Some comments on applications of cosmogenic radionuclides for determining groundwater flow, with special reference to ^{32}Si ands ^{10}Be$^{@)}$

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1. Introduction

In principle, any of the long lived radio-nuclides of half-lives exceeding one year, produced naturally by cosmic radiation in the earth's atmosphere, can serve to provide useful information on processes relating to transport of water through the upper layers of soil. Very useful information was in fact obtained from studies of the transient tracers, ^{3}H (half-life = 12.3 years) and ^{137}Cs (half-life = 30.2 years), produced in the detonations of nuclear weapons, based on observations on their dispersion in the sub-surface ground matrix (cf. Ritchie and McHenry, 1975; Phillips et. al. 1988). Naturally produced cosmogenic radiotracers have the advantage that their source functions are well known (Lal and Peters, 1967), which allows one to make meaningful models for their transport to the ground matrix, either by air-water exchange or by direct penetration through the soil.

Cosmic rays produce nine radio-nuclides of half-lives ranging between 10 years and 1.5 my, and five, between 2 weeks and 1 year (Table 1). These can serve as important tracers for measuring ground water movement on time scales of few weeks to millions of years, but surprisingly, they have not been studied to date with this view in mind. Earlier studies were concerned with their fall-out on the earth's surface, and estimation of their production rates. In the case of ^{10}Be, its studies were primarily directed towards using it for determining the soil formation ages (see references in Barg et. al. 1997). In the case of ^{36}Cl, a potentially important tracer, very large amount was produced in marine nuclear weapon's testing in late Feb. 1954, which overwhelmed the natural inventory of ^{36}Cl in the hydrosphere and in ground waters (Elmore et. al. 1983). In the case of ^{32}Si (half-life ~ 150 years), its studies were primarily directed towards examining the possibility of using it as a tracer for dating ground waters (Nijampurkar et. al. 1966). In recent years, however, realizing the necessity of developing reliable natural tracer methods, combined with the fact that it is progressively becoming easier to measure their weak activities, which result from the weak cosmic ray flux, there has been a revival in efforts to examine the suitability of cosmogenic tracers in hydrology.

The cosmogenic ^{32}Si has now been selected to study ground water infiltration rates at the University of Arizona, as a part of NSF SAHRA project, as recently discussed by Einloth et. al. (2001). This program would make use of the recently developed sensitive method for measuring ^{32}Si activity by measuring the beta-activity of its daughter nuclide, ^{32}P using a liquid scintillation spectrometer, as developed by Morgenstern (priv. comm.) and by Benitez-Nelson and Buessler (1998). In this presentation, I would not go into the details of the measurement techniques, but rather discuss in an overview what can be learnt from the various cosmogenic radiotracers in problems of hydrology, while pointing out their special merits.

a) Paper presented at the SAHRA- Recharge Workshop held at New Mexico Tech (Socorro), March 22-23, 2001

Table 1. Cosmogenic nuclide production rates and their inventories for radioisotopes of half-lives > 2 weeks $^{a)}$

	Half- life	Production Rate		Integrated	Integrated	Global
NUCLIDE	(years)	$(cm^2.sec)^{-1}$		inventory	inventory	Inventory
	(unless spec.)	troposphere	total	(dpm/cm^2)	$(atoms/cm^2)$	(grams)
			atmosphere			
^{10}Be	1.5×10^6	1.5×10^{-2}	4.6×10^{-2}	2.70	3.07×10^{12}	2.6×10^8
^{26}Al	7.1×10^5	3.8×10^{-5}	1.4×10^{-4}	8.40×10^{-3}	4.52×10^9	1.0×10^6
^{36}Cl	3.1×10^5	4.0×10^{-4}	1.1×10^{-3}	6.60×10^{-2}	1.50×10^{10}	4.6×10^6
^{81}Kr	2.3×10^5	5.2×10^{-7}	1.18×10^{-2}	7.10×10^{-5}	1.24×10^7	8.5×10^3
^{14}C	5730	1.10	2.50	1.50×10^2	6.52×10^{11}	7.7×10^7
^{39}Ar	268	4.3×10^{-3}	1.29×10^{-2}	7.75×10^{-1}	1.58×10^8	5.2×10^4
^{32}Si	150	5.4×10^{-5}	1.60×10^{-4}	9.60×10^{-3}	1.09×10^6	3.0×10^2
^{3}H	12.3	8.4×10^{-2}	2.50×10^{-1}	1.50×10^1	1.40×10^8	3.6×10^3
^{22}Na	2.6	2.4×10^{-5}	8.60×10^{-5}	5.16×10^{-3}	1.02×10^4	1.9
^{35}S	87 days	4.9×10^{-4}	1.40×10^{-3}	8.40×10^{-2}	1.52×10^4	4.5
^{7}Be	53 days	2.7×10^{-2}	8.10×10^{-2}	4.86	5.35×10^5	3.2×10^1
^{37}Ar	35 days	2.8×10^{-4}	8.30×10^{-4}	4.98×10^{-2}	3.62×10^3	1.1
^{33}P	25.3 days	2.2×10^{-4}	6.80×10^{-4}	4.08×10^{-2}	2.14×10^3	6.0×10^{-1}
^{32}P	14.3 days	2.7×10^{-4}	8.10×10^{-4}	4.86×10^{-2}	1.44×10^3	3.9×10^{-1}

a) Based on Lal and Peters (1967)

2. 2. Discussion on radio-nuclides which are useful for studying hydrological processes.

All the radio-nuclides listed in Table 1 have been extensively studied in the atmosphere, in wet precipitation, and in the hydrosphere, and in some cases, e.g. for ^{10}Be in sediments (cf. Lal and Peters, 1967; Lal, 1999). Their dispersion on the earth in different geospheres is principally controlled by two factors: their chemical properties and half-lives (Lal and Peters, 1967). In the case of long-lived isotopes, it is now possible to measure their concentrations using the accelerator mass spectrometry (AMS), usually at levels of > 10^6 atoms in a sample. We have therefore also given the expected steady state radio-nuclide inventories in atoms/cm^2 in Table 1. It can be observed that in the case of particle active nuclides, e.g. ^{10}Be and ^{26}Al, it should be very easy to determine their integrated deposition rates at a given site using the AMS from studies of sediments and soils. All long-lived nuclides, including ^{10}Be, ^{26}Al and ^{14}C, have sufficiently large inventories for convenient AMS determinations (the inventories of the gaseous nuclides are expected to be confined primarily within the earth's atmosphere). In the case of ^{3}H and shorter-lived radio-nuclides the depth of their dispersion in a geosphere is expected to be confined to shallow depths, in view of their short half-lives.

In ground waters, ^{32}Si exchanges appreciably with exchangeable (soluble) silica present in clays. Consequently, it has been observed that its concentration in ground waters is appreciably lower than in the feed waters (Lal et. al. 1970). The measured concentrations of ^{32}Si in rainwaters bracketed between 0.2-0.5 dpm/ 10^3 liters of rainwater. In several Indian river and lake waters, the corresponding values lie between 0.1-0.3 dpm/ 10^3 liters (). In ground waters, and in tube wells the values range between 0.01- 0.1dpm/ 10^3 liters (op. cit.). Thus, interaction with clays reduces the dissolved concentrations of ^{32}Si in lake, river and ground waters. The results of

Nijampurkar et. al. (1966) and Lal et. al. (1970) laid to rest the possibility of using ^{32}Si as a tracer for dating ground waters. Frohlich et. al. (1987) arrived at a similar conclusion, by making the direct observation that an appreciable fraction of ^{32}Si inventory was present in the soils in the top few meters of soils in the aquifer.

Based on the information to date about the chemical behavior of the cosmogenic tracers, ^{10}Be, ^{32}Si, ^{14}C and ^{39}Ar, we have summarized their expected behavior in ground waters in Table 2, along with comments whether they are suitable for dating ground waters, or for measuring ground water infiltration rates.

Table 2.Comments on behaviors of different tracers of half-lives exceeding 100 years in ground waters

	Cosmogenic nuclide			
COMMENTS	^{10}Be	^{32}Si	^{14}C	^{39}Ar
Tracer losses on exchange with *soil- matrix*	yes	yes	yes	no
Tracer losses on exchange with *rock- matrix*	yes	no	yes	no
Underground sources of tracer	*no*	*no*	*yes*	*yes*
Decrease of dissolved tracer *concentrations due to non-radioactive processes*	*yes*	*yes*	*yes*	*no*
Suitability as a tracer				
(i) *for dating ground waters*	no	no	yes[$)]	yes
(ii) for ground water infiltration rates	yes	yes	no[$)]	no

[$)] See text.

The three radio-nuclides, ^{10}Be, ^{32}Si and ^{14}C should potentially be useful as tracers for groundwater infiltration rates on a wide range of time scales. Extensive studies of ^{14}C/^{12}C ratios in the dissolved inorganic carbon (DIC) in ground waters show an appreciable exchange of ^{14}C with limestone and other carbonates, and effects of decomposition of organic matter. Measured values of the ^{14}C/^{12}C ratios in DIC in “young waters” are found to vary between 50 and 100% of modern carbon. Typical values of reduction in the ratio are of the order of 15%, corresponding to age overestimation by ~ 1300 years. By studying the chemical composition and δ^{13}C of the groundwater, one can obtain more reliable ages, especially relative ground water ages and the direction of flow of water. The uncertainties in the DIC ^{14}C/^{12}C ratios are however too large to estimate ground water infiltration rates!

Based on observations of behaviors of ^{32}Si and ^{10}Be in ground waters, they appear to be potential tracers for determining ground water infiltration rates. The mechanism of exchange of tracer in the two cases is however quite different. In the case of ^{32}Si, it exchanges with the soluble (exchangeable) silica in clays, whereas the nuclide ^{10}Be, being particle-active, is removed on surfaces by adsorption. It can be shown that in steady state, and in uniform soil horizons, the following equation (Lal and Ramesh, 2001) should well describe the expected changes in the concentrations of ^{32}Si and ^{10}Be in the ground matrix with depth, z:

$$C_s(z) = C_s(0).e^{-Az/v} \quad \ldots\ldots \quad (1)$$

where $C_s(z)$ and $C_s(0)$ are the concentrations of ^{32}Si (or ^{10}Be) in soil at depths z and at the surface, respectively, and A is the tracer exchange constant which depends on the tracer and the soil type, and ν is the water infiltration rate in the soil. The rate constants for different soil types can be easily determined from laboratory experiments, using the radio-nuclides ^{32}Si and ^{10}Be (or ^{7}Be), respectively, and in the case of ^{32}Si, from the rate of dissolution of silica in water for different soil types (Lal and Ramesh, 2001).

3. Concluding remarks

Several radio-nuclides are produced in the earth's atmosphere, which have been considered in earlier publications for determining ground water flow characteristics. We reviewed our present knowledge of the chemical behavior of different tracers and show that a great deal of useful work remains to be done using in particular the two radio-nuclides, ^{32}Si and ^{10}Be, which appear to be ideal for determining ground water infiltration rates in a variety of soil types. For measuring ground water infiltration rates, we need a tracer which exchanges with soils in a deterministic fashion! The rate constants for exchange of dissolved tracer with the soil matrix can easily be determined experimentally.

From the point of view of measurements of ^{32}Si and ^{10}Be activities in the ground matrix, it is very easy to measure ^{10}Be using the AMS (cf. Barg et. al. 1997). In the case of ^{32}Si, presently it is not convenient to use the AMS method for its measurement in ground waters in view of its expected low specific activity (^{32}Si / Si ratios are $<< 10^{-14}$). However, there exists an edge of advantage in the measurement of ^{32}Si since it decays to ^{32}P, which has a relatively short half-life (14.3 days), and emits an energetic beta particle. Thus it becomes possible to easily measure ^{32}Si activity by milking ^{32}P from even large amounts of ^{32}Si containing compounds (e.g. kilograms of silica), and measuring the ^{32}P activity using conventional low level beta detectors. Most of the early work (op. cit.) on measuring ^{32}Si activities in the ground matrix, and in ocean waters was carried out in this manner by counting its daughter nuclide, ^{32}P, using low level beta counters (Lal et. al. 1970; Frohlich et. al. 1987; Somayajulu et. al. 1991). The new technique of using the liquid scintillation counter as a low level detector for measuring ^{32}P beta activity, seems to hold considerable promise, and may make it possible to measure ^{32}Si in ground matrix more conveniently.

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