

Using Naturally Occurring Radionuclides To Determine Drinking Water Age in a Community Water System

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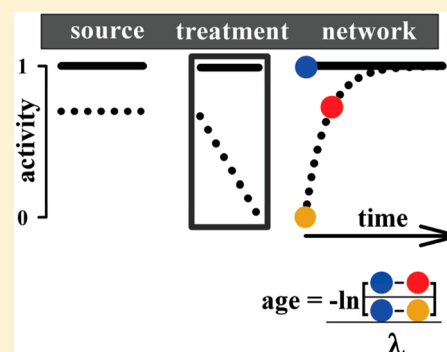
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Supporting Information

ABSTRACT: Drinking water quality in a community water system is closely linked to the age of water from initial treatment to time of delivery. However, water age is difficult to measure with conventional chemical tracers; particularly in stagnant water, where the relationship between disinfectant decay, microbial growth, and water age is poorly understood. Using radionuclides that were naturally present in source water, we found that measured activity ratios of $^{90}\text{Y}/^{90}\text{Sr}$ and $^{234}\text{Th}/^{238}\text{U}$ in discrete drinking water samples of known age accurately estimated water age up to 9 days old ($\sigma_{\text{est}}: \pm 3.8 \text{ h}$, $P < 0.0001$, $r^2 = 0.998$, $n = 11$) and 25 days old ($\sigma_{\text{est}}: \pm 13.3 \text{ h}$, $P < 0.0001$, $r^2 = 0.996$, $n = 12$), respectively. Moreover, ^{90}Y -derived water ages in a community water system ($6.8 \times 10^4 \text{ m}^3 \text{ d}^{-1}$ capacity) were generally consistent with water ages derived from an extended period simulation model. Radionuclides differ from conventional chemical tracers in that they are ubiquitous in distribution mains and connected premise plumbing. The ability to measure both water age and an analyte (e.g., chemical or microbe) in any water sample at any time allows for new insight into factors that control drinking water quality.



INTRODUCTION

Roughly 300 million people in the United States receive drinking water from community water systems.¹ This water is distributed through ~ 2 million km of water main and another ~ 10 million km of premise plumbing.² Water quality within the distribution system can be compromised by the breakdown of any added disinfectant that results in elevated concentrations of toxic disinfection byproducts (e.g., trihalomethanes and haloacetic acids) or microbial pathogen growth.^{3,4} A key factor in degrading water quality is water age.⁵

Water age or retention time in a community distribution system can be measured with a conventional chemical tracer, where the travel time of a chemical pulse or step signal is measured between upstream and downstream nodes.⁶ To create the signal, a water utility must purposely alter the chemistry of the system either through the addition or removal of a substance (e.g., a salt or fluoride), or by switching disinfectants (chlorine or chloramine) or water sources.

Naturally occurring radionuclides in the environment have been used to measure transport rates and residence times in aquatic systems (e.g., refs 7–9), but they have not been exploited as tracers in community water systems. Radionuclide tracers have an advantage over conventional chemical tracers in that they are ubiquitous (i.e., a natural component of the source water matrix and present throughout the distribution system at all times).

Water ages can be determined using supported and unsupported radionuclide tracers (Figure 1). Both tracer types are defined by chemical properties of the daughter/parent nuclide pair. Supported tracers, as shown in Figure 1a, are dependent on a conservative parent and the removal of a particle-reactive daughter in either the source water (via particle scavenging and settling) or the water treatment plant by means of flocculation, settling and rapid sand filtration. For unsupported tracers, as shown in Figure 1b, it is the daughter nuclide that is chemically conservative. Chronometry with both tracer types relies on an initial disequilibrium between the parent and daughter and either growth (supported) or decay (unsupported) of the daughter toward equilibrium with the parent nuclide in the distribution system.

In a community water system, the change in activity of a daughter nuclide, D , with time can be expressed as

$$\frac{dD}{dt} = G + C - S + R \quad (1)$$

where G represents the net growth or decay of daughter nuclide activity due to radioactive decay, C is the convective sum of advective and diffusive fluxes, S is the scavenging of the

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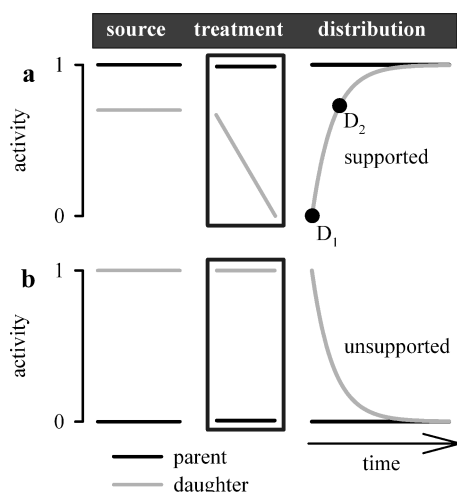


Figure 1. Use of naturally occurring radionuclides for measuring water age in drinking water depends on an initial disequilibrium between a parent and daughter nuclide pair in the community water system and an observed decrease in disequilibrium between two points in space or time. (a) For supported radionuclide tracers, daughter nuclide activity increases over time (e.g., D_1 and D_2). (b) For unsupported radionuclide tracers, daughter nuclide activity decreases over time.

daughter nuclide to either the pipe wall or through loss by particle settling, and R is the resuspension of daughter nuclide either through mobilization of sedimented deposits and pipe scale or the dissolution or desorption of nuclides from sediment deposits or pipe scale back to the water stream.

If, under ideal conditions, the terms on the right-hand side of eq 1 are dominated by G , then the activity of the daughter nuclide over time can be expressed as

$$D_2 = \frac{\lambda_D P}{\lambda_D - \lambda_P} (e^{-\lambda_P t} - e^{-\lambda_D t}) + D_1 (e^{-\lambda_D t}) \quad (2)$$

where P and D are the parent and daughter nuclide activities, λ is the decay constant of the daughter (D) or parent (P) nuclide ($\lambda = \ln(2)/\text{half-life}$), subscripts 1 and 2 relate to initial and subsequent sampling periods, and t is the time interval between sampling.

When the half-life of the daughter is much less than the half-life of the parent nuclide (e.g., $\ll 1\%$), eq 2 can be simplified and rearranged to solve for t , such that the relative water age between any two water masses in a distribution system can be calculated as

$$\text{water age} = \frac{-\ln\left(\frac{P - D_2}{P - D_1}\right)}{\lambda_D} \quad (3)$$

where P and D are the parent and daughter nuclide activities in the water at time of sample collection, and subscripts 1 and 2 relate to upstream (initial) and downstream sampling locations, respectively.

For supported tracers with particle-reactive daughters and conservative parents, any increase in D_2 in eq 3 results in an increase in water age. If the term G in eq 1 indeed dominates, then any increase in D_2 can correctly be attributed to time. However, convective (C), scavenging (S), and resuspension (R) fluxes may also contribute to the activity of the daughter nuclide and must ultimately be considered.

The use of radionuclides as tracers of water age depends on measurable activity in source and treated waters.^{10–12} Moreover, the ingrowth or decay of the tracer nuclide must be on a time scale that is proportional to water movement and age in the community water system. Using these criteria, we chose to examine naturally occurring daughter/parent activities of yttrium-90/strontium-90 ($^{90}\text{Y}/^{90}\text{Sr}$) and thorium-234/uranium-238 ($^{234}\text{Th}/^{238}\text{U}$). ^{90}Sr , a fallout nuclide from atmospheric nuclear weapons testing,¹³ is generally conservative in natural waters (K_d [mL g^{-1}]: $\sim 1 \times 10^2$),^{14,15} relatively long-lived (half-life: 28.8 years), and decays to ^{90}Y , which is short-lived (half-life: 64 h) and particle-reactive (K_d : $\sim 1 \times 10^5$).¹⁶ ^{238}U , a primordial radionuclide (half-life: 4.47×10^9 years), is chemically conservative (K_d : $\sim 1 \times 10^3$),¹⁷ measurable in all natural surface and ground waters, and decays to ^{234}Th , which has a half-life of 24.1 days and is highly particle-reactive (K_d : $\sim 1 \times 10^6$).¹⁶

Our goal in this study was to determine (i) if low activities of naturally occurring radionuclides in drinking water provide accurate water age estimates and (ii) if radiotracer derived water ages in a community water system are consistent with age estimates derived from a calibrated hydraulic model. To accomplish this, we (i) measured naturally occurring daughter/parent activities of $^{90}\text{Y}/^{90}\text{Sr}$ and $^{234}\text{Th}/^{238}\text{U}$ in Lake Michigan-sourced drinking water from the North Shore Water Commission (NSWC) treatment plant in Glendale, Wisconsin and (ii) compared tracer derived water ages from $^{90}\text{Y}/^{90}\text{Sr}$ measurements in the NSWC community water system, shown in Figure 2, with water ages derived from an extended period simulation model of the same network.

MATERIALS AND METHODS

Study Site. The NSWC community water system supplies drinking water to $\sim 35\,000$ customers over 259 km of pipe ($\sim 90\%$ unlined ductile iron, $\sim 10\%$ PVC). Particulate matter in Lake Michigan source water is removed in the treatment plant by flocculation (using polymers and aluminum sulfate) and sedimentation followed by rapid sand filtration. Additional details concerning the facility and its treatment procedures can be found in the NSWC water quality report.¹⁸

Water Sampling. Discrete water samples (~ 50 L each, $n = 11$) were collected in plastic barrels over a 45 min period on March 10, 2014 at the NSWC treatment plant (postfiltration; Figure 2, site a) and sequentially analyzed for ^{90}Y ($n = 10$) and ^{234}Th ($n = 11$) over a 25 day period. Sample times, sample volumes, and time of analysis can be derived from Table S1 in the Supporting Information.

Water samples (~ 55 L each, $n = 12$) were collected throughout the NSWC community water system over a 13 day period beginning on July 7, 2006 at 12 sites (a–l) shown in Figure 2. Samples were stored in plastic barrels until sample analysis (usually within 3 h). Water from the treatment plant (site a) was drawn from the clear well (postfiltration). Water from the distribution system (sites b–l) was drawn from both private premise plumbing (P) and fire hydrants (H). All water sources were flushed for ~ 10 min before sample collection. Collection times, sample volumes, and water source types (P or H) are listed in Table S2 in the Supporting Information.

Radionuclide Measurements. Our methods for measuring ^{90}Y and ^{234}Th are described in detail in our previous works.^{16,19} Briefly, ^{90}Y and ^{234}Th were coprecipitated onto newly formed iron hydroxide and removed from the water

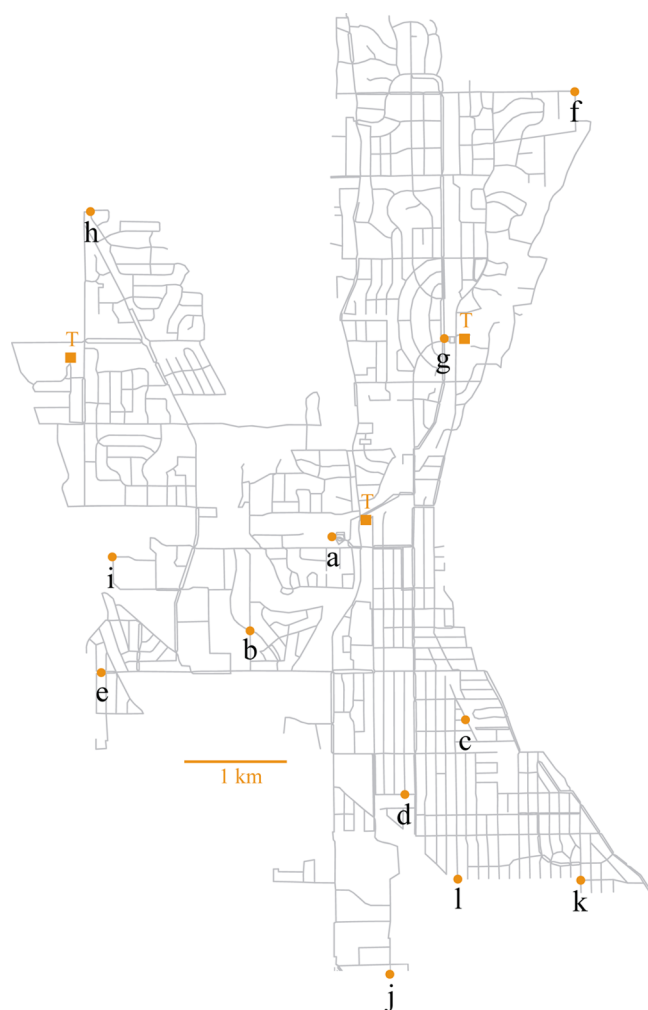


Figure 2. North Shore Water Commission (NSWC) community water system. Water samples were collected from sites a–l for analysis of $^{90}\text{Y}/^{90}\text{Sr}$ activity ratios. Site a is the NSWC treatment plant (postfiltration). Water storage tanks are identified with the letter “T”.

sample by filtration. The nuclides were separated and isolated on an ion-exchange column, transferred to counting plates by electrodeposition (^{234}Th) or iron hydroxide precipitation (^{90}Y), and β counted on a low background gas-flow proportional detector with anticoincidence circuitry. Yield monitors of ^{229}Th and ^{88}Y (Eckert & Ziegler Isotope Products), which were added to the samples at the beginning of the measurement procedure, were counted by α and γ spectrometry, respectively, to determine sample recovery. ^{90}Sr activities in the NSWC community water system, listed in Table S2 in the [Supporting Information](#), were determined by ^{90}Y analysis of water samples that were stored for >14 days until secular equilibrium between ^{90}Y and ^{90}Sr was achieved. Lake Michigan ^{90}Sr activities on specific distribution system sampling dates were calculated using a ~ 40 year data set of measured ^{90}Sr activities.¹⁶

Water Age Calculations. Radiotracer derived water ages in each discrete sample were calculated with eq 3, where D_2 was the measured activity of either ^{90}Y or ^{234}Th in each discrete sample, and D_1 was the initial (time zero) activity of either daughter. Radionuclide activities in samples collected in 2006 (listed in Table S2 in the [Supporting Information](#)) were corrected back to time of sampling.

Error Analysis. Counting errors (± 1 SD) for all radionuclide measurements were propagated through water age estimates and are listed in Tables S1 and S2 in the [Supporting Information](#). Our calculation of counting error is described in our previous works.^{16,19} Replicate sample analyses have shown true error to be approximately twice that calculated by simple counting statistics because of sampling errors and other processing uncertainties that are not accounted for. We therefore emphasize the standard error of estimate (σ_{est}) of the linear regression between measured water ages and radionuclide-derived water ages as a better estimate of the true error.

Hydraulic Modeling. The hydraulic model was developed and calibrated by Stantec to complete master planning, system evaluation, and Initial Distribution System Evaluation (IDSE) modeling for the NSWC community water system.²⁰ The hydraulic model was run with WaterCAD V8i (Bentley) and includes the treatment plant high service pumps, the municipal distribution systems shown in Figure 2, and all water storage and pumping facilities. Water demands were assigned by customer classification data from annual reporting and composite demands were distributed to the hydraulic model based on existing land use mapping. Large water users were identified and metered data were added individually to the hydraulic model. Minute-by-minute supervisory control and data acquisition (SCADA) data from three typical days in September 2009, including pump flows and tank levels, were used to determine water demand and an averaged diurnal curve. The hydraulic model utilizes logical controls to replicate high service pumps and tower operation, including variable-frequency drive (VFD) pumping and controlled tower filling, allowing for consistent extended period simulation (EPS) modeling. Field flow tests from all three distribution systems and SCADA data were used to complete steady state and EPS calibration in 2009. EPS calibration was completed in accordance with U.S. EPA guidance. Water demand data from the July 2006 sampling period (average: $2.49 \times 10^4 \text{ m}^3 \text{ d}^{-1}$) was globally scaled with the calculated diurnal curve to create an EPS run that replicated July 2006 conditions. The model was run for a 30 day simulation, with repeatable daily water age appearing after ~ 10 days. Model results for this study show the last 24 h period of the model run.

RESULTS AND DISCUSSION

Radionuclide Tracer Accuracy. To determine the accuracy of our radionuclide-derived water ages, we collected 11 replicate drinking water samples over a 45 min period from the NSWC treatment plant (post filtration) and sequentially measured each sample for ^{90}Y and ^{234}Th over a period of 25 days. Measured activities of both daughters and derived activities of their respective parents were used to calculate water sample ages at the time of sample processing (when daughter and parent nuclides were separated). The calculated water sample ages were then compared to known water sample ages based on elapsed time between sample collection and sample processing.

Activities of ^{90}Y and ^{234}Th increased with time between sample collection and measurement, as shown in Figure 3a, indicating significant disequilibrium between both daughters and their respective parents in water exiting the treatment plant filtration system. Initial daughter nuclide activities in a 2.4 h old sample were $0.90 \pm 0.05 \text{ mBq } ^{90}\text{Y L}^{-1}$ ($50.2 \pm 2.9 \text{ mBq } ^{90}\text{Y sample}^{-1}$) and $0.23 \pm 0.01 \text{ mBq } ^{234}\text{Th L}^{-1}$ ($13.0 \pm 0.3 \text{ mBq }$

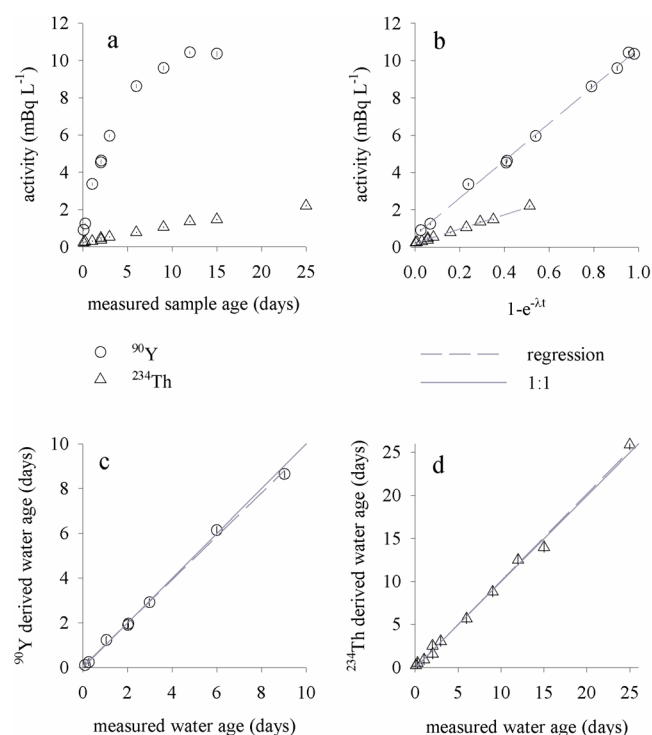


Figure 3. Discrete samples of newly filtered water were collected over a 45 min period from the NSW treatment plant and measured for ^{90}Y and ^{234}Th activity over a 25 day period. (a) Measured sample activity of ^{90}Y (± 1 SD, $n = 10$) and ^{234}Th (± 1 SD, $n = 11$) increased exponentially with measured sample age. (b) Measured sample activity of ^{90}Y and ^{234}Th increased linearly with sample age expressed as $1 - e^{-\lambda t}$ where λ is the decay constant for ^{90}Y or ^{234}Th and t is the measured sample age. ^{90}Y regression: $y = (10.0 \pm 0.2)x + (0.6 \pm 0.1)$, $P < 0.0001$, $r^2 = 0.998$. ^{234}Th regression: $y = (3.82 \pm 0.08)x + (0.20 \pm 0.02)$, $P < 0.0001$, $r^2 = 0.996$. (c) Measured water sample age versus ^{90}Y -derived water sample age ($\sigma_{\text{est}} = \pm 3.8$ h). (d) Measured water sample age versus ^{234}Th -derived water sample age ($\sigma_{\text{est}} = \pm 13.3$ h).

^{234}Th sample $^{-1}$). The activity of ^{90}Y (half-life = 2.67 days) grew faster than the activity of ^{234}Th (half-life = 24.1 days) because the rate of growth of the daughter nuclide is inversely proportional to its half-life.

Parent activities of ^{90}Sr (10.6 ± 0.2 mBq L^{-1}) and ^{238}U (4.02 ± 0.08 mBq L^{-1}) were calculated as the sum of the slope and zero intercept of the linear regression of measured water sample age versus daughter nuclide activity, as shown in Figure 3b, where measured age (t) was expressed as the daughter/parent equilibrium fraction ($1 - e^{-\lambda t}$) and $\lambda = 0.25993$ d^{-1} for ^{90}Y and 0.02876 d^{-1} for ^{234}Th . Both parent activities were consistent with ^{90}Sr (10.7 ± 2.0 mBq L^{-1} on March 10, 2014) and ^{238}U (3.8 ± 0.3 mBq L^{-1}) activities in Lake Michigan source water.¹⁶

Zero intercepts for both nuclide regressions, as shown in Figure 3b, indicated initial (time zero) water sample activities of 0.6 ± 0.1 mBq ^{90}Y L^{-1} and 0.20 ± 0.02 mBq ^{234}Th L^{-1} , giving initial daughter/parent activity ratios of 0.06 ± 0.01 and 0.05 ± 0.01 , respectively. $^{90}\text{Y}/^{90}\text{Sr}$ and $^{234}\text{Th}/^{238}\text{U}$ activity ratios in nearshore Lake Michigan are typically above ~ 0.5 .¹⁶ Lower activity ratios in NSW treatment plant outflow water indicated removal of the particle-reactive daughter in the filter treatment process.

The ^{90}Y -derived water age, as shown in Figure 3c, increased linearly with measured water age over the first 9 days with a standard error of estimate (σ_{est}) of ± 3.8 h over the 9-day

interval (equation: ^{90}Y derived water age (days) = $(0.97 \pm 0.02) \times$ measured water age (days) + (0.04 ± 0.08) , $P < 0.0001$, $r^2 = 0.998$, $n = 11$). In water samples older than 9 days, $^{90}\text{Y}/^{90}\text{Sr}$ activity ratios exceeded ~ 0.9 , with small errors in ^{90}Y measurements leading to large errors in calculated age, as listed in Table S1 in the Supporting Information.

The ^{234}Th -derived water age, as shown in Figure 3d, increased linearly with measured water age over the entire 25 day period with a standard error of estimate (σ_{est}) of ± 13.3 h over the 25 day interval (equation: ^{234}Th derived water age (days) = $(1.01 \pm 0.02) \times$ measured water age (days) - (0.1 ± 0.2) , $P < 0.0001$, $r^2 = 0.996$, $n = 12$). Because ^{234}Th has a half-life that is 9 times longer than the half-life of ^{90}Y , it reaches equilibrium with its parent more slowly. The advantage of using a longer-lived nuclide is the ability to measure older water. However, small errors in long-lived nuclide measurement result in relatively larger errors in calculated age.

Model versus Tracer Derived Water Ages in a Distribution System. To determine water ages in the NSW community water system, we collected discrete drinking water samples from 12 sites (a–l) shown in Figure 2. Measured activities of ^{90}Y and ^{90}Sr were then used to calculate water sample ages at the time of sample collection at each site using eq 3, which assumes that the change in daughter nuclide activity is a function of time only.

^{90}Sr activity (12.9 ± 0.3 mBq L^{-1} , $n = 5$, Table S2 in the Supporting Information) was measured in water collected at sites a, c, i, j, and k. We observed no significant difference in activity between point of entry and dead-end junctions at the distribution system periphery. Calculated ^{90}Sr activity in Lake Michigan source water was 13.0 ± 2.5 mBq L^{-1} on July, 20, 2006. ^{90}Y was measured in water samples collected from all 12 sites (a–l) with activities ranging from 0.8 ± 0.1 mBq L^{-1} at site a to 6.3 ± 0.2 mBq L^{-1} at site j (Table S2 in the Supporting Information).

^{90}Y -derived water ages in the NSW community water system ranged from the operationally defined age of ~ 0 h in the treatment plant clear well to ~ 56 h along the distribution system periphery, and were generally consistent with water ages derived from the extended period simulation model, as shown in Figures 4 and 5 and listed in Table S2 in the Supporting Information. At sites a–f, in particular (Figure 5a), tracer derived water ages agreed with modeled ages with a standard error of estimate of ± 2.5 h (equation: ^{90}Y derived water age (hours) = $(1.02 \pm 0.08) \times$ modeled water age (hours) - (0.43 ± 1.43) , $P = 0.0002$, $r^2 = 0.978$, $n = 6$).

Tracer and model derived water ages disagreed at sites g–l, as shown in Figures 4 and 5b, where tracer derived water ages were as much as 32 h older (site i) and 41 h younger (site g) than their modeled counterparts. Reasons for these discrepancies can be attributed to faults with either the tracer or model. We examine both possibilities below.

Tracer derived water ages would be in error if any factor other than time influenced the daughter/parent nuclide ratio. As shown in eq 1, the three most likely factors to influence the daughter/parent nuclide ratio (excluding radioactive decay over time) are convection (C), scavenging (S), and resuspension (R).

For supported tracers, convective fluxes (C) will tend to increase the activity of D_2 (e.g., ^{90}Y) and water age as slower moving (and older) water along the pipe boundary layer is mixed into the main channel flow and any diffusive flux of higher downstream daughter nuclide activity moves upstream.

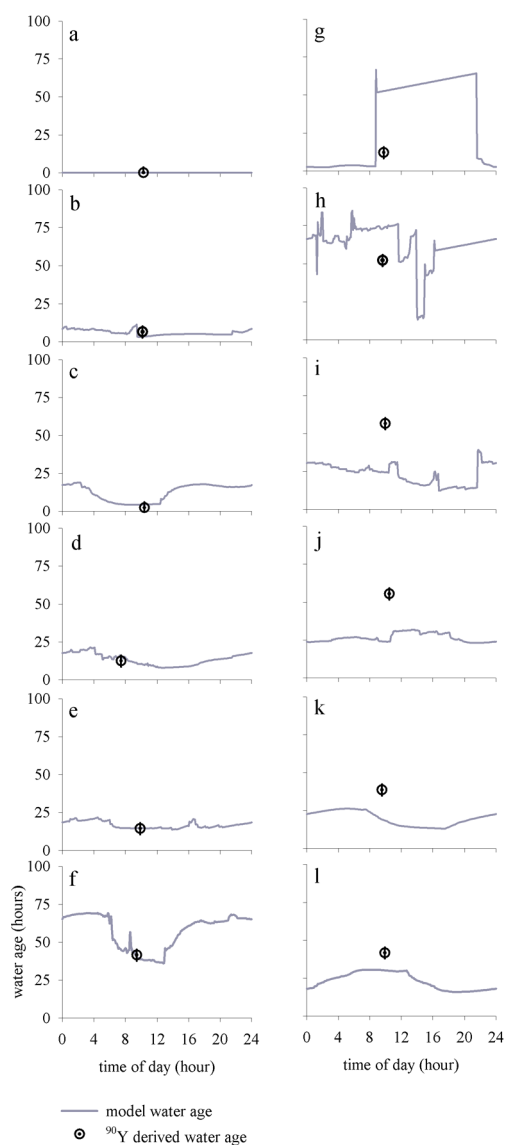


Figure 4. Comparison of ^{90}Y -derived (open circle) and modeled (line) drinking water ages at NSW community water system sites a–l. ^{90}Y -derived and modeled water ages were normalized to an age of 0 at site a. Error bars (σ_{est}) = ± 3.8 h.

However, inasmuch as any resultant increase in apparent water age reflects an actual incorporation of older water, we regard these convective influences on water age as a legitimate indicator of age.

The scavenging (S) of either daughter or parent nuclides, by sorption to pipe wall or loss through particle settling, will ultimately result in a decrease in daughter nuclide activity (D_2) and, for supported tracers, a decrease in water age, as indicated in Figure 5b. The accumulation of radionuclide activity on pipe walls and in sediment deposits has been documented in several studies (e.g., refs 21–24), and chemical analysis of iron water-pipe scale has revealed measurable concentrations of elements strontium and yttrium.^{15,25} However, the presence of an inventory of any particular element or nuclide does not necessarily translate to a measurable influence of S on reducing calculated water age. As a first approximation, an estimate of nuclide scavenging from the water stream to the pipe wall or deposit can be calculated as the product of the areal inventory of unsupported nuclide activity on the wall/deposit and its

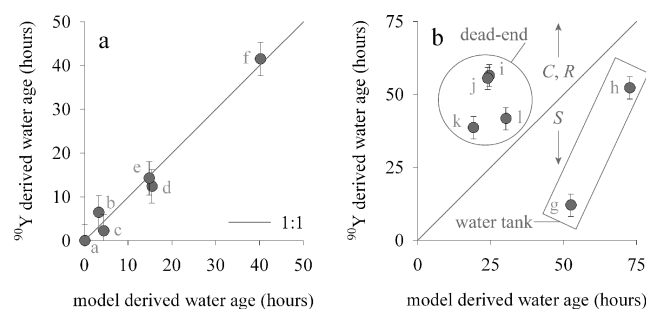


Figure 5. ^{90}Y -derived and modeled drinking water ages at NSW community water system sites a–l. Error bars (σ_{est}) = ± 3.8 h. (a) Sites a–f. (b) Sites g–l. Circled sites labeled “dead-end” refer to sites located near dead-end junctions. Rectangle enclosed sites labeled “water tank” refer to sites located near water storage tanks. “C” and “R” refer to convective and resuspension fluxes that increase the activity of the daughter nuclide and the apparent water age. “S” refers to a scavenging flux that will decrease the activity of the daughter nuclide and apparent water age.

decay constant (i.e., $\text{Bq m}^{-2} \times \lambda [\text{d}^{-1}]$). If the resultant scavenging flux is \ll than the production or decay or the daughter nuclide activity (i.e., $\lambda(P - D)$), then the effect of scavenging on water age is negligible. We were not able to analyze pipe scale in this study; however, inspection of our measured nuclide activities and calculated water ages shows no obvious impact of nuclide scavenging. Parent activities of ^{90}Sr were consistent throughout the distribution system, as listed in Table S2 in the Supporting Information, and tracer-derived water ages were significantly lower than modeled ages at only two sites, as shown in Figure 5b. Modeled water ages at sites g and h were the oldest of the 12 sites visited, which would conform with the idea that increased exposure time in the distribution system leads to increased scavenging. However, there was no correlation between modeled water age and the deviation of the tracer-derived age from the modeled age, which we would expect if exposure time was a factor that influenced scavenging.

Alternatively, the deviation of tracer-derived water ages from modeled ages at sites g and h might be explained by their proximity to water storage tanks. The modeled age estimates showed significant variation over a 24 h period (as shown in Figure 4) due to the close proximity of water storage tanks, labeled “T” in Figure 2. Drinking water age in the proximity of a water tank is low during tank filling and high during tank draining. If young and old water was mixed in the tank, then the ^{90}Y -derived age of water leaving the tank would be lower than the arithmetic mean of the two original water mass ages.^{26,27} On the other hand, if water was not completely mixed in the storage tank, then channelized flow out of the tank may also have been younger than the mean mixed age. Measuring $^{90}\text{Y}/^{90}\text{Sr}$ activity ratios in discrete samples from the water storage tank would reveal if water within the tank was completely mixed. If two radionuclide tracers with different half-lives were used in tandem, the blending ratio of new and old water could in some cases be calculated.^{27,28} Although both mixing scenarios are possible, it is important to remember that these hydraulic model results are based on a generalized diurnal demand curve. Therefore, system operation time is not necessarily identical to actual field sampling time. If the system operation time was advanced by ~ 1 h at site g, then tracer and model derived water ages would have been in agreement.

In general, hydraulic disturbances or changes in water chemistry (caused by, e.g., switching water sources, temperature change, or modified treatment processes) can lead to the mobilization, dissolution or desorption of nuclides in sediment deposits or pipe scale to the mobile phase.^{21,29} In certain instances, where the accumulation of a parent nuclide in pipe deposits results in substantial activity of the supported daughter nuclide, the desorption of the daughter nuclide to the water stream must also be considered.^{23,24} For supported tracers, resuspension (*R*) of daughter nuclides will increase the activity of D_2 and water age, as indicated in Figure 5b.

In our study of the NSW community water system, ^{90}Y -derived water ages were significantly older than modeled ages at four sites (i–l), as shown in Figure 5b. Water samples from sites i–l were collected from a fire hydrant, as listed in Table S2 in the Supporting Information, and hydraulic disturbances may have mobilized nuclides from pipe walls or sediment deposits. However, water samples from sites f and h were also collected from fire hydrants, with tracer-derived water ages either in agreement (site f) or less than (site h) modeled ages. Moreover, simultaneously measured ^{90}Sr activities at sites i, j, and k showed no significant increase in activity, as listed in Table S2 in the Supporting Information. We therefore do not believe that elevated water ages at sites i–l were due to the mobilization of supported ^{90}Y in pipe deposits.

We similarly found no evidence for a systematic change in water chemistry in the NSW system. Although elevated water ages were measured at sites k and l on July 18, and at sites i and j on July 20, other tracer-derived water ages were either in agreement (site c) or less than (site h) modeled ages on the same sampling dates (Table S2 in the Supporting Information).

Finally, the release of significant ^{90}Y activity from ^{90}Sr that has accumulated in pipe scale is not plausible.³⁰ Gerke et al.¹⁵ measured stable strontium in drinking water and in pipe scale from four water utilities. From their measurements, we calculate an average $\text{Sr } K_d$ of 180 ± 120 , which is close to the value of $\sim 1 \times 10^2$ that we present above. Taking the product of the $\text{Sr } K_d$ and the average measured ^{90}Sr activity in drinking water from the NSW system ($12.9 \pm 0.3 \text{ mBq L}^{-1}$), we estimate a ^{90}Sr activity of $2400 \pm 1500 \text{ mBq kg}^{-1}$ in NSW pipe scale deposits. If supported ^{90}Y activity in the pipe scale is in secular equilibrium with its parent, then a rough estimate of dissolved ^{90}Y activity in equilibrium with the pipe scale is given by the ratio of the sorbed ^{90}Y over the $^{90}\text{Y } K_d$ that we have measured in Lake Michigan source water ($2400 \pm 1500 \text{ mBq kg}^{-1} / 1 \times 10^5 \text{ L kg}^{-1}$) = $0.02 \pm 0.01 \text{ mBq } ^{90}\text{Y L}^{-1}$. This equilibrium activity is 2 orders of magnitude lower than the average measured ^{90}Y activity in drinking water at sites i–l.

Another and perhaps more plausible explanation for elevated water ages at sites i–l is related to the sites' location on the periphery of the distribution system, close to dead-end junctions, as shown in Figure 2. Modeled water age on dead-end water mains was directly attributed to the assigned water demand in the hydraulic model and model demand was assigned by customer class. Customer class at sites i, j, and l is industrial/commercial area with a higher assumed demand. If demand at these sites was actually less than what was assumed, then modeled water ages would underestimate the true age. The discrepancy between ^{90}Y -derived and modeled water ages at these sites highlights the potential merit of calibrating hydraulic models with direct tracer measurements.^{31–33}

Radiotracer Availability. The use of naturally occurring radionuclides as tracers of drinking water age depends on their

activity in source waters. For supported tracers, as shown in Figure 1a, we have focused on the $^{90}\text{Y}/^{90}\text{Sr}$ and $^{234}\text{Th}/^{238}\text{U}$ daughter/parent pairs because the ingrowth of both daughters is on a time scale that is proportional to water movement and age in the NSW community water system. Use of these particular tracers in other community water systems will depend on measurable activities of ^{90}Sr and ^{238}U .

By 1980, $6.04 \times 10^{17} \text{ Bq}$ of ^{90}Sr were deposited over the entire planet.^{13,34} Because ^{90}Sr is soluble, nominal activities are measurable in many surface and young (<50 year) ground waters. In freshwater systems in the Northern Hemisphere, relatively high activities of ^{90}Sr (~ 5 to 15 mBq L^{-1}) appear common enough that the use of the $^{90}\text{Y}/^{90}\text{Sr}$ tracer pair for measuring water age and retention time in drinking water distribution systems appears feasible.^{14,35–37}

Activities of ^{238}U can vary by over 3 orders of magnitude in surface waters.^{10,19} However, the activity or concentration of total uranium ($^{238}\text{U} + ^{235}\text{U} + ^{234}\text{U}$) is often reported by public water suppliers in their annual water quality reports (e.g., ref 18). Older surveys of uranium abundance in source and finished drinking water are also available for larger cities in the U.S.^{10,38,39} Specific activities of ^{238}U can be approximated knowing the natural abundance of ^{238}U (99.275% of total uranium by weight) or the contribution of ^{238}U activity to total uranium activity ($\sim 45\%$ but variable; refs 10, 40, 41).

The use of unsupported tracers, as shown in Figure 1b, has not been tested. However, for community water systems using groundwater with measurable radium, we speculate that daughter/parent activities of radium-224/thorium-228 (^{224}Ra half-life: 3.63 days) may also be used for chronometry.

Additional Work and Recommendations. In water systems that use multiple water sources, changes in daughter and parent nuclides must be measured carefully. Scavenging and resuspension fluxes can affect daughter/parent nuclide activities in water in any distribution system and must be considered when calculating water ages. The effect of pipe material (e.g., PVC, concrete, or iron), pipe scale composition, and biofilm on radionuclide sorption/desorption will differ for each radionuclide. Added phosphorus, as well as variations in source water chemistry (e.g., dissolved organic matter) might also affect the rate of radionuclide transfer between drinking water and pipe walls and deposits. These factors can potentially affect the accuracy of calculated water ages and need further study. As an initial test, we strongly recommend that water ages should be calculated using two radionuclide pairs whenever possible (e.g., $^{90}\text{Y}/^{90}\text{Sr}$ and $^{234}\text{Th}/^{238}\text{U}$). Any discrepancy between the two tracer-derived water ages will indicate either mixing of different aged water masses or the preferential uptake/release of one of the tracer nuclides from pipe and sediment deposits. The blending of different aged water masses can to some extent be isolated from other processes because, for supported tracers, the tracer with a shorter lived daughter nuclide (e.g., $^{90}\text{Y}/^{90}\text{Sr}$) will always yield a slightly younger water age than the tracer with a longer lived daughter nuclide (e.g., $^{234}\text{Th}/^{238}\text{U}$). Finally, the use of naturally occurring radionuclides to measure water age needs to be tested against established protocol. Water ages derived from naturally occurring radionuclides need to be compared with water ages derived from a conventional (e.g., salt) pulse/step tracer test.

Application. The use of naturally occurring radionuclides as tracers of drinking water age could greatly facilitate hydraulic model calibration because water age can be measured at any node of the distribution system, at any time. We speculate,

however, that the primary advantage of using naturally occurring radionuclide tracers will be to measure water age in stagnant water that can be found outside of the community water system in premise plumbing, pools, and tanks. Pathogens in premise plumbing now constitute a leading source of waterborne disease outbreak in the developed world,⁴² and water age is intrinsically linked with both disinfectant decay and microbial growth.^{43–45} Drinking water ages in community water systems are expected to rise with the increasing use of water saving technology and conservation measures.² The ability to measure water age and an analyte (e.g., microbe or chemical) in the same water sample will allow for new insight into factors that control drinking water quality.

■ ASSOCIATED CONTENT

Supporting Information

NSWC treatment plant sample measurements and age calculations and NSWC distribution system sample measurements and age calculations. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b03227.

(PDF)

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Notes

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