Earth and Planetary Science Letters 456 (2016) 78–86

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Cosmogenic ^{22}Na as a steady-state tracer of solute transport and water age in first-order catchments

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ARTICLE INFO

Article history:
Received 5 May 2016
Received in revised form 29 September 2016
Accepted 1 October 2016
Editor: M. Frank

Keywords:
cosmogenic
radionuclide
sodium
tracer
groundwater
dating

ABSTRACT

Naturally-occurring cosmogenic ^{22}Na ($T_{1/2} = 2.6$ yr) is a potentially powerful tracer of solute and water movement in catchments. However, due to its low abundance in precipitation ($\sim 10^{-20}$ mol L^{-1}), there are only a handful of datasets documenting cosmogenic ^{22}Na atmospheric fluxes and concentrations in surface waters. Here we present the first record of cosmogenic ^{22}Na fallout to North America and test its use as a radiometric tracer of water age in three small catchments in the Eastern United States. We show that ^{22}Na deposition to southeastern Virginia, USA during 2012–2014 was 187 ± 10 mBq m^{-2} yr^{-1} and that flux is largely additive with precipitation amounts. Our measurements of fallout combined with previous ^{22}Na deposition data from other regions indicate that approximately 77% of the variability in the annual global ^{22}Na atmospheric flux is controlled by precipitation. Export of ^{22}Na in drainage waters from three first-order forested catchments ranged from 12.5 to 174 mBq m^{-2} yr^{-1} and can be explained by a flux-based radioactive decay model, indicating that the watersheds are in steady-state with respect to cosmogenic ^{22}Na on annual timescales. We conclude that in temperate climates with no systematic changes in rainfall amounts at the annual timescale, ^{22}Na may be useful for quantifying the recharge age of relatively young (<20 yr) surface waters and groundwaters and for tracing solute transport at the watershed scale.

1. Introduction

Industrial and agricultural practices, urbanization, and climate change all affect the quantity and quality of freshwater resources available for human consumption (Vorosmarty et al., 2000). The most valuable approach for characterizing available freshwater resources and sustainable practices will be to focus on measuring flows in the hydrologic cycle rather than just standing stocks (Oki and Kanae, 2006). To do this, methods are needed to quantify rates of flow within different hydrologic systems and calculate reservoir recharge over appropriate timescales (Dirmeyer and Brubaker, 2006). Natural surface waters and groundwaters are typically a mixture of water sources with a spectrum of ages that take a range of flowpath geometries and lengths through the subsurface. The most common approach for characterizing and quantifying flows in hydrologic systems is to measure and model the behavior of a soluble tracer (McGuire and McDonnell, 2006), which can be used to determine the average "age" of water (defined as the time elapsed since a water molecule was precipitation, sometimes phrased as "recharge age") and mean transit time of a molecule through a particular system of the hydrologic cycle.

A wide range of natural and artificial tracers have been developed and applied to measure recharge age. The ideal hydrologic tracer would conservatively trace water flow and have a well-defined single input function, but no single atom or molecule has emerged as a universal tool for all environments. One of the most common tracers used in hydrologic studies is tritium (^{3}H, $T_{1/2} = 12.3$ yr), which qualifies nicely as a water tracer but it has a very complicated input function because of cosmogenic production and a large artificial pulse introduction to the atmosphere in the 1950s–1960s. Applying ^{3}H as a dating tool is thus very sensitive to recharge age and conditions, particularly in the Northern Hemisphere. While this problem can be largely overcome by normalizing ^{3}H to its daughter He, losses and gains of He by degassing and rock interactions as well as diffusive fractionation can complicate its application (LaBolle et al., 2006). Consequently, ^{3}H must be treated as a non-steady-state tracer in most systems and multiple age solutions are possible (Rose, 2007). Furthermore, where locally anthropogenic ^{3}H is still being released by nuclear power plants

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http://dx.doi.org/10.1016/j.epsl.2016.10.002
0012-821X/

and waste disposal sites, its application as a precise chronological tool becomes further hampered (Hughes et al., 2010).

Anthropogenic chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6) gases have also been widely applied to measure groundwater ages and calculate aquifer recharge rates for relatively young (<40 yr) waters (Busenberg and Plummer, 2000; Darling et al., 2012). While these tracers can be very useful in certain situations, they cannot be used for surface waters because streams, lakes, and reservoirs are open systems that will rapidly exchange gases with "modern" air. Moreover, the use of these gases can be limited by geologic and environmental conditions, as igneous rocks can produce SF_6 (Harnisch et al., 2000; Koh et al., 2007), and microbial breakdown of CFCs occurs under anoxic conditions (Darling et al., 2012). Finally, both gases have relatively complicated input functions where steady-state assumptions are not valid and may further change if limits are placed on production or emissions (Busenberg and Plummer, 2000; Darling et al., 2012).

Cosmogenic ^{22}Na ($T_{1/2} = 2.602$ yr) is naturally produced in the atmosphere when cosmic rays spallate Ar atoms (Lal et al., 1979; Rodel, 1965). As with ^{3}H, a large pulse of ^{22}Na was introduced into the atmosphere during the 1950–1965 weapons testing era, but this anthropogenically produced sodium has now decayed over more than 15 half-lives, making natural cosmogenic production the only significant source in today's environment (Fleishman, 2008). This isotope of sodium has several properties that make it ideal as a hydrologic tracer. Given that short-lived cosmogenic radionuclides created in the atmosphere are removed nearly entirely through wet deposition (Kaste and Baskaran, 2012; Landis et al., 2014), ^{22}Na fluxes to the Earth's surface should be relatively constant in most regions with no systematic changes in precipitation rates. While production rates of cosmogenic radionuclides do vary inversely with the 11-yrs solar cycle (Hernandez-Ceballos et al., 2015), based on cosmogenic ^{7}Be records in air, this is likely to introduce a relatively small (±20%) but regular fluctuation in annual ^{22}Na deposition over a ~5–6 yr timescale. Moreover, sodium is one of the most soluble of all the cations, and conservative behavior would be predicted in temperate to humid climates. Its 2.6 yr half-life makes it valuable over the 1–20 yr characteristic timescale of many catchment-scale transport processes for surface waters and shallow groundwater systems (McGuire and McDonnell, 2006). Finally, generic sodium (stable ^{23}Na, "Na" hereafter) is nearly ubiquitous and relatively simple to measure in meteoric, surface, and groundwaters. By measuring Na regularly in samples during the collection and sample processing stages, concentration and recovery yields for ^{22}Na can be monitored accurately.

To date, cosmogenic ^{22}Na is one of the most poorly documented natural isotopic systems. While a number of studies documented bomb-produced ^{22}Na in the atmosphere and rainfall during the 1960s and 1970s (Bhandari et al., 1970; Cigna et al., 1970; Lal et al., 1979), there have been only a few studies that quantify natural (cosmogenic) ^{22}Na atmospheric fluxes for an appreciable amount of time and even fewer that measure ^{22}Na in surface or groundwaters (Fleishman, 2008). As far as we are aware, there are no published studies that have measured annual cosmogenic ^{22}Na deposition in North America. The primary reason for the lack of ^{22}Na measurements in various segments of the hydrologic cycle is its low abundance. Natural fallout rates of ^{22}Na are documented to typically range from 100–300 mBq m^{-2} yr^{-1}, making the ^{22}Na specific concentrations and specific activities in rainwater to be ~10^4 atoms L^{-1} and 0.05 to 0.25 mBq L^{-1}, respectively (Fleishman, 2008; Sakaguchi et al., 2005). For comparison, the more commonly measured cosmogenic radionuclide in rainfall, ^{7}Be, has specific radioactivities (Bq L^{-1}) 10,000 times this amount (Baskaran et al., 1993; Kaste and Baskaran, 2012). Thus, large collection volumes (50–500 liters), radionuclide preconcentration, and long photon counting times are needed for ^{22}Na measurement.

^{22}Na was first utilized as a tracer of hydrologic processes in freshwater basins in northwestern Russia during the 1970s, when atmospheric and lake water ^{22}Na concentrations were elevated due to bomb-produced inputs (Fleishman, 1982, 2008). Despite non-steady state conditions, ^{22}Na was utilized for residence time calculations because the long-term atmospheric depositional patterns of both artificial and natural ^{22}Na in the region had been previously documented. Since the complete decay of bomb-produced ^{22}Na and the return of atmospheric ^{22}Na fluxes to natural levels in the 1980s, only a handful of studies have explored the potential of ^{22}Na as a freshwater tracer, and these have focused on using ^{22}Na to calculate water and solute residence times in large basins. The most recent examples are when ^{22}Na was successfully applied to calculate the residence times of water in Lake Ladoga in Europe (Fleishman, 2008) and Lake Biwa in Japan (Sakaguchi et al., 2005) by measuring ^{22}Na inputs and outputs to these freshwater reservoirs.

The objective of this study is to develop and test ^{22}Na as a tracer of solute transport and radiometric water age in three small (<100 ha) undisturbed vegetated catchments where recharge ages are expected to be 1–20 yrs. At the primary site in southeastern Virginia (14.7 ha), annual ^{22}Na atmospheric and stream discharge fluxes were measured between 2012–2014 and 2012–2016, respectively, and recharge age was independently determined with SF6. We also measured ^{22}Na discharge fluxes in two other first order catchments where ages have been determined by previous studies (SF6, Plummer et al., 2001; high resolution water isotopic analyses, Benettin et al., 2015).

2. Methods

2.1. Study site description

2.1.1. Atmospheric deposition and Pogonia watershed in Williamsburg, VA, USA

During 2012–2014, we measured Na and ^{22}Na in precipitation in Williamsburg, (37°15′N; 76°45′W), which is on the Coastal Plain geologic province of Virginia. Williamsburg typically receives 1.1 m of wet precipitation that is distributed approximately evenly across the entire year. Mean annual temperature is 15 °C, so only a minor fraction (<10%) of the precipitation is frozen as ice or snow. Wet precipitation was collected from February 2012 through August 2014 from a 4.25 m^2 roof section of a vinyl-clad storage shed using a gutter system that drained into a 185 L rain barrel. Depending on the amount of rainfall, the barrel was emptied every 2 to 4 weeks, and a 60–80 L sample was collected for Na and ^{22}Na analysis. In one instance, we analyzed rainfall from different portions of a single large storm. On October 28–29th, 2012, Hurricane Sandy hit southeastern Virginia and delivered ~12 cm of rain over the period of 35 h. We analyzed the first, middle, and final third of this storm to quantify the temporal variability of ^{22}Na deposition in a single event.

The first-order 14.7 ha watershed that we measured for Na and ^{22}Na fluxes during 2012–2016 has a gently sloping perennial stream (Fig. 1) which drains into Lake Matoaka. The watershed and the lake are on the property of the College of William & Mary in Williamsburg, VA. The stream is approximately 1.5 km in length, and drains over Quaternary sands of the Bacon's Castle fluvial geologic unit. Soils here are sandy loam Ultisols with no carbonate minerals, and a digital-elevation model based on LiDar data of the watershed modeled with ArcHydro indicates that the mean straight flow-path length here is 360 m. The total relief along the stream length from the drainage divide to the sampling point is about 25 m, and base flow is relatively constant at ~1.5 L s^{-1} except for time periods immediately following large storms. In this part of southeastern VA, evapotranspiration is 60–70% of annual