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

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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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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 $\text{mBq}\,\text{m}^{-2}\,\text{yr}^{-1}$, making the ^{22}Na specific concentrations and specific activities in rainwater to be $\sim 10^{4}$ $\text{atoms}\,\text{L}^{-1}$ and 0.05 to 0.25 $\text{mBq}\,\text{L}^{-1}$, respectively (Fleishman, 2008; Sakaguchi et al., 2005). For comparison, the more commonly measured cosmogenic radionuclide in rainfall, ^{7}Be, has specific radioactivities ($\text{Bq}\,\text{L}^{-1}$) 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 $\text{L}\,\text{s}^{-1}$ except for time periods immediately following large storms. In this part of southeastern VA, evapotranspiration is 60–70% of annual

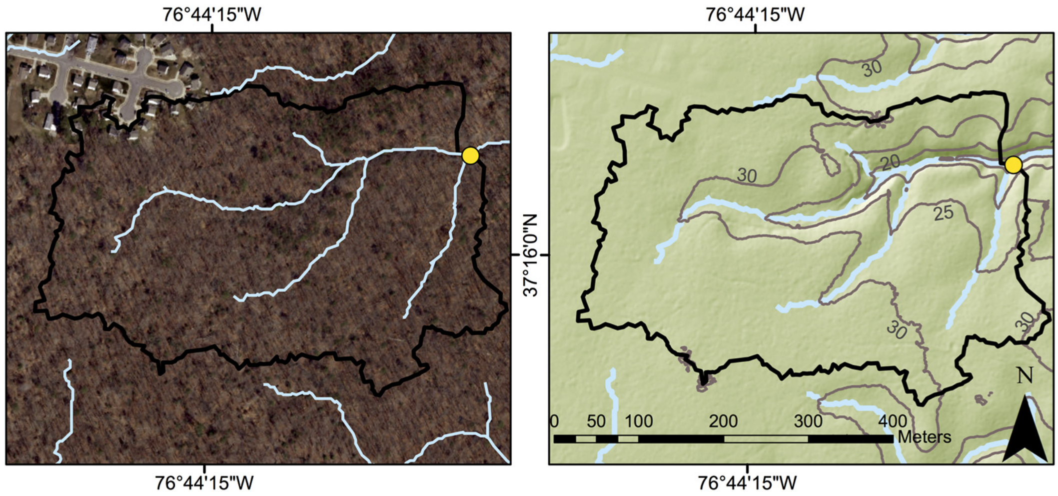

Fig. 1. Satellite photo (left) and topographic map (right) of forested Pogonia watershed in Williamsburg, VA where Na and ^{22}Na exports were measured between 2012–2016. Yellow circle indicates sampling point. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

precipitation (Sanford and Selnick, 2012). Thus, annual surface and groundwater discharges for Pogonia are calculated to be 0.33 to 0.44 m compared with the 1.1 m of annual precipitation. Given that the regolith here is predominantly quartz, Pogonia stream has a low dissolved load (~10 mg L^{-1}) and is mildly acidic with a pH ranging from 5–6. The watershed is relatively undisturbed with no irrigation and is covered almost entirely by mature native deciduous vegetation that is dominated by oak, hickory, beech, and tulip poplar.

2.1.2. *Hubbard Brook Experimental Forest, New Hampshire, USA*

We also measured Na and ^{22}Na in base flow drainage waters from Watershed 3 in the Hubbard Brook Experimental Forest (43°56′N; 71°45′W) in central New Hampshire, USA. This watershed has been monitored for hydrologic and elemental budgets beginning in 1957 and is a member of the Long-Term Ecological Research Network (LTER). Watershed 3 is a 42 ha catchment draining the Silurian Rangeley unit, which consists primarily of quartz mica schist and quartzite. Since this region was glaciated multiple times during the Pleistocene, thin (~1–50 cm) soils (Spodosols) are developed on till. This watershed has a total relief of about 60 m and is vegetated with mature northern deciduous forest dominated by American beech, sugar maple, yellow birch, and some red spruce at higher elevations. Average annual precipitation here is 1.5 m with nearly one-third of this falling as snow, and annual runoff is calculated using high resolution (30 min during steady flow and 6 minutes during changing flow) gauge height data measured in a v-notch weir. Mean annual runoff from Watershed 3 is 1.1 m. Watershed 3 has a slightly acidic pH (~6) and a relatively low dissolved load (<2 mg L^{-1}). Given that Watershed 3 has been the hydrologic reference catchment for a wide range of paired catchment and hillslope studies for the last 50 years (Bailey et al., 2003; Benettin et al., 2015; Johnson et al., 1969; Lawrence and Driscoll, 1990) and has well-characterized hydrology, soils, and climate, we considered this an ideal field site to test ^{22}Na as a tracer.

2.1.3. *Jones Run, Shendandoah National Park, Virginia, USA*

Shenandoah National Park encompasses approximately 800 km^2 of relatively undisturbed forest on the Blue Ridge Mountains of Northern Virginia. Our sampling site at Jones Run is approximately 40 km south of the Big Meadows Air Quality Monitoring Station, which is part of the National Atmospheric Deposition Program (NADP, 2015). Here, rainfall, temperature, and precipitation chemistry have been collected since 1981, and we use these data to calculate total precipitation and atmospheric Na fluxes. Annual precipitation here is 1.46 m, and annual discharge from forested watersheds here is calculated at 0.66 m ± 0.08 based on an evapotranspiration model (Sanford and Selnick, 2012). We sampled Jones Run for ^{22}Na, a small first-order stream that drains the ridgeline beginning at about 850 m in elevation. Our sampling point for this study is at 750 m in elevation where the stream becomes perennial (38°13.688′N; 78°43.365′W). Soils here are relatively thin Inceptisols and overlie Cambrian age siliclastic metasedimentary rocks of the Chilhowee Group which overlie the Catoctin Greenstone. As with the other streams studied here, Jones Run is mildly acidic, with a pH ranging from 6 to 7 and a relatively low total dissolved load of 6 to 8 mg L^{-1}.

2.2. *Streamwater sampling*

We used two methods to sample adequate volumes of streamwater for ^{22}Na determination during 2012–2016. During the first three years, we used a peristaltic pump to collect 70–80 L of water during base flow in the summer and fall from the Pogonia Watershed. Suspended matter was removed in the field by passing the water through a column of 8 μm pyrex glass wool. The filtered water was transported back to the laboratory using plastic carboys where the ^{22}Na was extracted and concentrated using Amberlite™ 120 or Dowex™ G26 H+ form cation exchange resin. However, because transporting such large volumes of water from remote regions is challenging, in 2014 we developed a second, in-situ method for collecting and concentrating ^{22}Na from up to 200 L of surface waters that relies on the use of total Na as a yield monitor. We found that ~100 g (wet) of Dowex™ G26 H+ form resin, which comes in a relatively uniform bead size (650 ± 50 μm), could be packaged in a polypropylene bag with a mesh size of 250 μm and anchored just above the stream bed, allowing flowing streamwater to gradually equilibrate with the resin over the course of 5 to 8 days. Weights were sealed into the bag with the resin to keep the bag stationary in a current. This method works best during steady flow conditions (i.e., avoiding large storms) and requires that the concentration of total dissolved Na (mg L^{-1}) is measured in the water by collecting 30 mL samples at the beginning and end of the resin bag's deployment. The resin can then be analyzed for total Na (mg), and then the liters of water that have equilibrated with the resin can be calculated using the known concentration (mg L^{-1}) of generic Na in the stream. We used both methods (pumping and transporting 80 L of water back to the lab for separation and processing vs. the in-situ method) and found that the calculated ^{22}Na concentrations were indistinguishable.

At Pogonia Stream, groundwater samples were collected for SF_6 measurements as a way to provide independent constraints on base flow age. A polyvinyl chloride monitoring well placed in the stream valley floor near the ^{22}Na collection point was sampled with a peristaltic pump and collected in 1-L plastic safety coated amber glass bottles with zero headspace. Extreme care was taken to prevent contact of the water sample with the atmosphere by placing one end of the tubing in the well and the other end in the sample bottle and maintaining a relatively high ($2\ \mathrm{L\,min^{-1}}$) flow rate. The bottle overflowed three times its volume before it was capped. The bottle was examined to ensure that there were no air bubbles, and then replicate samples were sent to the US Geological Survey in Reston, VA for dissolved anthropogenic gas analysis (Busenberg and Plummer, 2000). Recharge temperature for Pogonia was determined to be 15 °C using a weather station situated within 2 km of the site, excess air was 2 mL, recharge elevation is 20 m above sealevel, and recharge age is calculated using a piston-flow model (Busenberg and Plummer, 2000; Plummer et al., 2001).

2.3. Sample processing

2.3.1. Water samples: direct collections

After the precipitation or runoff samples were taken back to the lab, the water was placed in 50–75 L high-density polyethylene tanks, and a 10 mL volume was removed for the determination of major cation content with a Dionex ICS2000 Ion Chromatography system. The ICS2000 uses suppressed conductivity detection and can measure as low as $0.01\ \mathrm{mg\,Na\,L^{-1}}$. The tank containing the water sample drained to a storage tub through a half-meter length of 1/4 inch inner-diameter Tygon tubing that was packed with cation exchange resin (Amberlite™ IR120H). Drainage through the resin was driven by gravity at a rate of approximately $15\ \mathrm{L\,d^{-1}}$. To ensure the most efficient gamma detection of ^{22}Na, we determined the smallest amount of resin that was required for efficient Na removal from the water and found that 1.8 g (wet) was required for every mmol of cation charge for near total removal of sodium. We typically used approximately 10 g of resin for precipitation samples and approximately 35 g of resin for Pogonia drainage waters. After the water sample flowed through the resin-packed tubing, the resin was extracted, dried, and combusted in a fused quartz crucible for 7 h at 650 °C. The ash was collected in 2.5 mL of 1 M HCl, which was transferred to a 2-cm diameter vial for gamma counting. After the separation process, the storage tub containing the water that had passed through the resin was measured for major cations once again to calculate sodium recovery yields, which were typically >95%. Total generic sodium was also measured in the dissolved ash sample to cross-check the recoveries.

2.3.2. Surface water samples: resin bag analysis

After the resin bags that were deployed in the stream were recovered, the bags were split open and the resin was placed in a small 250 micron sieve and gently rinsed with a small amount (∼400 mL) of de-ionized water to remove silt and debris that passed through the polypropylene mesh and got trapped within the resin. The cleaned resin was then placed in a glass column and eluted using 1 M HCl at a flow rate of $1\ \mathrm{mL\,s^{-1}}$ maintained by a peristaltic pump. We found that most of the Na was removed from the resin with the first ∼300 mL of acid, and much of the smaller monovalent and divalent cations including potassium, calcium, etc. remained in the column. Separating Na from other ions in surface water or groundwater samples is useful because naturally occurring ^{40}K and ^{238}U-series radionuclides decay by gamma emission, and can increase the Compton-continuum background in gamma spectrums and thus degrade the sensitivity for ^{22}Na (Sakaguchi et al., 2003). The Na solutions were then evaporated to ∼10 mL and then run for ^{22}Na. A small (30 μL) subsample of the 10 mL concentrate was run for total Na to calculate a final yield (and used to calculate liters of solution that equilibrated with the resin).

2.4. Gamma analysis of ^{22}Na

We measured cosmogenic ^{22}Na in rainwater and streamwater samples by ultralow background gamma-counting the burned cation exchange resin or concentrated Na solutions in a high efficiency geometry. The ash residue and small volume of HCl rinse were put in a vial that had a diameter of 2 cm, and sample heights were typically <1 cm. The vial was placed directly in the center of a Canberra 5030 “Broad Energy” intrinsic germanium (Ge) detector, which has a 50 cm^2 surface area and 2 keV full-width half maximum energy resolution at 1333 keV. These detectors have an ultralow background cryostat design and a remote detector chamber that keeps the preamplifier and detector hardware outside of the shield. The gamma analysis laboratory is housed in the lowest level of a 4-story science building at the College of William and Mary, and each detector is surrounded by 10 to 15 cm of lead in every direction. We calibrated the intrinsic Ge detectors with a mixed isotope source (Isotope Products 7503) that contained radionuclides decaying at energies ranging from 46–1800 keV. A source of pure ^{22}Na (Perkin–Elmer) was used to correct the detection efficiency for peak-summing of the 1275 keV gamma emission with the 511 keV annihilation photons, which is significant given the high nuclear yield of the latter (180%). Our absolute detection efficiency for ^{22}Na ranged from 2.6–3.1%, depending on the height of the sample, which was determined by the volume of the resin ash. Count times for each sample typically ranged from 7 to 20 days. Detector background in the ^{22}Na region of interest from 1272–1278 keV is 0.7 ± 0.1 counts per 1000 s, indicating a detection (95% confidence) limit of 2 mBq ^{22}Na.

3. Results

3.1. Total Na fluxes to and from watersheds

Total Na inputs via atmospheric deposition and outputs via stream discharges in the Pogonia, Hubbard Brook, and Jones Run watersheds were quantified either through measurements done in this study or measurements compiled from other datasets. In the Pogonia watershed, average annual atmospheric Na flux was $497\ \mathrm{mg\,m^{-2}\,yr^{-1}}$ while the average annual total Na discharge was $928\ \mathrm{mg\,m^{-2}\,yr^{-1}}$. In all three watersheds as well as watersheds analyzed in other regions, the ratio of Na outputs to Na inputs is greater than 1 (up to ∼10), indicating that Na is generally gained but not lost as waters move through the watershed (Fig. 2).

3.2. ^{22}Na concentrations in precipitation and atmospheric ^{22}Na fluxes

We found ^{22}Na concentrations in precipitation samples to be on the order of $10^{-4}\ \mathrm{Bq\,L^{-1}}$. ^{22}Na in precipitation samples varied greatly from rain event to rain event over the three-year period, ranging from $0.02–0.4\ \mathrm{mBq\,L^{-1}}$ (volume-weighted mean $= 0.14 \pm 0.08\ \mathrm{mBq\,L^{-1}}$). ^{22}Na fluxes for each 2–4 week collection period correlated linearly with precipitation ($r^2 = 0.57$), indicating that ^{22}Na flux is primarily controlled by precipitation amounts (Fig. 3). However, significant dilution of ^{22}Na and Na is observed during single large precipitation events (Fig. 4). We found that during Hurricane Sandy, ^{22}Na concentrations declined from $0.2\ \mathrm{mBq\,L^{-1}}$ to $0.03\ \mathrm{mBq\,L^{-1}}$ between the beginning third of the storm to the final third of the storm, and total Na followed a similar declining pattern (Fig. 4). Annual atmospheric

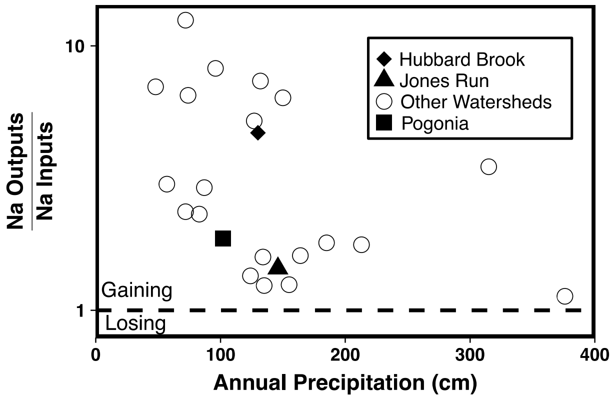

Fig. 2. Summary of watershed-scale sodium budgets comparing inputs from atmospheric deposition with exports via drainage waters calculated for a wide range of climates tabulated by others (Likens and Bormann, 1995) and made in this study. Note that the *x*-axis has a linear scale while the *y*-axis has a logarithmic scale.

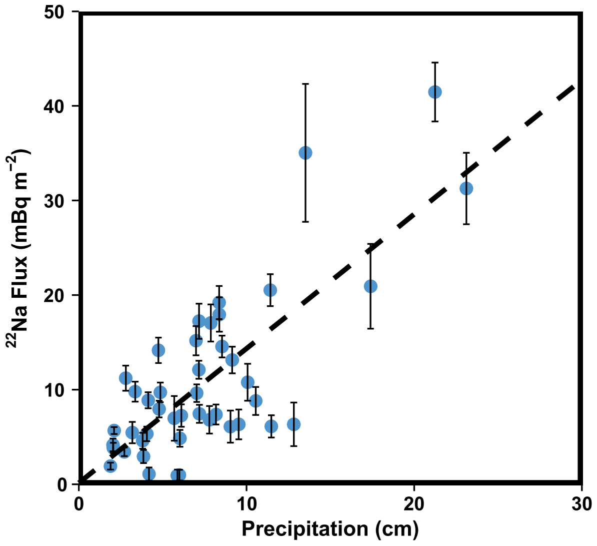

Fig. 3. Comparison of precipitation and ^{22}Na flux measured in 44 atmospheric deposition samples collected in Williamsburg, VA during 2012–2014. Each datapoint represents 2 to 4 weeks of collection. The linear fit is $y = 1.42x + 0.138$ ($p < 0.01$), with an r^2 of 0.571.

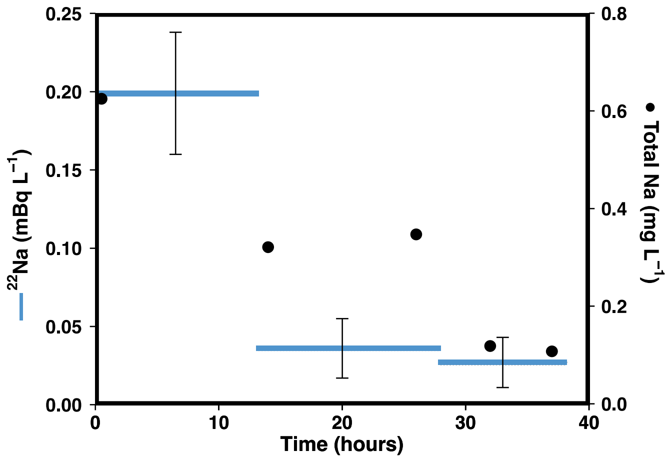

Fig. 4. Concentration of ^{22}Na and Na measured in precipitation during Hurricane Sandy. The horizontal line represents the duration of time that each ^{22}Na measurement integrates, and the circles represent discrete measurements of total Na.

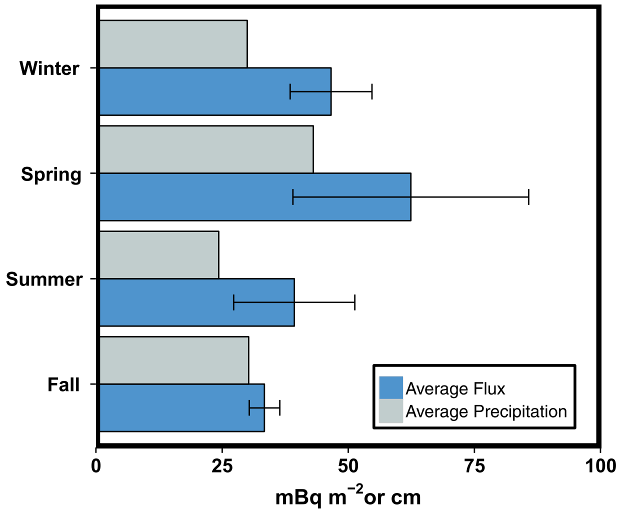

Fig. 5. Seasonal variability of precipitation and atmospheric ^{22}Na flux measured in Williamsburg, VA during 2012–2014.

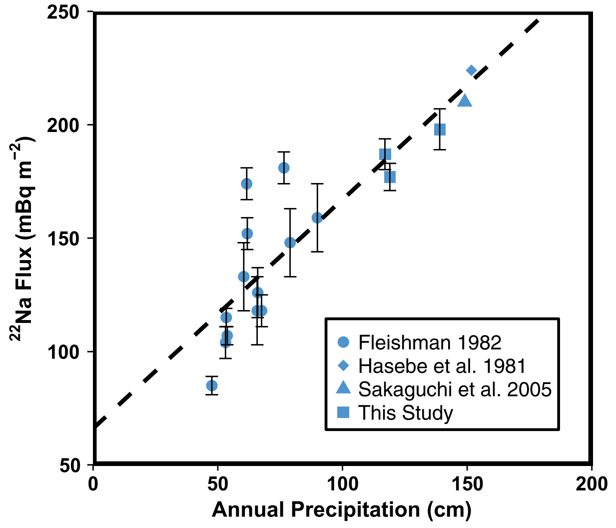

Fig. 6. Annual rainfall and annual ^{22}Na flux measured in this study compared with all other published global deposition data. The linear fit is $y = 1.01x + 66.1$ ($p < 0.01$), with an r^2 of 0.775.

fluxes of ^{22}Na to the Pogonia watershed in 2012, 2013, and 2014 were 187, 198, and 177 mBq m^{-2}, respectively, with an overall mean of 187 ± 10 mBq m^{-2} ($\pm 1\sigma$). ^{22}Na fluxes varied on a seasonal timescale with the highest average seasonal ^{22}Na flux in the spring (Apr to Jul mean = 62 ± 23 mBq m^{-2}) and lowest in the fall (Oct–Dec mean = 33 ± 3 mBq m^{-2}); average seasonal precipitation amounts were also highest in the spring (mean = 43 cm) (Fig. 5).

Our annual atmospheric ^{22}Na flux measurements combined with annual ^{22}Na flux data generated in previous studies from other regions in the world indicates that from 0.5 to 1.5 m of annual precipitation, a liner relationship of the form $y = 1.01x + 66.1$ ($r^2 = 0.77$) holds, where y is annual ^{22}Na flux (mBq m^{-2} yr^{-1}) and *x* is annual precipitation (cm) (Fig. 6). We used this linear regression to calculate the ^{22}Na atmospheric deposition to the Jones Run watershed in Virginia and the Hubbard Brook watershed in New Hampshire based off of local annual precipitation values. Calculated fluxes were found to be 214 ± 46 mBq m^{-2} yr^{-1} for Jones Run and 222 ± 47 mBq m^{-2} yr^{-1} for Hubbard Brook (95% prediction interval given).

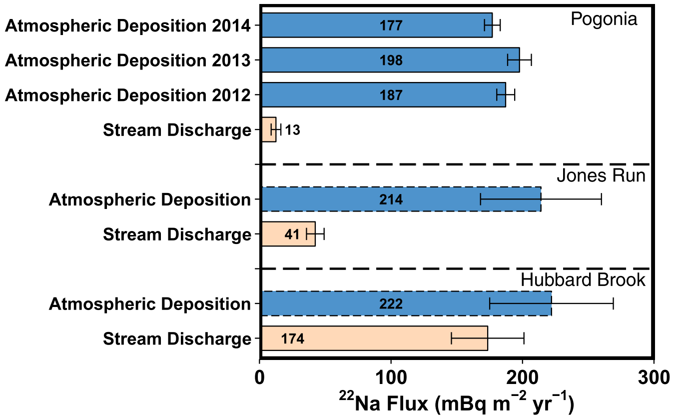

Fig. 7. Atmospheric fluxes of ^{22}Na compared with drainage water exports for three first-order forested watersheds in Virginia and New Hampshire, USA. Dotted outlines indicate that fluxes were estimated using the linear regression $y = 1.01x + 66.1$.

3.3. ^{22}Na concentrations in surface runoff and watershed ^{22}Na exports

^{22}Na concentrations were directly measured in drainage waters of all three watersheds studied here and calculated annual ^{22}Na discharge fluxes were found to be lower than the annual atmospheric deposition at the same site (Fig. 7). Concentrations of ^{22}Na in surface runoff across all watersheds ranged from 0.035 to 0.162 mBq L^{-1}. Variations in ^{22}Na exports from the Pogonia stream were not found to be significantly different from year to year. We found that when streamwater was analyzed for ^{22}Na by pumping a known volume (65 to 80 L) of streamwater into plastic containers and then processing that water in the lab, the ^{22}Na concentration was 0.042 ± 0.02 mBq L^{-1}, but when using the in-stream resin bag method we found 0.035 ± 0.01 mBq L^{-1}. While these numbers are statistically indistinguishable, we note that the uncertainty is smaller when using the resin bag method, because hundreds of liters of Pogonia Stream equilibrated with the resin bag, which yielded more Na for the gamma analysis. The average annual ^{22}Na export from Pogonia Watershed was 12.5 ± 3.7 mBq m^{-2}, while measured annual watershed exports were higher in the Jones Run and Hubbard Brook Watersheds at 41.4 and 174 mBq m^{-2} respectively (Fig. 7).

4. Discussion

4.1. Atmospheric deposition of ^{22}Na to watersheds

While measurements of atmospheric ^{22}Na deposition are sparse due to the low abundance of ^{22}Na in precipitation, measurements of ^{22}Na atmospheric fluxes have been carried out in Heidelberg, Germany (Rodel, 1965), Rome, Italy (Cigna et al., 1970), St. Petersburg, Russia (Fleishman, 1982, 2008), Tokyo, Japan (Hasebe et al., 1981), Fukui City, Japan (Tokuyama and Igarashi, 1998), Lake Biwa Japan (Sakaguchi et al., 2005), and Bombay, India (Lal et al., 1979). These measurements show elevated rates of ^{22}Na deposition up to ~2200 mBq m^{-2} yr^{-1} in St. Petersburg from the early to mid 1960s due to nuclear weapon testing. By the beginning of the 1970s, bomb produced ^{22}Na had disappeared from the environment entirely due to decay, and ^{22}Na concentrations in precipitation returned to natural background levels (Fleishman, 2008). As a result, much lower deposition rates, ranging from approximately 100 to 300 mBq m^{-2} yr^{-1}, were observed in the late 20th century, which are the same range that we observed in 2012–2014 (Figs. 6, 7).

We found that annual wet deposition of ^{22}Na from 2012–2014 in Williamsburg, VA ranged from 177–198 mBq m^{-2} yr^{-1} (187 ± 10 mBq m^{-2} yr^{-1} mean $\pm 1\sigma$). These measurements are similar to those measured by Fleishman (1982, 2008) who found that between 1968–1984, ^{22}Na deposition was 85–181 mBq m^{-2} yr^{-1}, with median of 125 mBq m^{-2} yr^{-1}. The similarity in deposition rates that we quantified is remarkable given that our two studies were made decades apart, at significantly different latitudes, and in contrasting climates. The Fleishman dataset showing ^{22}Na deposition to St. Petersburg (60°N latitude) is the only other long-term cosmogenic flux record available for comparison, and when it is normalized to annual precipitation the deposition is 211 ± 33 mBq m^{-2} yr^{-1} per meter of precipitation. Despite the various factors that can control cosmogenic production and atmospheric deposition, including latitude, solar activity, cosmic ray fluxes, and climate (Feely et al., 1989), this study combined with available datasets indicate that annual ^{22}Na deposition at a single site is relatively constant from year to year, with standard errors of the annual mean on the order of 10–15%.

Our 44 flux measurements made for 2 to 4 week collection periods show that ^{22}Na wet deposition fluxes are additive, with ^{22}Na fluxes correlating positively with precipitation ($r^2 = 0.57$; Fig. 3). Locally, others have observed strong linear correlations between precipitation and fallout radionuclide fluxes (Landis et al., 2014). Interestingly, a linear relationship between flux and precipitation cannot hold across a large precipitation gradient, because eventually the atmosphere becomes depleted in ^{22}Na. We find evidence of this during our Hurricane Sandy observations (Fig. 4); this "wash out effect" has been shown for cosmogenic ^{7}Be as well (Ishikawa et al., 1995). It is clear that aerosols containing Na and radionuclides are preferentially scavenged from the atmosphere during the initial part of the storm. While spring and summertime thunderstorms deliver somewhat higher ^{22}Na fluxes, and larger volume fall storm systems tend to have lower ^{22}Na fluxes, we find that year-to-year atmospheric ^{22}Na flux variability is less than its seasonal variability.

All published post-bomb era ^{22}Na fluxes made across the globe combined with our measurements show that flux correlates linearly with annual local precipitation and that precipitation is the dominant control on ^{22}Na flux to the earth's surface ($r^2 = 0.77$; Fig. 6). Latitude is most likely the next most important variable controlling deposition given that cosmic rays are deflected towards to the poles. The annual ^{22}Na flux per meter of precipitation that we measured at 37°N was 150 mBq m^{-2}, somewhat lower than the 210 mBq m^{-2} measured at 60°N by Fleishman (2008), but more measurements are needed to quantify the relationship between latitude and deposition, particularly because snow and rain reportedly have different atmospheric scavenging efficiencies (McNeary and Baskaran, 2003).

4.2. Basis for a steady state model of ^{22}Na in watersheds

Sodium is a relatively soluble element with a low affinity for cation exchange sites and of little biological relevance compared to other common cations in forested watersheds (Bailey et al., 2003; Waring and Schlesinger, 1985). At the Hubbard Brook Experimental Forest, for example, Vitousek (1977) estimated that annual Na accumulation by a mature hardwood forest was on the order of 25 g ha^{-1} yr^{-1}, which was <1% of the annual sodium inputs to the watersheds by atmospheric deposition and chemical weathering and trivial compared to the annual net ecosystem production of 3600 kg ha^{-1} yr^{-1}. In soils with relatively high rainfall (>1 m annually), especially where rain is mildly acidic, cation exchange sites on soil minerals are typically dominated by Al^{3+} or H^{+}, rather than Na^{+} (David and Lawrence, 1995). In organic horizons, Ca often dominates the exchange surfaces, but Na is usually documented to have a very low or even undetectable presence here (Bailey et al., 2003).

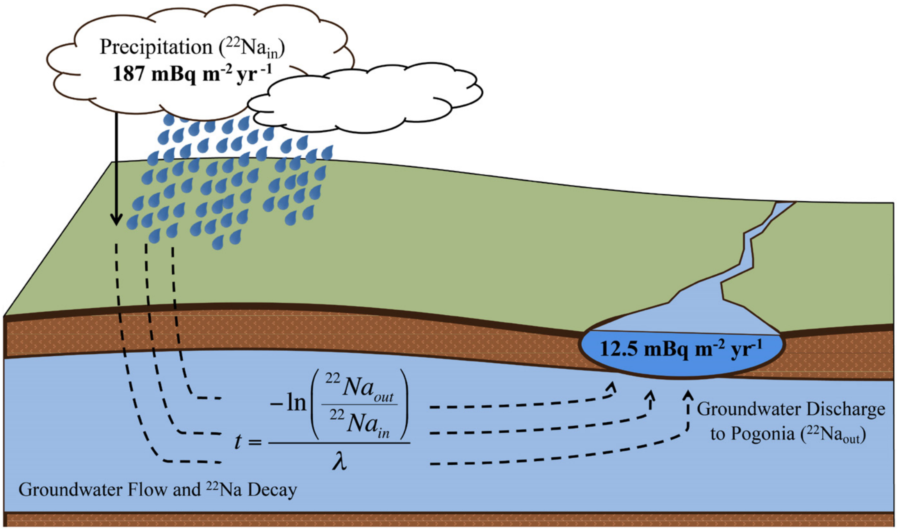

Fig. 8. Conceptual diagram for applying a steady-state model for ^{22}Na transport in a small watershed, with measured fluxes given for Pogonia Watershed in Williamsburg, VA. ^{22}Na inputs via atmospheric deposition are in balance with groundwater discharge and radioactive decay. In this case, discharge fluxes to Pogonia Stream indicate 10 ± 3 yrs of decay, which is consistent with SF6 derived recharge age of 12 ± 1 yrs for this system.

Because biological uptake of Na is typically very low, and soils in all but the driest climates have relatively small pools of exchangeable sodium or secondary sodium-bearing minerals, watershed budget calculations made across a wide range of environments indicate no net sodium storage (Fig. 2). Our measurements of Na inputs via atmospheric deposition to the Pogonia Watershed in Virginia were significantly lower than streamwater exports, and our calculations made for Jones Run and those made at Hubbard Brook also indicate larger annual Na outflows compared with inflows (Fig. 2). Given that Na atoms are not being taken up by the biosphere or soils in significant quantities, then ^{22}Na can be expected to pass through many watersheds and radioactive decay will be the primary loss term for this radionuclide in catchments. While catchments are rarely in steady-state with respect to total atmospheric Na because of geogenic sources (e.g., mineral weathering), in many cases, they may be in steady-state with respect to atmospheric ^{22}Na.

Despite seasonal variation in atmospheric ^{22}Na deposition (Fig. 5), the annual inputs of ^{22}Na into the watershed were relatively constant year-to-year from 2012–2014. Between 2012–2016, annual ^{22}Na exports from the Pogonia stream were also relatively constant but an order of magnitude lower than inputs (Fig. 7). We hypothesize that the loss of dissolved ^{22}Na as it moves through the watershed can be explained solely by radioactive decay such that the atmospheric input of ^{22}Na to a watershed is equal to radioactively decayed ^{22}Na plus discharged ^{22}Na. Given this, the annual ^{22}Na discharge flux $[^{22}\mathrm{Na}]_{\mathrm{output}}$ from watersheds and the annual ^{22}Na input flux $[^{22}\mathrm{Na}]_{\mathrm{input}}$ to watersheds can be related using a flux-based radioactive decay model:

$$[^{22}\mathrm{Na}]_{\mathrm{output}} = [^{22}\mathrm{Na}]_{\mathrm{input}} e^{-\lambda t} \tag{1}$$

where λ is the ^{22}Na decay constant (0.266 yr^{-1}), and t is the time elapsed since recharge. This model indicates that the average water age in the Pogonia watershed during base flow conditions is 10.0 ± 3 yrs (Fig. 8). Modeled fluxes and measured discharges of ^{22}Na in the Jones Run and Hubbard Brook watersheds indicated younger mean ages of 6.2 and 0.92 yrs, respectively, which is consistent with the relatively higher ^{22}Na discharge fluxes of these streams compared to the Pogonia stream (Fig. 7).

We evaluate the results of our ^{22}Na age dating method in the three study sites with independent age dating methods. The SF_6 measurements in Pogonia yielded a recharge age of 12.2 ± 1 yrs, which is statistically indistinguishable from our ^{22}Na derived age. This timespan is also consistent with the average flow path length of 360 m in Pogonia and a hydraulic conductivity of ~0.1 m d^{-1} that would be expected for the sandy clay loam texture that is typical of the watershed (Rawls et al., 1982). In Shenandoah National Park, several detailed studies showed that the thin, unconfined colluvium aquifers that overlie metabasalts and metasedimentary rocks along the ridge consistently show ages of 2–5 yrs (Busenberg and Plummer, 2000; Plummer et al., 2001). During relatively low flow conditions, we found Jones Run to have a ^{22}Na age of 6.2 ± 1.1 yrs, which is consistent with these other studies. The age of water in the Hubbard Brook watershed was independently determined with an integrated transport model that was calibrated with high-resolution time series of water hydrogen isotope data for rainfall and streamwater (Benettin et al., 2015). This indicates that streamwater near our collection point in Watershed 3 had an average age of approximately 150–250 d (0.4–0.7 yrs) during dry periods (Benettin et al., 2015). Our ^{22}Na-derived recharge age for Hubbard Brook Watershed 3 base flow ranged from 0.1 to 2.1 yrs (95% confidence interval), with a mean of 0.92 yrs.

4.3. Potential of ^{22}Na as a chronological tool in watersheds

The power of ^{22}Na as a freshwater chronological tool is greatest in low-order catchments that meet certain criteria with respect to water age, water chemistry, and soil type. Its 2.6 yr half-life makes it a valuable tracer in watersheds where characteristic solute flushing times operate on 1–20 yr timescales, because ^{22}Na becomes increasingly difficult to detect after approximately 6 half-lives have elapsed since recharge. Our work and others have focused on the use of H+ form cation exchange resin to concentrate Na from large volumes of water (Komura et al., 2006; Sakaguchi et al., 2003). Commercially-available cation exchange resin is not selective to Na, and Ca is typically the most common cation in natural waters. Therefore, concentrating ^{22}Na from large volumes of ground, stream, or lake water becomes more difficult as the total dissolved load increases because calcium dilutes the number of sites available for Na adsorption.

We found that we could efficiently concentrate Na from 100–200 L of streamwater having <10 mg L^{-1} total dissolved load with small bags of resin placed in the field. However, in waters draining carbonate rocks where total dissolved loads could be >200 mg L^{-1} and solutions are dominated by Ca^{2+} and Mg^{2+}, many kg of cation resin would be needed for a single sample making the subsequent processing of Na for efficient gamma analysis difficult. More research is needed to evaluate the potential of ^{22}Na as a tracer in waters that drain landscapes where clay mineral cation exchange sites have relatively high Na proportions, as isotopic dilution during cation exchange would complicate our steady-state approach. Our work indicates that ^{22}Na will conservatively trace water in catchments with relatively thin acidic soils (Hubbard Brook and Shenandoah National Park) or in thicker quartz-rich soils that are highly weathered typical of the Atlantic Coastal Plain.

While it hasn't been quantified routinely, cosmogenic ^{22}Na fallout in precipitation should be measurable nearly everywhere on earth. In the absence of systematic changes in precipitation, our data combined with other records indicates that atmospheric fluxes should be relatively ($\pm 15\%$) constant from year to year. Using the linear regression developed in this study to model ^{22}Na deposition based on local precipitation, we show that average base flow recharge age can be determined solely from measuring the ^{22}Na discharge flux. While more measurements of ^{22}Na flux are needed for different parts of the world, a first-order estimate of mean recharge age may be calculated by measuring drainage water discharges for ^{22}Na, annual precipitation data, and the relationships between precipitation and annual atmospheric ^{22}Na flux developed here. Our efforts at developing the use of ^{22}Na as a tracer of recharge age in watersheds focused on base flow conditions to keep the number of flowpath geometries as simple as possible (Fig. 8), and so that total Na ($\mathrm{mg\,L^{-1}}$) was constant. We acknowledge that even during base flow conditions, groundwater that discharges into streams has a spectrum of recharge ages, and that the ages we determined here are best described as a weighted mean of the various flowpaths. If we had sampled during storm events, we would have expected to measure higher daily ^{22}Na export from the watersheds compared with the daily average base flow flux. Thus, ^{22}Na may be further developed as a novel tool for hydrograph separation, as ^{22}Na concentrations in base flow should be distinguishable from relatively higher ^{22}Na concentrations in storm runoff or shorter-flowpath subsurface flow.

5. Conclusions

Cosmogenic ^{22}Na is delivered to southeastern Virginia, USA at a relatively constant rate with precipitation. Our measurements of ^{22}Na deposition to the East Coast of the United States compared with deposition rates made on two other continents indicate that global atmospheric ^{22}Na fluxes scale with precipitation. ^{22}Na outputs from a watershed can be explained by atmospheric fluxes and radioactive decay, indicating that this naturally occurring isotope of sodium can serve as a "clock" for solute flushing times and water age over timescales of 1–20 yrs. Given that ^{22}Na is naturally occurring, has a relatively stable input function, and readily remains dissolved in many waters, it can serve as a very useful hydrologic tracer that can resolve age over the relatively valuable timescale of 1–20 yrs.

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