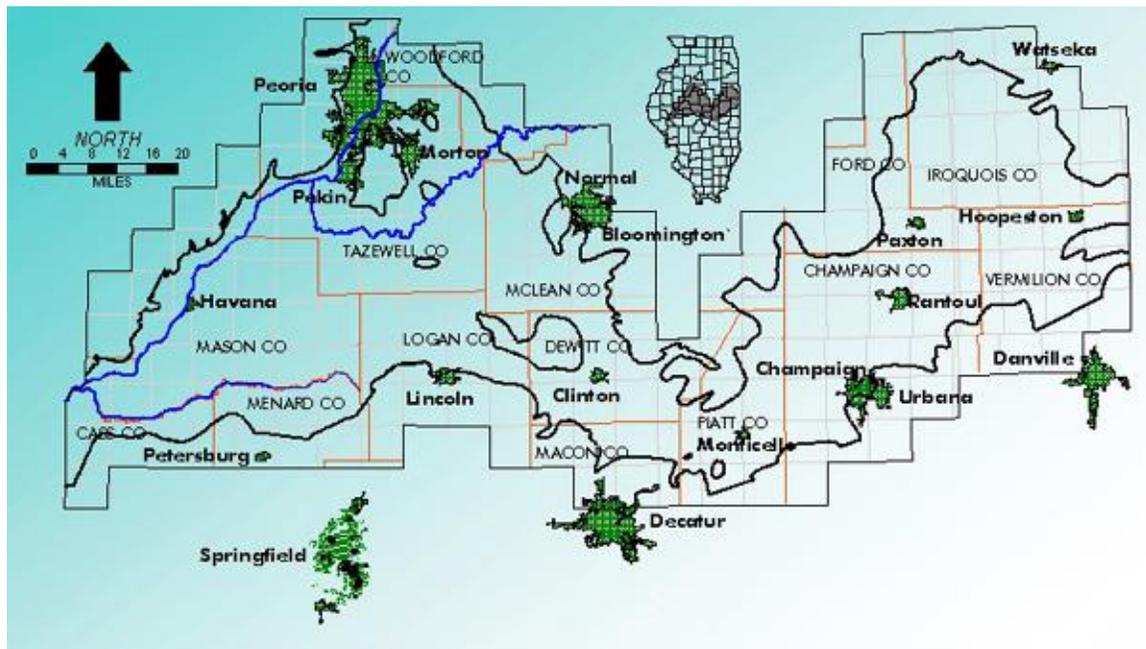


Figure 8. Extent of the Mahomet Aquifer in Central Illinois, USA.

Electrical utilities that could not obtain permits to build power plants on the East Coast of the USA, such as Public Service Enterprise Group (PSEG) from New Jersey are building gas turbine power plants in the Midwest and connecting them to the national power grid. A project was considered to build such a power plant at water-poor Sidney,

Illinois, east of Champaign-Urbana would obtain its plant coolant needs by pumping the aquifer water through a pipeline to Sidney, providing tax dollars revenue to the city.

There has been plans to use the aquifer water to provide the needs of projected corn ethanol production plants which would use 6-10 gallons of water per gallon of produced ethanol, as well as for a coal gasification plant using a futuristic name: Future-Gen, exposing the aquifer with potential rapid depletion in addition to possible pollution by what are essentially industrial processes.

Two areas in the State of Illinois have been identified as at risk for water shortages and conflicts: the North East Illinois Deep Aquifer and the Mahomet Aquifer. The twin city of Champaign Urbana in Central Illinois obtains its water from the Mahomet aquifer; a 3,700 square miles area of water saturated gravel and sand, but is reaching its local yield capacity. The aquifer is held by a bed-rock on the sides and bottom and topped by impervious clay rich glacial till. It extends from Danville on the Indiana and Illinois border to the south east of Tazewell County. The recharge of the aquifer occurs at the rate of about one inch per year of water movement, completing its recharge function with a time constant of 3,000 years.

Even though ground water is a renewable resource, it is not an infinite resource. It is finite in size and can be depleted by over-pumping which lowers the water table. Continued growth and withdrawal from the same part of the aquifer would lead to "dewatering," a situation that would compromise the quality of water in the aquifer. Precluding climate change and population growth and urbanization, under the present conditions, the Illinois State Water Survey (ISWS) estimates that an additional 16-17 million gallons per day can be pumped before starting to dewater of the aquifer.

The manufacture of ethanol requires 6-10 gallons of water per gallon of ethanol. Most manufacturing processes use water in some form or another: 62,000 gallons per ton of steel and 39,000 gallons per average automobile. A typical ethanol plant producing 100,000 gallons of ethanol per day would need 600,000-1,000,000 gallons per day of water. Ethanol plants were at some time contemplated around the cities of Royal, Tuscola, Farmer City, Champaign and elsewhere in the state of Illinois. The Ohio based company: The Andersons, planned a plant in Champaign that would withdraw 1.9 million gallons of aquifer water per day by its grain elevator, bringing 35 jobs to the county. The company owns the mineral rights under its property according to state law and is entitled to withdraw that water. Under "reasonable use" standards water rights come with property rights, unless challenged in court. The courts would listen to the competing claims of the current users. A fraction of the withdrawn water would be discharged into the Kaskaskia River after being used in the ethanol fermentation and evaporative cooling processes and the company needs only the granting of a pollution permit for waste water discharge from the Environmental Protection Agency (EPA) to proceed with its project.

As water resources become scarcer, in the water wars the losers will have to move or face death, with the winners prospering and surviving. One billion people, or about 1/6 of humanity, lack access to safe drinking water, and 1/3 of the world population people lives in regions with water scarcity.

Agriculture absorbs 74 percent of all water taken by humans from rivers, lakes, aquifers and wetlands against 18 percent for industry and 8 percent for municipalities. Demand for water is rocketing with a rising population. In many places, 30-40 percent of water is lost because of leaks in pipes and canals and illegal tapping into them.

Governments set a Millennium Goal in 2000 of halving the proportion of people with no access to safe drinking water by 2015.

Diarrhea and malaria, the main water related diseases, killed 1.8 million and 1.3 million people respectively in 2002, with most of them children under the age of five.

Achieving the 2015 drinking water goal would require \$10-\$30 billion extra a year on top of the amounts already invested.

The amount of water needed for crop production is projected to rise by 60-90 percent by 2050, to 11,000-13,500 km³ from 7,200 km³ in 2006.

One calorie of food needs about a liter of fresh water to produce. The typical food consumption is 3,000 calories per day per person, or 3,000 liters of water. A kilogram (kg) of grain takes 500-4,000 liters to produce, and a kg of industrially produced meat uses 10,000 liters. The rising production of biofuels from crops such as corn, soybeans or sugar cane will complicate the efforts to feed the world and may add strains to irrigation, increase soil erosion and deplete fresh water supplies. For instance, it is estimated that it takes 6-10 gallons of water to produce one gallon of corn ethanol.

DISCUSSION

Deep aquifers are unlikely to be contaminated under present use conditions. However, the future safety of these aquifers and the potential for shallow aquifer water migrating to deeper aquifers, need to be evaluated before making substantial policy and financial investments.

The potential for groundwater mining is clearly evident and the sustainability of this resource needs to be fully considered.

REFERENCES

1. I. D. Clark and Peter Fritz, "Environmental Isotopes in Hydrogeology," New York, Lewis Publishers, p. 328, 1997.
2. T. B. Coplen, "Uses of Environmental Isotopes," in W. M. Alley, ed., "Regional ground-water quality," New York, Van Nostrand Reinhold, pp. 227-254, 1993.
3. L. N. Plummer, D. L. Parkhurst and D. C. Thirstiness, "Development of Reaction Models for Ground-water Systems," *Geochimica et Cosmochimica Acta*, v. 47, pp. 665-686, 1983.
4. L. N. Plummer, E. C. Prestemon, and D. L. Parkhurst, "An Interactive Code (NETPATH) for Modeling Net Geochemical Reactions along a Flow Path," version 2.0: 94-4169, p. 130, 1994.
5. International Atomic Energy Agency (IAEA), "Statistical Treatment of Environmental Isotope Data in Precipitation," Vienna, IAEA, Technical Report Series No. 206, 1981.
6. R. M. Michel, R.M., "Tritium Deposition in the Continental United States, 1953-1983," U.S. Geological Survey Water-Resources Investigations Report 89-4072, p. 46, 1989.
7. Peter Schlosser, "Tritium/³He Dating of Waters in Natural Systems," in: "Isotopes of Noble Gases as Tracers in Environmental Studies," Vienna, IAEA, p. 123-145, 1992.

8. Eurybiades Busenberg, and L. N. Plummer, "Use of Chlorofluorocarbons (CCl₃F and CCl₂F₂) as Hydrologic Tracers and Age-dating tools," *The alluvium and terrace system of central Oklahoma, Water Resources Research*, v.28, no. 9, pp. 2257-2283, 1992.
9. S. Derra, S., "CFCs--No easy solutions," *Research and Development*, v. 32, pp. 54-66, 1990.
10. M. Molina and F. S. Rowland, "Stratospheric Sink for Chlorofluoromethanes," Chlorine atom catalyzed destruction of ozone, *Nature*, no. 249, pp. 810-812, 1974.
11. L. N. Plummer, and Eurybiades Busenberg, "Chlorofluorocarbons," in: P. G. Cook and Andrew Herczeg, eds., *Environmental tracers in subsurface hydrology*, Klumer Academic Press, 1999.
12. R. S. Bradley, "Quaternary Paleoclimatology," Boston, Unwin Hyman, p. 472, 1997. Clark, I.D., and Fritz, Peter, 1997, *Environmental isotopes in hydrogeology*: New York, Lewis Publishers, 328 p.
13. T. B. Coplen, "Uses of Environmental Isotopes," in W. M. Alley, ed., *Regional Ground-water Quality*, New York, Van Nostrand Reinhold, pp. 227-254, 1993.
14. Pradeep K. Aggarwal, Asish R. Basu, Robert J. Poreda, K. M. Kulkarni, K. Froelich, S. A. Taradfar, Mohamed Ali, Nasir Ahmed, Alamgir Hussain, Mizanur Rahman, and Syed Reazuddin Ahmed, "Isotope Hydrology of Groundwater in Bangladesh: Implications for Characterization and Mitigation of Arsenic in Grounwater," IAEA-TC Project: BGD/8/016 Report, December 2000,
15. L. Aragua-Araguas, K. Froehlich, and K. Rozanski, "Stable isotope composition of precipitation over Southeast Asia," *Journal of Geophysical Research*, 103 (D22), 28, pp. 721-28 742, 1998.
16. S. V. Navada, S.M. Rao, "Study of Ganga River - Groundwater Interaction Using Environmental Oxygen-18," *Isotopenpraxis* 27 (8), pp.380 – 384, 1991
17. R. V. Krishnamurthy, S. K. Bhattacharya, "Stable oxygen and hydrogen isotope ratios in shallow groundwater from India and a study of the role of evapotranspiration in the Indian monsoon," In: "Stable isotope geochemistry. A tribute to Samuel Epstein. Special publication No. 3," Eds: H. P. Taylor, J. R. O'Neil, I. R. Kaplan, The Geochemical Society, San Antonio, Texas, pp. 187-194, 1991.
18. P.S. Datta, S.K. Tyagi and H. Chandrasekharan, "Factors controlling stable isotope composition of rainfall in New Delhi," *India. Journal of Hydrology*, 128, pp. 223-226, 1991.
19. V. Thapaliyal, "Stratosphere circulation in relation to summer monsoon over India," *Proc. Intern. Symposium on Hydrological Aspects of Droughts*, New Dehli, I: 347-369, 1979.
20. P. S. Datta, S. K. Bhattacharya, and S. K. Tyagi, "¹⁸O Studies on recharge of phreatic aquifers and groundwater flow-paths of mixing in the Delhi area," *Journal of Hydrology* 176, pp.25-36, 1996.
21. J.C. Duplessy, E. Bard, M. Arnold, N. J. Shackleton, J. Duprat and L. Labeyrie, "How fast did the ocean – atmosphere system run during the last deglaciation?" *Earth and Planetary Science Letters*, 103, pp.27-40, 1991.
22. K.W.Burton, and D. Vanc, "Glacial-interglacial variations in the neodymium isotope composition of seawater in the Bay of Bengal recorded by planktonic foraminifera," *Earth and Planetary Science Letters*, 176, pp.425-441, 2000.

23. M. Umitsu, "Late Quaternary sedimentary environments and landforms in the Ganges Delta," *Sedimentary Geology* 83, pp. 177-186, 1993.
24. M. Banerjee and P. K. Sen , "Palaeobiology in understanding the change of sea level and coast line in Bengal Basin during Holocene period," *Indian Journal of Earth Sciences*, Vol. 14, Nos. 3-4, pp. 307-320, 1987.
25. International Atomic Energy Agency, IAEA, "Statistical Treatment of Environmental Isotope Data in Precipitation," Technical Reports Series No. 331, IAEA, Vienna, 1992.
26. International Atomic Energy Agency, IAEA, "Statistical Treatment of Environmental Isotope Data in Precipitation," Technical Reports Series No. 206, IAEA, Vienna, 1981.
27. K. Rozanski, L. Araguas-Araguas, and R. Gonfiantini, "Relation between long-term trend of oxygen-18 isotope composition of precipitation and climate," *Science*, Vol. 258, pp. 981-985, 1992.
28. C. B. Taylor and W. Roether, "A uniform scale for reporting low-level tritium measurements in water," *Int. J. Appl. Radiat. Isot.*, Vol. 33, pp.377-382, 1982.
29. H. Craig, "Standard for reporting concentrations of deuterium and oxygen-18 in natural waters," *Science*, Vol. 133, pp. 1833-1834, 1961.
30. R. Gonfiantini, "Standards for stable isotope measurements in natural compounds," *Nature* , London, Vol. 271, pp. 534-536, 1978.
31. W. Dansgaard, "Stable isotopes in precipitation," *Tellus*, Vol. 16, pp. 436-468, 1964.