

GEOCHRONOLOGY VIII: COSMOGENIC NUCLIDES

INTRODUCTION

As the name implies, cosmogenic nuclides are produced by cosmic rays, specifically by collisions with atoms in the atmosphere (and to a much lesser extent, the surface of the solid Earth). Cosmogenic nuclides, like the U decay series nuclides, have half-lives sufficiently short that they would not exist in the Earth if they were not continually produced. Assuming that the production rate is constant through time, then the abundance of a cosmogenic nuclide in a reservoir isolated from cosmic ray production is simply given by:

$$N = N_0 e^{-\lambda t} \quad 12.1$$

Hence if we know N_0 and measure N , we can calculate t . Table 12.1 lists the cosmogenic nuclides of principal interest. As we shall see in the next lecture, cosmic ray interactions can also produce rare stable nuclides, and their abundance can also be used to measure geologic time.

Cosmogenic nuclides are created by a number of nuclear reactions with cosmic rays and by-products of cosmic rays. "Cosmic rays" are high energy (several GeV up to 10^{19} eV!!) charged particles, mainly protons, or H nuclei (since, after all, H constitutes most of the matter in the Universe), but nuclei of all the elements have been recognized. Only in the last 15-20 years or so has it been possible to achieve energies as high as several GeV in accelerators: cosmic rays have been a useful source of high energy particles for physicists for decades (the Cornell Electron Storage Ring produces energies up to 15 GeV). A significant fraction originates in the Sun, though these are mainly of relatively low energies. The origin of the remainder is unclear; it is thought that many may originate in supernovae or similar high energy environments in the cosmos.

The cosmic ray flux decreases exponentially with depth in the atmosphere as these particles interact with matter in the atmosphere. This observation has an interesting history. Shortly after the discovery of radioactivity, investigators noticed the presence of radiation even when no known sources were present. They reasonably surmised that this resulted from radioactivity in the Earth. In 1910, an Austrian physicist named Victor Hess carried his detector (an electroscope consisting of a pair of charged gold leaves: the leaves would be discharged and caused to collapse by the passage of charged particles) aloft in a balloon. To his surprise, the background radiation increased as he went up rather than decreased! It thus became clear that cosmic rays originated from outside, rather than inside, the Earth.

The primary reaction that occurs when cosmic rays encounter the Earth is *spallation*, in which a nucleus struck by a high energy particle shatters into a number of pieces, including stable and unstable nuclei, as well as protons and neutrons. Unstable particles such as muons, pions, etc. are also created. The interaction of a cosmic ray with a nucleus sets off a chain reaction of sorts as the secondary particles and nuclear fragments, which themselves have very high energies, then strike other nuclei producing additional reactions of lower energy. ^{14}C is actually produced primarily by reactions with secondary particles, mainly by the $^{14}\text{N}(n,p)^{14}\text{C}$ reaction involving relatively slow neutrons.

^{14}C DATING

Carbon-14 is by far the most familiar and useful of the cosmogenic dating schemes. Its usefulness results from its relatively short half-life, a relatively high production rate, and the concentration of carbon in biological material. The short half-life has the advantage of producing accurate dates of

TABLE 12.1. COSMOGENIC NUCLIDES OF GEOLOGICAL INTEREST

Nuclide	Half-life, years	Decay constant, γ^{-1}
^{14}C	5730	1.209×10^{-3}
^3H	12.33	5.62×10^{-2}
^{10}Be	1.500×10^6	4.62×10^{-5}
^{26}Al	7.16×10^5	9.68×10^{-5}
^{36}Cl	3.08×10^5	2.25×10^{-6}
^{32}Si	276	2.51×10^{-2}

(geologically speaking) young samples and easy determination by counting the decays. The traditional method of ^{14}C determination is counting of the β rays produced in its decay. ^{14}C decays without emitting a gamma, which is unfortunate because γ -rays are more readily detected. Carbon is extracted from a sample and converted into CO_2 and placed in a very well shielded counting tube. Typically, several grams or tens of grams of carbon are required, which results in a substantial volume of CO_2 , so the counting tube is quite large, with a capacity of several liters.

In the last decade or so, a new method, accelerator mass spectrometry, has been used with considerable success. Greater accuracy is achieved with considerably less sample. Unfortunately, such instruments are expensive and rare (though they are becoming less so), and most radiocarbon work is still done (and will be for the foreseeable future) by conventional beta counting.

Because of the way in which it is measured, ^{14}C is generally reported in units of *specific activity*, or disintegrations per minute per gram carbon rather than as a ratio to ^{12}C or ^{13}C . Atmospheric carbon, and carbon in equilibrium with the atmosphere (carbon in living plant tissue and the surface of the oceans) has a specific activity of 13.56 dpm/g. This is, in effect, the value of N_0 in equation 12.1.

The cosmic ray flux varies latitudinally because of the effect of the Earth's magnetic field on the paths of charged particles. One would expect, then, the production rate of ^{14}C to be higher at the poles, and this is indeed the case. However, because the mixing time of the atmosphere is short compared to the residence time of ^{14}C in the atmosphere, the ^{14}C concentration in the atmosphere is uniform.

Can we really assume, however, that the atmosphere specific activity today is the same as in the past? From equation 12.1, we can see that knowing the initial specific activity is essential if an age is to be determined. To investigate the variation of the specific activity of ^{14}C with time in the atmosphere, the specific activity of ^{14}C in wood of old trees (dendrochronology) has been examined. The absolute age of the wood is determined by counting tree rings. The result of such studies shows that the specific activity has indeed not been constant, but has varied with time (Figure 12.1). There are a number of effects involved. Most recently, there has been injection of bomb-produced ^{14}C into the atmosphere raising the specific activity. Then, over the past hundred years or so, the specific activity has decreased because of addition of "old" (i.e., ^{14}C -free) carbon in CO_2 from fossil fuel burning (*the Suess effect*). There are also several 'excursions' over the last 1000 years, known as the *deVries events* whose origin is unknown, but probably relates to variation in the cosmic ray flux. Whether this results from solar activity, supernovae events, etc. is unclear. In any case, a correction must be applied to ^{14}C dates because of these variations. Calibration of ^{14}C through dendrochronology

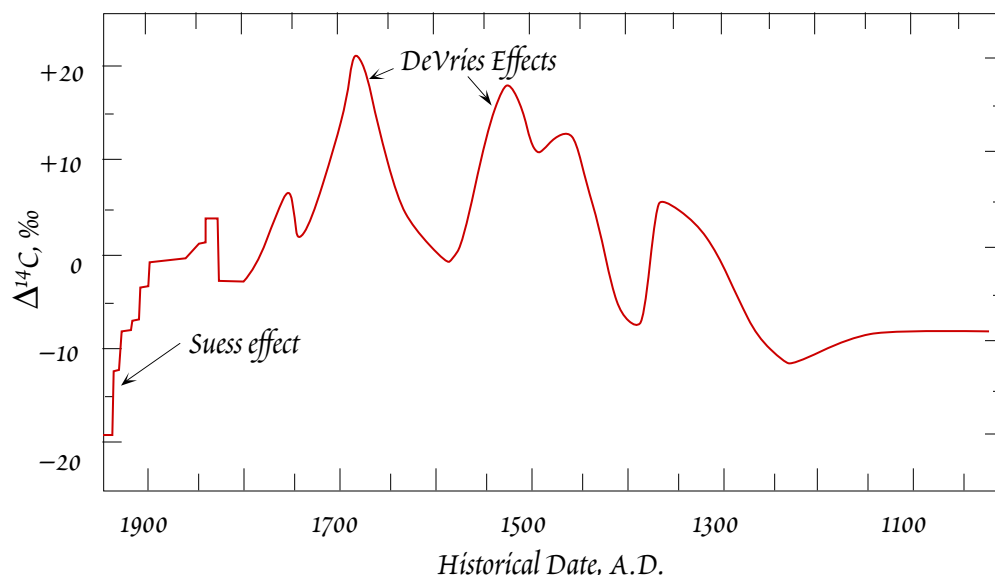


Figure 12.1. Variation of initial specific activity of ^{14}C in the past.

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has now been done back many thousands of years. Extension of this calibration back 10,000 years and more through comparison of ^{14}C and $^{238}\text{U}/^{230}\text{Th}$ ages is now underway.

Most of the applications of ^{14}C dating are probably in archaeology, but geological applications include volcanology (^{14}C dating is an important part of volcanic hazard assessment), Holocene stratigraphy, and oceanography. It is also used to determine the time of prehistoric earthquakes, and thus part of earthquake hazard assessment. In oceanography, the age of bottom water (age meaning the time since the water last equilibrated with the atmosphere) can be determined with ^{14}C . Typically, this age is of the order of 1000 yrs.

A more recent oceanographic application, which utilizes accelerator mass spectrometry, is the determination of paleo-bottom water ages. The ice ages affected ocean circulation, but the exact nature of the effect is still uncertain. Of particular interest are the changes in the ocean circulation pattern that occurred as the last glaciation ended. Because planktonic foraminifera live in the upper part of the ocean, which is in equilibrium with the atmosphere, one can date a sedimentary stratum by measuring ^{14}C in planktonic foraminiferal tests. Benthic foraminifera live at the bottom of the ocean, and build their tests from CO_2 dissolved in bottom water. Thus a ^{14}C date of a modern benthic foram would give the age of the bottom water. By comparing the ^{14}C ages of planktonic and benthic foraminifera, one may determine the "ages" of bottom waters in the past. This in turn reveals something of paleocirculation patterns.

^{10}Be , ^{26}Al , AND ^{36}Cl

We now consider some of the other nuclides produced by cosmic ray interactions with atmospheric gases. These include ^{10}Be , ^{26}Al , and ^{36}Cl . These nuclides have much longer half-lives than ^{14}C and thus are applied to longer time-scale problems, such as Pleistocene chronology, and dating of groundwater. Of these, ^{10}Be has been the most extensively utilized, for several reasons. First, its production rate is higher ($10^{-2} - 10^{-3}$ atoms/cm²/sec versus 10^{-5} – 10^{-6} for ^{26}Al and ^{36}Cl). It also has the advantage over ^{36}Cl that, once absorbed onto clays, it is relatively immobile, and that while a small amount of ^{36}Cl will be produced within the earth by neutron capture on ^{35}Cl (with neutrons arising from fission of U, as well as secondary neutrons produced by (α, n) reactions), there is effectively no internal 'nucleogenic' production of ^{10}Be in the Earth.

^{10}Be is created by spallation reactions between cosmic rays and N and O nuclei. Since these are the most abundant nuclei in the atmosphere, the production rate of ^{10}Be is comparatively high. ^{26}Al is produced by spallation of ^{40}Ar , and ^{36}Cl is produced by $^{40}\text{Ar}(p, \alpha)^{36}\text{Cl}$ reactions (probably mainly with secondary protons). Unlike carbon, Be, Cl and Al do not form gases under ambient conditions at the surface of the Earth[‡], so residence time of ^{10}Be , ^{26}Al , and ^{36}Cl in atmosphere are quite short. Once they form, they are quickly extracted from the atmosphere by rain. Since we know the cosmic ray flux varies latitudinally, we might expect latitudinal variation in, for example, the ^{10}Be production rate and flux to the surface of the Earth. Subareal variations in ^{10}Be show the expected latitudinal dependence. However, the distribution in oceans is uniform because ^{10}Be spends sufficient time in oceans that its distribution is homogenized (the residence time of Be is somewhat uncertain, but seems to be about 4000 years). Be is readily scavenged and absorbed by clay particles, both subareally and in the oceans. The concentration in soils is quite high. In the oceans ^{10}Be is extracted from seawater by adsorption on suspended clay particles. Because of its low activity, ^{10}Be is analyzed primarily by accelerator mass spectrometry. The applications include dating marine sediments, paleosols, Mn nodules, etc.

Let's now consider some examples of how these nuclides can be used for geochronology. We will begin with ^{10}Be dating of sediments and they go on to show how ages can be improved if we use both ^{10}Be and ^{26}Al . We will then consider how ^{36}Cl and bomb-produced ^3H are used in hydrology.

Let's now see how ^{10}Be can be used for age determination. The relevant equation is

[‡] In the laboratory, elemental chlorine is, of course, a gas, but it is so reactive that it quickly reacts with electronegative atoms (e.g., alkalis, metals) in nature to form chlorides.

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$$^{10}\text{Be} = ^{10}\text{Be}_0 e^{-\lambda_{10}t} \quad 12.2$$

We assume the rate of deposition of ^{10}Be in the ocean depends only on the production rate, hence,

$$^{10}\text{Be} \propto \Phi e^{-\lambda t} \quad 12.3$$

where Φ is the production rate. The concentration of ^{10}Be in a given amount of sediment may nonetheless vary because it can be variably diluted depending on how fast other components in the sediment are deposited. In other words, we must also consider the sedimentation rate. The amount of ^{10}Be in a given amount of sediment then becomes:

$$[^{10}\text{Be}] = \frac{\Phi}{a} e^{-\lambda t} \quad 12.4$$

where a is the sedimentation rate. If sedimentation rate is constant, then the depth, d , of a given horizon in the sediment is given by

$$d = a \times t \quad 12.5$$

and

$$t = \frac{d}{a} \quad 12.6$$

We can substitute equ. 12.6 into 12.4 to obtain

$$[^{10}\text{Be}] = \frac{\Phi}{a} e^{-\lambda d/a} \quad 12.7$$

Taking the log of both sides, we have:

$$\ln[^{10}\text{Be}] = -\lambda \frac{d}{a} \ln\left(\frac{\Phi}{a}\right) \quad 12.8$$

From this we can see that the slope of a plot of $\ln[^{10}\text{Be}]$ vs. depth will be inversely related to sedimentation rate.

In a more general case, the sedimentation rate will not be constant, but will be a function of time. A general equation will then be

$$[^{10}\text{Be}] = \frac{\Phi(t)}{a(t)} e^{-\lambda d/a} \quad 12.9$$

In a sedimentary sequence such as a piston core, we do not necessarily know t (indeed, that is what we wish to determine), but we do know the depth in the core, which we know is some function of time. It is convenient then to transform equation 12.8 to a function of depth rather than time:

$$[^{10}\text{Be}](d) = \frac{\Phi}{a(d)} e^{-\lambda t(d)} \quad 12.10$$

The sedimentation rate a is simply

$$a = \frac{dd}{dt(d)} \quad 12.11$$

Substituting for a and integrating, we obtain:

$$\int_0^d [^{10}\text{Be}](d) dd = -\frac{\Phi}{\lambda} (e^{-\lambda t(d)} - 1) \quad 12.12$$

This equation in turn can be solved for $t(d)$:

$$t(d) = -\frac{1}{\lambda} \ln \left[1 - \frac{\Phi}{\lambda} \int_0^d [^{10}\text{Be}](d) dd \right] \quad 12.13$$

The integral is simply the sum of the activity of ^{10}Be down the core to any depth d .

This method has been used successfully to date sediments. However, since there are a number of ways of determining the age of young marine sediments, a more interesting application is determination of growth rates of manganese nodules, for which age determination is quite difficult.

Somewhat more accurate dates may be achieved when two cosmogenic nuclides are used. For example, ^{10}Be and ^{26}Al . In this case we can write two equations:

$$^{10}\text{Be} = ^{10}\text{Be}_0 e^{-\lambda_{10}t} \quad (12.2)$$

$$^{26}\text{Al} = ^{26}\text{Al}_0 e^{-\lambda_{26}t} \quad 12.13$$

Dividing one by the other, we obtain

$$\frac{^{26}\text{Al}}{^{10}\text{Be}} = \left(\frac{^{26}\text{Al}}{^{10}\text{Be}} \right)_0 e^{(\lambda_{10} - \lambda_{26})t} \quad 12.14$$

The advantage of this approach is that the initial $^{26}\text{Al}/^{10}\text{Be}$ ratio should be independent of the cosmic ray flux.

COSMOGENIC AND BOMB-PRODUCED RADIONUCLIDES IN HYDROLOGY

Determining the age of water in underground aquifers is an important problem because of the increasing demands placed in many parts of the world on limited water resources. A prudent policy for water resource management is to withdraw from a reservoir at a rate no greater than the recharge rate. Determination of recharge rate is thus prerequisite to wise management. Cosmogenic radionuclides are swept out of the atmosphere by rain and into the groundwater system. If we know the concentration of a radionuclide in rainwater, N_0 , and if we can assume that it is not produced within the Earth or lost from solution (this is our closed system requirement), then the 'age' of water in an aquifer is determined simply from equation 12.1, where we define 'age' as the time since the water left the atmosphere and entered the groundwater system.

In addition to cosmogenic production, ^3H and other radionuclides were produced in significant quantities during atmospheric thermonuclear tests between 1952 and 1963. The pulse of ^3H in precipitation during this period is illustrated in Figure 12.2. Tritium is readily detected by beta counting, and therefore bomb-produced tritium is potentially useful for tracing precipitation that fell during the 1950's and 1960's through groundwater systems. There are limitations on using it as a geochronological tool because the precipitation history of ^3H is not well known in most areas. In most cases, tritium has been used simply to distinguish pre-bomb from post-bomb waters. Older ground waters would be essentially free of atmospherically produced ^3H because of its short half-life (12.3 years), but contain

some ^3H produced *in situ* by fission-generated neutrons.

^{14}C has been used successfully for dating groundwater for decades. Since the concentration of ^{14}C in the atmosphere is uniform, its concentration in precipitation is also uniform. However, there are several problems with ^{14}C dating. The first is that ^{14}C is present in water principally as HCO_3^- and CO_3^{2-} . Both isotopic exchange reactions with carbonates in soils and the aquifer matrix and precipitation and dissolution

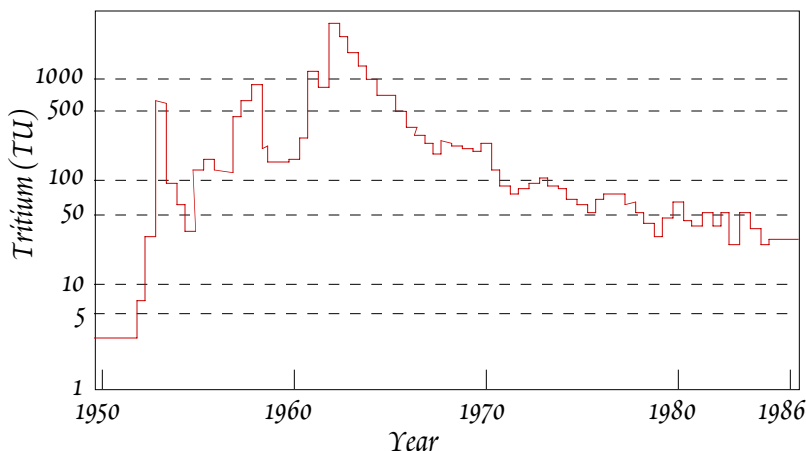


Figure 12.2. ^3H in precipitation recorded at Ottawa, Canada from 1950 to 1956. Vertical scale is in "Tritium Units", which are 10^{-18} atoms ^3H /atom ^1H .

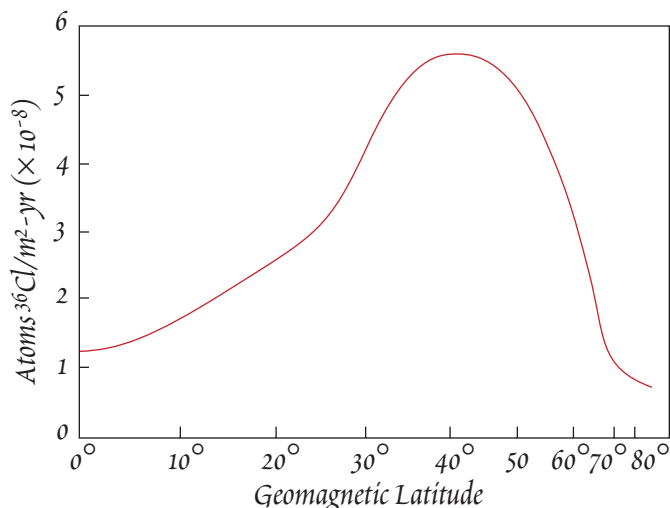


Figure 12.3. Latitudinal dependence of the fallout of atmospheric ^{36}Cl (from Bentley et al., 1986).

and neutron capture by ^{36}Ar . The former process has been estimated to produce about $11 \text{ atoms}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$, while the latter produces about half that, for a total production of about $15 \text{ atoms}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$. The residence time of ^{36}Cl in the atmosphere (about 1 week) is not long enough to homogenize its concentration, so the fallout varies with latitude as shown in Figure 12.3.

As usual, dealing with just the number, or concentration, of ^{36}Cl atoms can have disadvantages, and can be misleading. Evaporation, for example, would increase the number of ^{36}Cl atoms. Thus the $^{36}\text{Cl}/\text{Cl}$ ratio (Cl has two stable isotopes: ^{35}Cl and ^{37}Cl) is generally used. Stable chlorine can be leached from rocks. This chlorine will be nearly, but not entirely, free of ^{36}Cl . Some ^{36}Cl will be produced naturally by ^{35}Cl capturing neutrons generated by fission and (α, n) reactions on light elements. Further complications arise from the bomb-produced ^{36}Cl . Dissolved chlorine can also capture neutrons. Thus ^{36}Cl will build up in groundwater water according to:

$$N_{36} = \frac{\phi_n f}{\lambda_{36}} (1 - e^{-\lambda_{36} t}) \quad 12.15$$

where N_{36} is the number of ^{36}Cl atoms per mole, ϕ_n is the neutron flux, and f is the fraction of neutrons captured by ^{35}Cl . The secular equilibrium value, i.e., the concentration at $t = \infty$ is simply:

$$N_{36} = \frac{\phi_n f}{\lambda_{36}} \quad 12.16$$

This *in situ* production must be taken into account.

Stable Cl derived from sea spray is also present in the atmosphere and in precipitation. Its concentration decreases exponentially from coasts to continental interiors. Thus the initial $^{36}\text{Cl}/\text{Cl}$ ratio in precipitation will be variable and must be determined or estimated locally before groundwater ages can be estimated. The age of groundwater may then be determined from:

$$t = \frac{-1}{\lambda_{36}} \ln \left(\frac{C^{\text{Cl}} [^{36}\text{Cl}/\text{Cl} - ^{36}\text{Cl}/\text{Cl}_{se}]}{C_0^{\text{Cl}} [^{36}\text{Cl}/\text{Cl}_0 - ^{36}\text{Cl}/\text{Cl}_{se}]} \right) \quad 12.17$$

where C^{Cl} is the chloride concentration and the subscripts "0" and "se" denote initial and secular equilibrium values respectively.

Bentley et al. (1986) used this approach to determine the age of groundwater in the Great Artesian Basin aquifer. The Great Artesian Basin aquifer is one of the largest artesian aquifers in the world and underlies about a fifth of Australia (Figure 12.4). The primary aquifer is the Jurassic Hooray

of carbonates will alter the concentration of ^{14}C in groundwater. This, of course, violates the closed-system requirement. A second disadvantage is its relatively short half-life, which restricts the use of ^{14}C dating to waters less than 25,000 years old. While this is sufficient for shallow, localized groundwater systems, regional systems often contain much older water.

In contrast to ^{14}C , ^{36}Cl is essentially conservative in groundwater solutions, and has a half-life suitable for dating a water in regional aquifers as old as 1 Ma. The disadvantage is that it has a much lower production rate in the atmosphere than ^{14}C , and its analysis requires accelerator mass spectrometry.

In the atmosphere, the primary means of production of ^{36}Cl are spallation of ^{40}Ar

sandstone, which outcrops, and is recharged, along the eastern edge of the basin. Bentley et al. (1986) sampled 28 wells from the system. They estimated an initial $^{36}\text{Cl}/\text{Cl}$ ratio of 110×10^{-15} and a secular equilibrium value of 9×10^{-15} atoms per liter. Some well samples showed evidence of ^{36}Cl addition, probably from upward leakage of water from evaporate-bearing Devonian sediments beneath the aquifer. Other wells, particularly those in the recharge area, showed evidence of evaporation, which increases Cl concentrations before the water penetrated the groundwater system, not surprising in an arid environment. On the whole however, ^{36}Cl ages were comparable to calculated hydrodynamic ages, as illustrated in Figure 12.5.

In a somewhat different application, Paul et al. (1986) have used ^{36}Cl to determine the accumulation time of dissolved salt in the Dead Sea. The Dead Sea is a particularly simply hydrologic system because it has no outlet. In such a simple system, we can describe the variation of the number of ^{36}Cl atoms with time as the rate of input less the rate of decay:

$$\frac{dN}{dt} = I - \lambda N \quad 12.18$$

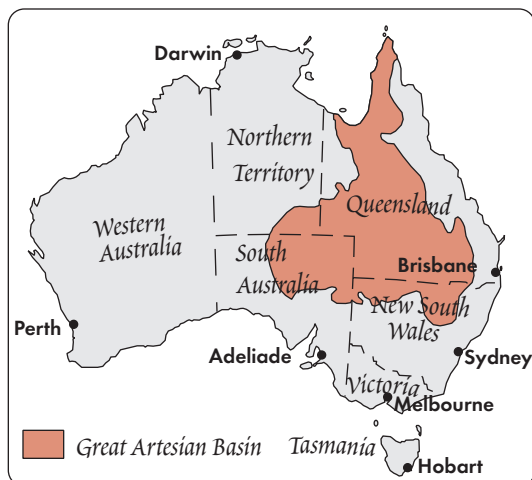


Figure 12.4. Extent of the Great Artesian Basin aquifer in Australia. From Bentley et al. (1986).

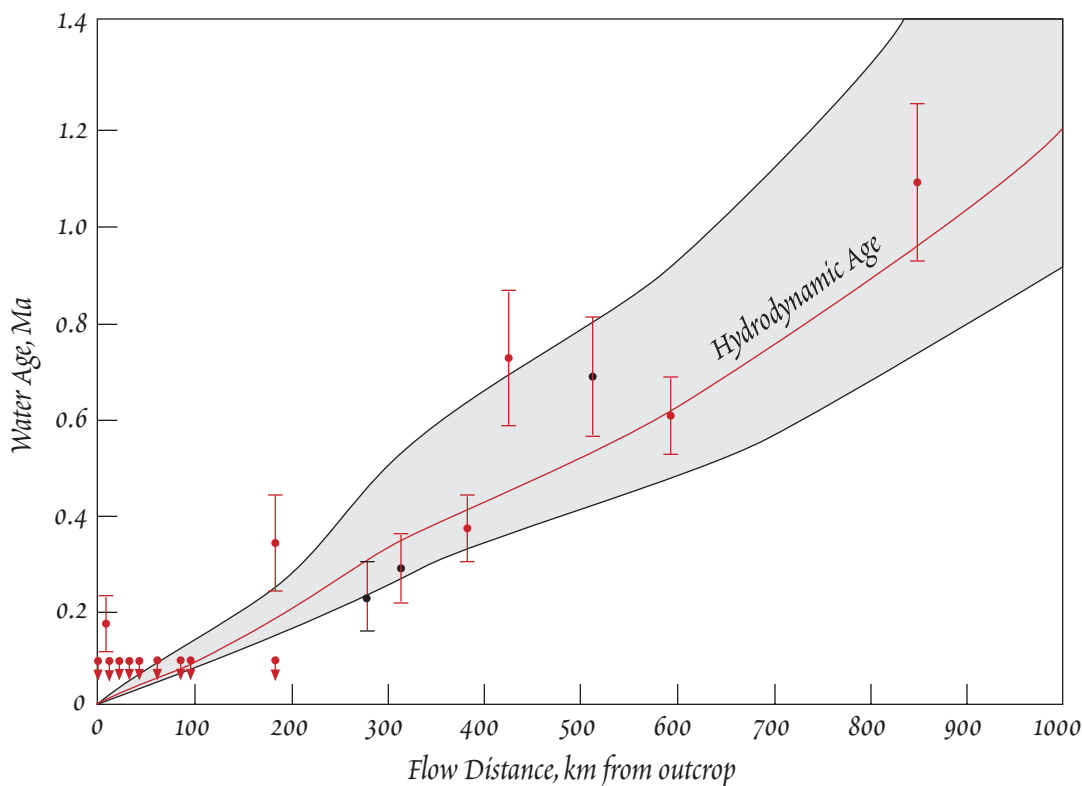


Figure 12.5. Comparison of ^{36}Cl ages with “hydrodynamic age”, i.e., the age estimated from hydrologic flow parameters. From Bentley et al. (1986).

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where I is the input rate (precipitation of chloride is assumed negligible). Integration of this equation yields:

$$N = \frac{I}{\lambda} (1 - e^{-\lambda t}) \quad 12.19$$

Paul et al. measured $^{36}\text{Cl}/\text{Cl}$ in Mt. Hermon snow, in various rivers in the Dead Sea system, and in saline springs in the Dead Sea basin. These results are summarized in Table 12.2. Using equation 12.19, they estimated an accumulation time of 20,000 years for the salt in the Dead Sea. The Dead Sea basin has been estimated to be 15,000 years old based on ^{14}C . The difference suggests some of the Cl now in the Dead Sea was inherited from its less saline Pleistocene predecessor, Lake Lisan. The data in Table 12.2 also illustrates how a combination of Cl and ^{36}Cl data can distinguish between addition of Cl from rock leaching and evaporation, both of which are processes that will increase the concentration of Cl. Evaporation should not significantly change the $^{36}\text{Cl}/\text{Cl}$ ratio, while addition of Cl derived from rock leaching should decrease this ratio. There is a general southward (downstream) increase in Cl concentration in the Jordan River–Dead Sea system. It is apparent from the data in Table 12.2 that this is due to both addition of rock-derived Cl and evaporation.

TABLE 12.2. ^{36}Cl MEASUREMENTS IN THE DEAD SEA SYSTEM

Site	$^{36}\text{Cl}/\text{Cl}$ (10^{-15})	Cl mg/l	^{36}Cl 10^6 atoms/l
Mt. Hermon Snow	1580±120	1.50	40±5
Banias River	400±60	11.9	80±15
Snir River	430±125	11.0	80±20
Dan River	725±140	10.5	129±25
Lake Kinneret	49±15	252	210±65
Jordan River	121±19	646	1,320±210
Dead Sea	17±2	2.30×10^5	6.6×10^4
Ashlag Spring (saline spring)	4±2	2.6×10^5	

REFERENCES AND SUGGESTIONS FOR FURTHER READING

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