

# $^{90}\text{Y}$ – $^{90}\text{Sr}$ disequilibrium in surface waters: investigating short-term particle dynamics by using a novel isotope pair

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## Abstract

We demonstrate the use of the disequilibrium between  $^{90}\text{Sr}$  ( $t_{1/2} = 29.1$  yr) and its particle-reactive daughter  $^{90}\text{Y}$  ( $t_{1/2} = 64$  h) to estimate particle removal rates and settling velocities in the epilimnion of a freshwater lake during varying conditions of stratification caused by seasonal changes. The estimated rates of removal obtained from the  $^{90}\text{Sr}$ – $^{90}\text{Y}$  disequilibrium showed good agreement with (a) measured rates of mass removal obtained from settling particle fluxes in sediment traps and the inventories of suspended material and (b) independently obtained removal coefficients for the scavenging behavior of two different isotopes of particle-reactive plutonium, present in the water column because of different processes. Because  $^{90}\text{Sr}$  is widespread and readily measurable in freshwater systems as a result of fallout from nuclear weapons testing, the  $^{90}\text{Sr}$ – $^{90}\text{Y}$  disequilibrium is a potentially valuable resource for examining particle dynamics in surface waters.

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## 1. Introduction

In the absence of other processes, a radioactive isotope should eventually occur in equilibrium with its progeny, especially when the progeny has a relatively short half-life. Where equilibrium does not occur, the presence of processes that re-

move the progeny from the environment of the parent can be inferred, and the rates of these processes can be estimated. The disequilibrium between soluble parent isotopes and particle-reactive progeny can be used to estimate particle settling rates.

Studies in marine systems over the past three decades have demonstrated that the measurement of disequilibrium between natural radionuclides such as generally soluble uranium and its surface-active thorium progeny can provide useful information about particle dynamics related to

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sedimentation, resuspension, and the transport of particle-active species [1–15]. Particle settling velocity, an important physical control on transport and nutrient cycling, has been obtained directly from measurements of the  $^{238}\text{U}$ – $^{234}\text{Th}$  disequilibrium in salt water [5,11].

Coale and Bruland [9] have used the  $^{238}\text{U}$ – $^{234}\text{Th}$  disequilibrium to estimate both the rate of particle settling and the rate of particle scavenging of ions (i.e.  $^{234}\text{Th}$ ) from solution. In contrast to the frequent use of disequilibrium measurements in marine systems, their use in freshwater systems has been limited by the low  $^{238}\text{U}$  concentrations and attendant difficulties of measuring the concentrations of  $^{234}\text{Th}$  [14]. Alternative approaches using low-level radiometric techniques or other relevant isotope pairs of sufficient abundance and detectability are needed for the more dilute waters.

In this work we expand the measurement of radiogenic disequilibrium to a freshwater system by using a new pair of radionuclides to obtain information about particle dynamics in the freshwater column. The objective of this study was to develop and test a procedure for using the disequilibrium between the soluble isotope  $^{90}\text{Sr}$  ( $t_{1/2} = 29.1$  yr) and its particle-reactive daughter  $^{90}\text{Y}$  ( $t_{1/2} = 64$  h) to estimate particle settling behavior in a freshwater system. In addition, the opportunity was presented to employ a widely dispersed but overlooked pair of radioisotopes as a novel device for limnological study.

Deposition of  $^{90}\text{Sr}$  in the environment from nuclear weapons testing in the atmosphere was significant and widespread. By 1970, the northern mid-latitudes lying between  $30^\circ\text{N}$  and  $60^\circ\text{N}$  had received from  $1.33 \times 10^5$  to  $1.78 \times 10^5$  dpm  $\text{m}^{-2}$  of this long-lived fission product [16]. As a result, many surface waters now have sufficient concentrations of fallout  $^{90}\text{Sr}$  [17–19] for studies of particle dynamics employing the  $^{90}\text{Sr}$ – $^{90}\text{Y}$  disequilibrium. This is especially advantageous in freshwaters, in which the use of the  $^{238}\text{U}$ – $^{234}\text{Th}$  disequilibrium is impractical because of low uranium concentrations (e.g.  $< 0.02$  dpm  $\text{l}^{-1}$ ).

## 2. The lake

The study site is Pond B, an 82-ha (203-a) warm monomictic reservoir on the Department of Energy's Savannah River Site in Barnwell Co., South Carolina. Constructed in 1961, the system was used as a cooling water source for a nuclear production reactor until 1964. During the operational period, radionuclides including  $^{90}\text{Sr}$  were released to the reservoir. No additional releases of radionuclides have occurred since 1964, and the reservoir has remained undisturbed. Presently in a semi-natural state, this aquatic system supports a thriving community of aquatic plants, fish and other biota [20]. Physical and limnological characteristics have been described by Bowling et al. [21]. Of particular importance are annual cycles of thermal stratification featuring recurring physical and chemical properties [22–24].

## 3. Sampling and analytical methods

Because of the short half-life (64 h) of  $^{90}\text{Y}$ , two considerations are necessary to measure the  $^{90}\text{Sr}$ – $^{90}\text{Y}$  disequilibrium accurately. First, water samples need to be filtered in the field to immediately separate the  $^{90}\text{Y}$  in the particle phase from the  $^{90}\text{Y}$  in the dissolved phase. Second is the timely separation of  $^{90}\text{Y}$ , still in the soluble phase, from the conservative  $^{90}\text{Sr}$  parent source. The field techniques and sample preparation used in this exercise were similar to those used previously for the measurement of Pu, Am, and Cm concentrations [25–27]. Certain details of sampling and processing of samples are presented here to emphasize any differences associated with the recovery and radiometric analysis of  $^{90}\text{Y}$  (and  $^{90}\text{Sr}$ ).

For each field exercise, raw water samples in triplicate (hereafter referred to as A, B, and C) of 24 l volume were pumped directly from the lake through 0.45- $\mu\text{m}$  membranes of 293 mm diameter, resulting in corresponding sets of suspended solids and filtered water from each depth selected. Samples A and B were used to provide duplicate measures of  $^{90}\text{Y}$  concentrations. Sample C was used to assay  $^{90}\text{Sr}$  concentrations by mea-

asuring the fully regrown  $^{90}\text{Y}$  daughter activity after 14 d.

Each 24-l filtrate (A, B, C) was acidified with 250 ml of concentrated hydrochloric acid (i.e. 1% by volume in 12 M acid). To each acidified filtrate, the following were added, with mixing: ferrous ion ( $1 \text{ mg l}^{-1}$ ), stable strontium ion ( $5 \text{ mg l}^{-1}$ ), and known activities of isotopic diluent radionuclides including  $^{88}\text{Y}$  and  $^{242}\text{Pu}$ . After 2 h the acidified filtrate solutions of samples A and B were made neutral to basic with ammonium hydroxide (e.g. 250 ml of 14 M solution) to precipitate the iron. The insoluble hydrous iron oxide, bearing all coprecipitated or scavenged nuclides including the ambient  $^{90}\text{Y}$  and its  $^{88}\text{Y}$  diluent ( $t_{1/2} = 107 \text{ d}$ ), was filtered out by using a  $0.45\text{-}\mu\text{m}$  membrane (293 mm diameter). Directly, the sample membrane filters with recovered iron carrier precipitates were transferred moist into 250-ml Pyrex beakers. The beakers were covered and placed in a muffle furnace already at  $520^\circ\text{C}$ . The covers were removed after 1 h, and the samples ashed for another 2 h. After a delay of 14 d, a similar coprecipitation procedure was applied to each sample C filtrate to begin the radiometric assay of the ambient  $^{90}\text{Sr}$  concentration by measuring the re-equilibrated  $^{90}\text{Y}$  daughter activity. The  $0.45\text{-}\mu\text{m}$  filters with the collected suspended solids for samples A and B were transferred moist into ceramic 150-ml Coors crucibles, covered, and ashed at  $600^\circ\text{C}$  for 2 h. Covers were removed after 1 h. Sample C filters, which were to be held for assay of  $^{90}\text{Sr}$  concentrations in suspended solids, were air-dried and weighed, then remoistened and ashed at  $520^\circ\text{C}$  overnight in tared Pyrex beakers.

The exact times of the initial phase separation and the separation of the ambient  $^{90}\text{Y}$  from the conservative  $^{90}\text{Sr}$  parent in the filtrates were recorded. These times were later used to correct for growth or decay of  $^{90}\text{Y}$  during the analytical procedure.

All ashed materials resulting from ignition of filters containing either the suspended solids or the iron hydroxide precipitates from samples A, B and C were leached or solubilized with hot 6 M HCl. Known activities of isotopic diluents including  $^{88}\text{Y}$  and  $^{242}\text{Pu}$  were added to each sample so-

lution, which was then clarified by centrifugation, evaporated to dryness, and – with the exception of samples from set C – taken up in 8 M  $\text{HNO}_3$ . The  $^{90}\text{Y}$  (and  $^{88}\text{Y}$ ) was recovered by using ion exchange and radiochemical separations similar to those described for plutonium, thorium, uranium, and americium [25–30]. The yttrium, a rare-earth-like element, was recovered in a manner similar to that for americium, an actinide rare earth. The separated  $^{90}\text{Y}$  fraction was taken up in a small volume (10 ml) of dilute hydrochloric acid to which 0.5 mg of iron (+3) was added. The solution was made ammoniacal with 7 M of  $\text{NH}_4\text{OH}$ , and the resulting iron hydroxide precipitate carrying the  $^{90}\text{Y}$  and  $^{88}\text{Y}$  was filtered onto a 25-mm-diameter membrane disk ( $0.45\text{-}\mu\text{m}$  pore size) by using a standard glass filtration chimney with a filter pump aspirator. After the iron- $^{90}\text{Y}$  precipitate was rinsed with dilute  $\text{NH}_4\text{OH}$  and then deionized water, the filter disk was removed, still moist, from the holder and mounted on a flat 1.5-in. (38-mm) stainless steel disk (A.F. Murphy Die and Machine Co., North Quincy, MA, USA). The sample was covered with a polyethylene film ( $1 \text{ mg cm}^{-2}$ ) that was held down with an application of glue (stick) around the uncovered perimeter of the support disk. The  $^{90}\text{Y}$   $\beta$  particles were counted in a gas-flow proportional system with a background of 0.25 counts per minute (cpm). Initial  $\beta$  counts were made within 36 h of sample recovery time (time zero, or  $t_0$ ). Recounts were made to assess the radiochemical purity of the separated  $^{90}\text{Y}$  nuclide, which had a half-life equal to 64 h. Subsequent to the  $\beta$  counting, the yttrium chemical yield was obtained by counting the  $\gamma$  emissions from the  $^{88}\text{Y}$  isotopic diluent by using a sodium iodide (NaI) crystal coupled to a multi-channel analyzer. After a delay of 14 d, the suspended-solids fraction from sample C was taken up in 8 M  $\text{HNO}_3$  and analyzed for  $^{90}\text{Y}$  (i.e.  $^{90}\text{Sr}$ ) by using the same chemical separations and counting source preparation as applied to samples A and B. The delay allowed for the re-establishment of secular equilibrium between any  $^{90}\text{Sr}$  present and its  $^{90}\text{Y}$  daughter. The general steps of the separation scheme are outlined in Fig. 1.

Duplicate concentration values for  $^{90}\text{Sr}$  in filtered water were provided by retaining one of

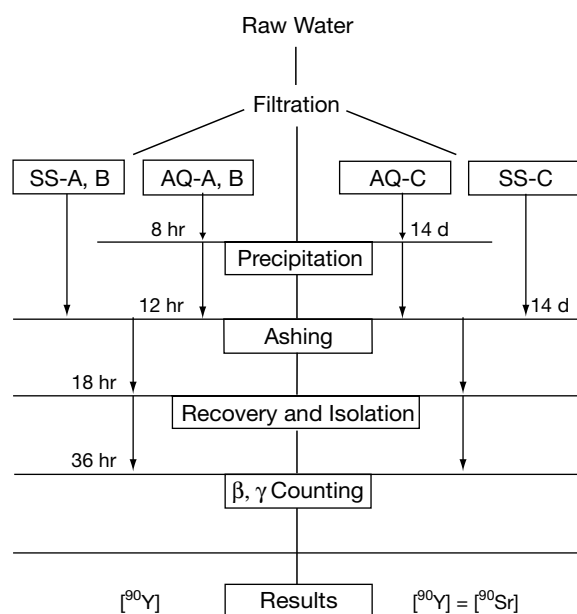


Fig. 1. General scheme of steps and timing for the collection, processing, and assessment of ambient  $^{90}\text{Y}$  (left-hand side) or ambient  $^{90}\text{Sr}$  after full regrowth of  $^{90}\text{Y}$  (right-hand side).

the supernatant solutions (A or B) that had been processed for recovery of ambient  $^{90}\text{Y}$ . The selected supernatants were simply re-acidified, held for a minimum of 2 weeks and reprocessed as separate samples after the re-equilibration of the  $^{90}\text{Y}$ - $^{90}\text{Sr}$  pair. These duplicate measurements were incorporated into the  $^{90}\text{Sr}$  values shown in Table 1.

For this study,  $^{90}\text{Sr}$ - $^{90}\text{Y}$  disequilibrium values were measured at various depths in March, June, and December of 1986. For March, values were measured at 1-, 5-, and 9-m water depths. For June and December, measurements were taken at 1-, 4-, 6-, 8-, and 10-m depths. All sampling was conducted in the deepest area of the lake, where the maximum depth was 12 m.

## 4. Results and discussion

### 4.1. Interferences and bias reduction

Blank phases obtained by passing demineralized water through unused filter membranes were processed like the samples and received the

Table 1  
Concentrations of  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  in the water column of Pond B at the Savannah River Site in December, early March, and June 1986<sup>a</sup>

Sample month	Depth (m)	[Dry] <sup>b</sup>	[Ash] <sup>c</sup>	[Sr] <sub>Aq</sub> <sup>d</sup>	[Y] <sub>Aq</sub> <sup>d</sup>	[Y] <sub>ss</sub> <sup>e</sup>	[Y] <sub>tot</sub> <sup>f</sup>
Dec. 1986	1	1.58	1.15	8.43 ± 0.16	2.96 ± 0.10	4.05 ± 0.12	7.00 ± 0.16
	4	1.92	1.40	8.36 ± 0.16	2.72 ± 0.09	4.30 ± 0.13	7.02 ± 0.16
	6	1.98	1.45	8.20 ± 0.15	2.65 ± 0.09	4.09 ± 0.12	6.74 ± 0.15
	8	2.0	1.46	8.39 ± 0.22	3.30 ± 0.10	3.80 ± 0.11	7.10 ± 0.15
	10	1.96	1.41	8.04 ± 0.15	3.02 ± 0.09	3.63 ± 0.10	6.65 ± 0.13
Mar. 1986	1	4.10	0.533	7.77 ± 0.22	3.53 ± 0.07	3.35 ± 0.06	6.88 ± 0.09
	5	5.23	0.701	7.79 ± 0.20	3.50 ± 0.07	3.48 ± 0.07	6.98 ± 0.10
	9	2.87	1.06	7.81 ± 0.21	3.41 ± 0.08	3.22 ± 0.07	6.63 ± 0.11
June 1986	1	6.06	0.590	6.86 ± 0.20	2.32 ± 0.12	3.64 ± 0.11	5.96 ± 0.16
	4	7.14	0.900	8.71 ± 0.17	2.06 ± 0.06	4.10 ± 0.12	6.16 ± 0.13
	6	7.41	1.88	10.01 ± 0.20	2.58 ± 0.07	5.31 ± 0.16	7.89 ± 0.17
	8	5.33	0.773	10.82 ± 0.14	8.21 ± 0.25	2.22 ± 0.07	10.43 ± 0.26
	10	5.39	0.700	12.17 ± 0.30	11.07 ± 0.33	0.70 ± 0.11	11.77 ± 0.35

<sup>a</sup> All data shown are simple means of duplicate measurements. Errors shown are standard counting errors.

<sup>b</sup> Concentration of suspended solids on the basis of dry weight (mg l<sup>-1</sup>).

<sup>c</sup> Ash weight concentration as mg l<sup>-1</sup>.

<sup>d</sup> Concentration (dpm l<sup>-1</sup>) in filtrate.

<sup>e</sup> Concentration (dpm l<sup>-1</sup>) on suspended solids.

<sup>f</sup> Total concentration in dpm l<sup>-1</sup>.

same additions. Control sources of  $^{88}\text{Y}$  (the isotopic diluent) were prepared and counted in the amount, form, and geometry used with the samples to provide the basis for chemical yield evaluation and to measure artifact  $\beta$  particles generated in the gas-proportional detectors by the  $\gamma$ -emitting  $^{88}\text{Y}$ . Stable strontium was added to the sample filtrates (vide supra) as a holdback carrier to prevent  $^{90}\text{Sr}$  from following the ambient  $^{90}\text{Y}$  daughter onto the hydrous iron oxide precipitate, thus avoiding the ingrowth of excess or ‘in vitro’  $^{90}\text{Y}$  from any coprecipitated  $^{90}\text{Sr}$  parent. Subsequent separation steps employed to isolate the  $^{90}\text{Y}$  also tended to eliminate  $^{90}\text{Sr}$  activity. Instrumental backgrounds on the four-detector system used for this exercise were close to 0.25 cpm and contributed less than 2% to the initial gross count rate of the two lowest-counting samples and less than 0.5% to the average gross count rate for the set of 73 field samples included in the study. The background-corrected  $\beta$  count rates of the phase blanks appeared to be essentially artifact pulses from the  $^{88}\text{Y}$  yield monitor. This determinate source contributed less than 10% to the initial gross count of the two lowest-counting samples and less than 3% to the average sample described above.

The minimum detectable  $^{90}\text{Y}$  activity for this procedure was  $0.05 \text{ dpm l}^{-1}$ . This estimate, derived from measurements made on phase blanks ( $n = 7$ ), included sample size (24 l), counter background ( $0.25 \pm 0.01 \text{ cpm}$ ), counting time (200 min), counting efficiency ( $0.5 \text{ cpm [dpm]}^{-1}$ ), and average chemical recovery (80%). Increasing the sample size, increasing the counting time, and using a stable isotope of yttrium for isotope dilution would decrease the minimum detectable activity. Appropriate decay and ingrowth corrections were applied to the  $^{90}\text{Y}$  measurements. These corrections were based on sample processing time before  $\beta$  counting (decay) and sample holding time before separation of ambient  $^{90}\text{Y}$  from the  $^{90}\text{Sr}$  parent source (ingrowth and decay). For example, the concentration value of artifact  $^{90}\text{Y}$  produced by  $^{90}\text{Sr}$  in the filtrate during the period between the initial phase separation and removal of  $^{90}\text{Y}$  by coprecipitation on hydrous iron oxide was equal to the product of the  $^{90}\text{Sr}$  concentration and the

expression  $[1 - \exp(-\lambda_d t)]$ , where  $\lambda_d$  and  $t$  are the  $^{90}\text{Y}$  decay constant and the elapsed time, respectively. The exponential expression represents the first-order approach to secular equilibrium between a long-lived source and a short-lived progeny.

#### 4.2. Disequilibrium calculations

The mathematical expressions employed here to relate the measurements of  $^{90}\text{Sr}$ – $^{90}\text{Y}$  disequilibrium to the physical dynamics of particles and particle-reactive species are similar to expressions developed and applied to uranium–thorium disequilibria in marine systems. The first consideration is a steady state between (a) the production of a daughter radionuclide and (b) its disappearance by radioactive decay, plus removal because of association with particulate matter. This steady state can be expressed as follows:

$$\lambda_p N_p = \lambda_d N_d + k N_d \quad (1)$$

Here  $\lambda_p$  and  $\lambda_d$  are the decay constants of the parent source (e.g.  $^{90}\text{Sr}$ ) and the daughter nuclide, respectively. The ‘ $N$ ’ terms are the atom concentrations of the parent and daughter nuclides in the water column. The  $k$  term is the first-order net removal rate coefficient (nonradiogenic) for the particle-active daughter nuclide. Solving for the removal coefficient and converting to activities ( $A$ , expressed in  $\text{dpm l}^{-1}$ ) by using the appropriate decay constants gives the following:

$$k = \lambda_d (A_p - A_d) / A_d \quad (2a)$$

or

$$k_c = \lambda_d (A_p - A_{d \text{ tot}}) / A_{d \text{ tot}} \quad (2b)$$

This expression, first used in similar form by Broecker et al. [2], involves the total concentration of the daughter nuclide  $A_d$  (e.g.  $A_{d \text{ tot}}$ ). Coale and Bruland [9] pointed out that in this form the rate coefficient (e.g.  $k_c$ ) would be related to the net removal of the daughter nuclide from the parent source by the combined processes of phase transfer (e.g. adsorption) and particle settling. If the  $A_d$  term is just the measured soluble-phase concentration of the daughter nuclide (e.g.  $A_{d \text{ aq}}$ ), the rate coefficient (e.g.  $k_t$ ) is related to the net transfer

rate of the daughter from the soluble phase to the particle phase [5,8,9,11] as follows:

$$k_t = \lambda_d(A_p - A_{d\text{ aq}})/A_{d\text{ aq}} \quad (3)$$

If the  $A_{d\text{ tot}}$  term in the denominator of Eq. 2b is replaced by the concentration of the daughter in the suspended solids phase only (i.e.  $A_{d\text{ ss}}$ ), normalized to unit volume, then the rate coefficient (e.g.  $k_r$ ) is related to the net removal rate of the particle mass:

$$k_r = \lambda_d(A_p - A_{d\text{ tot}})/A_{d\text{ ss}} \quad (4)$$

This last removal coefficient ( $k_r$ ) has been used to estimate the mass (or particle) flux and particle settling velocity [5,9,11,15].

The measurements presented in Table 1 represent the physical, biological, and chemical conditions prevailing in the water column at three different stages of stratification: (a) at the onset in early March, (b) at a fully developed state in June, and (c) in December during an unstratified period. The narrow range of all concentrations in the lake in December was a consequence of the well-mixed, isothermal water column established during the annual fall overturn in late October through late November. At that time, the hypolimnetic water (> 6 m), rich in ferrous ion [24], was reoxidized, causing the formation of insoluble ferric oxides. The particles collected in early December were essentially precipitated hydrous ferric oxide with an ash-to-dry ratio of greater than 70%. Following the surge in particle formation during the fall overturn, the concentrations of suspended matter in the epilimnion declined (as the material settled out) through January and into February (see Fig. 2). The higher suspended-solids concentration with lower ash content for March (Table 1) was a reflection of the increasing production of biogenic materials as epilimnetic waters warmed after mid-February. At this time, the  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  concentrations in the water column were uniform in vertical distribution.

By June, more than a month after the annual onset of stratification and development of anoxia in the water column below a depth of 6 m, the  $^{90}\text{Sr}$ – $^{90}\text{Y}$  concentrations showed a vertical profile. The  $^{90}\text{Y}$  was found to be nearly solubilized at 8 m

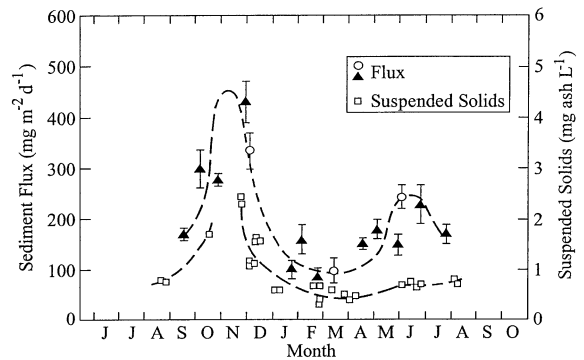


Fig. 2. Variation of settling mass fluxes (ash weight in  $\text{mg m}^{-2} \text{d}^{-1}$ ) over an annual cycle in near-surface waters of the study lake (upper plot), combining direct measurements of flux for sediment traps (closed triangles) and the fluxes estimated from  $^{90}\text{Y}$ – $^{90}\text{Sr}$  disequilibrium (open circles). The lower plot (open squares) shows suspended-solids concentrations (ash in  $\text{mg l}^{-1}$ ) measured in the near-surface waters of the lake.

and deeper. The increased solubility of the  $^{90}\text{Y}$  below depths of 6 m was similar to the behavior of other particle-active elements, including plutonium and thorium, that were present in the anoxic deeper waters of the lake [22]. The reductive dissolution of the hydrous manganese and iron oxides associated with the suspended materials falling into the anoxic hypolimnion tended to decrease the adsorptive capacity of the solids [23]. Alberts et al. [24] measured significant increases of dissolved organic carbon below the thermocline during the stratified period. Dissolved organic matter can effectively reduce the affinity of particulate matter for metal ions through formation of soluble metal complexes [25–27].

Small but measurable fractions (0.5–4%) of the total  $^{90}\text{Sr}$  concentrations were detected on suspended particulates in June. The vertical gradient in  $^{90}\text{Sr}$  values likely developed through a weak association with settling particles forming in the productive epilimnion (0–3 m) during the stratified period that began in April. With the volume estimates for the depth sectors of the lake given by Pinder et al. [22] and the measured  $^{90}\text{Sr}$  concentrations in Table 1, the total water column inventories calculated for  $^{90}\text{Sr}$  in the June, March, and December sampling events were  $14.2 \times 10^9$ ,  $13.9 \times 10^9$ , and  $14 \times 10^9$  dpm, respectively. The

Table 2

Rate coefficients related to the phase transfer of soluble  $^{90}\text{Y}$  onto particulates ( $k_t$ ), the net removal of the  $^{90}\text{Y}$  nuclide from the water column ( $k_c$ ), and the net removal of particulate mass from the water column ( $k_r$ )

Sampling dates	Depth (m)	$k_t$ ( $\text{d}^{-1}$ )	$k_c$ ( $\text{d}^{-1}$ )	$k_r$ ( $\text{d}^{-1}$ )
Dec. 1986	1	$0.480 \pm 0.023$	$0.053 \pm 0.010$	$0.092 \pm 0.015$
	4	$0.538 \pm 0.024$	$0.051 \pm 0.010$	$0.084 \pm 0.014$
	6	$0.533 \pm 0.040$	$0.056 \pm 0.010$	$0.093 \pm 0.014$
	8	$0.400 \pm 0.020$	$0.047 \pm 0.010$	$0.088 \pm 0.017$
	10	$0.432 \pm 0.020$	$0.054 \pm 0.010$	$0.099 \pm 0.015$
Mar. 1986	1	$0.312 \pm 0.010$	$0.034 \pm 0.010$	$0.069 \pm 0.010$
	5	$0.318 \pm 0.010$	$0.030 \pm 0.010$	$0.060 \pm 0.008$
	9	$0.335 \pm 0.013$	$0.046 \pm 0.010$	$0.095 \pm 0.020$
June 1986	1	$0.508 \pm 0.070$	$0.040 \pm 0.011$	$0.064 \pm 0.020$
	4	$0.840 \pm 0.033$	$0.107 \pm 0.010$	$0.161 \pm 0.010$
	6	$0.749 \pm 0.020$	$0.070 \pm 0.010$	$0.103 \pm 0.013$
	8	$0.083 \pm 0.010$	$0.009 \pm 0.010$	$0.046 \pm 0.030$
	10	$0.026 \pm 0.011$	$0.009 \pm 0.010$	$0.150 \pm 0.170$

gradient exhibited by the essentially soluble  $^{90}\text{Sr}$  was apparently a redistribution during the stratified period. Because of a short half-life (64 h), the  $^{90}\text{Y}$ – $^{90}\text{Sr}$  disequilibrium tended to adjust rapidly and reflect changes in the  $^{90}\text{Sr}$  concentration or in the  $^{90}\text{Y}$  removal rate, making a steady-state condition more likely.

Measured concentrations of  $^{90}\text{Y}$  and its parent  $^{90}\text{Sr}$ , presented in Table 1, were used with the disequilibrium Eqs. 2b–4 to derive rate coefficients related to (a) the net phase transfer of soluble  $^{90}\text{Y}$  onto particulates, (b) the net removal of the  $^{90}\text{Y}$  nuclide from the water column, and (c) the net removal of particulate mass from the water column. Table 2 was constructed with these coefficients. The uptake or phase transfer rate coefficient  $k_t$  (first column of Table 2) ranged from 0.32 to 0.84  $\text{d}^{-1}$ , indicating solution residence times ( $1/k_t$ ) of 1–3 d for the  $^{90}\text{Y}$  nuclide. The rate coefficient values in the second column of Table 2 represent the net removal of the  $^{90}\text{Y}$  from the water column by the combined processes of uptake onto suspended particulates and particle settling. This combined process coefficient ( $k_c$ ) ranged in value from 0.03 to 0.11  $\text{d}^{-1}$ , indicating water column residence times ( $1/k_c$ ) of 9–30 d for the  $^{90}\text{Y}$  nuclide during the three sampling periods. Values for the rate coefficient  $k_r$  are in the last column of Table 2. This coefficient, expressed as the fraction of the particulate mass

inventory removed per day, ranged from  $\leq 0.04$  to 0.16  $\text{d}^{-1}$ , corresponding to residence times ( $1/k_r$ ) from 6 to more than 25 d for an average particle in the sector of the water column examined during the measurement periods. The uniformity of values for the mass removal coefficient in December suggested a residence time of about 11 d for an average particle in the whole water column, corresponding to an average particle settling velocity of approximately 1 m  $\text{d}^{-1}$  over the 12-m depth.

#### 4.3. Mass flux calculations

Estimates of mass (expressed as ash weight) fluxes in the epilimnetic waters (0–3 m) of the lake were calculated for December, March, and June by using the corresponding mass removal coefficients ( $k_r$  values) from Table 2 and the suspended mass concentration from Table 1. These estimated fluxes (the product of the  $k_r$  value and the suspended-solids inventory in the 0–3-m sector) were then plotted in Fig. 2 with mass fluxes measured directly by sediment traps. The trap data (ash mass in  $\text{mg m}^{-2} \text{d}^{-1}$ ), covering nearly one annual cycle in the lake, were taken from table 1 in Bowling et al. [21]. Because the traps were set at 3 m and had collected material from more than the surface layer, the estimated fluxes were calculated by using an average of the two

upper water column  $k_r$  values and suspended-solids concentrations (e.g. at 1 and 4 m). Included in Fig. 2 is a plot of unpublished suspended-solids concentrations measured by the authors in the near-surface water of the lake over several years. The flux data and the suspended-solids concentrations used to construct the plots in Fig. 2 were based on ash, because the traps were not poisoned, and loss of dry weight (i.e. carbon) by bacterial remineralization was avoided.

The seasonal variation in the mass flux and suspended-solids concentrations shown in Fig. 2 reflects the biogeochemical processes occurring in the lake. The plot of suspended-solids concentrations (ashed basis) shows little change in the near-surface water of the lake from March through August. However, the ash content of the suspended materials in the upper water column decreased after March, reaching a minimum of just under 10% by late June. In terms of dry (not ashed) weight, a significant peak in suspended-solids concentration ( $>7 \text{ mg l}^{-1}$ ) occurred in late June, consistent with a relative peak in the mass flux at that time. The conformation of the mass fluxes estimated from the measurement of  $^{90}\text{Y}$ – $^{90}\text{Sr}$  disequilibria to the flux pattern observed by sediment trapping not only supported the trap measurements but, more importantly, gave credence to an independent assessment of particle or mass flux based on the disequilibrium of the ubiquitous but unexploited  $^{90}\text{Y}$ – $^{90}\text{Sr}$  radioisotope pair.

#### 4.4. Nuclide removal rates

Comparisons were made between the rate coefficients related to (a) the removal of the  $^{90}\text{Y}$  nuclide from the water column of the lake by the combined processes of sorption onto particles plus particle settling ( $k_c$  values in Table 2) and (b) the removal rates of two isotopes of plutonium, mass 239 and mass 238, also present in the lake but entering the water column from different sources. The fractional removal rate of the 239 isotope, present in the lake essentially from historically contaminated sediments, was equal to the ratio of the sediment trap collection rate of the 239 isotope to the total inventory of this iso-

tope in the water column standing over the traps. During the January–February period, this ratio, on a daily basis, was equal to 0.03 or 3% of the  $^{239}\text{Pu}$  inventory removed per day. After April and into June, the removal rate was observed to increase to near 0.07 of the  $^{239}\text{Pu}$  inventory per day. The numerical average for the January to June observations was 0.05 of the  $^{239}\text{Pu}$  inventory removed from the 0–3-m sector of the lake per day. Removal rate values for the 239 isotope were taken from table 3 in Bowling et al. [21].

On the basis of the average of the two upper (e.g. 1 and 4 m) water column removal coefficients or  $k_c$  values found in Table 2, the estimated daily fractional removal of  $^{90}\text{Y}$  inventory by particulates during December, March, and June ranged from 0.032 to 0.074  $\text{d}^{-1}$ , with an overall average of 0.053  $\text{d}^{-1}$  during the period. These removal rates were essentially the same as those quoted above, which were measured directly by sediment traps for plutonium, mass 239, in the 0–3-m sector of the lake.

Another isotope of plutonium, mass 238, originating on airborne particulates released from nearby operations, was deposited on the surface of the lake at the rate of approximately 20 000  $\text{dpm d}^{-1}$  [31–34]. The average standing inventory of the mass 238 isotope, present in the near-surface waters of the lake from atmospheric sources, was estimated to be 640 000  $\text{dpm}$  [22]. The fractional removal rate of the  $^{238}\text{Pu}$  inventory, equal to the ratio of daily inputs to standing inventory, was 0.03  $\text{d}^{-1}$ . This removal rate was in good agreement with the near-surface (1-m) removal coefficients for  $^{90}\text{Y}$  or the  $k_c$  values in Table 2, which averaged just over 0.04  $\text{d}^{-1}$  and ranged from 0.032 to 0.053  $\text{d}^{-1}$  during the December, March, June period.

## 5. Conclusions

In this work we have demonstrated the use of radiogenic disequilibria between a pair of ubiquitous but overlooked fallout isotopes,  $^{90}\text{Sr}$  and  $^{90}\text{Y}$ , to provide estimates of important components of particle dynamics in a surface water body. We have exploited the fact that the par-



ticle-reactive  $^{90}\text{Y}$  is produced at a precisely measurable rate by its conservative  $^{90}\text{Sr}$  parent. The  $^{90}\text{Y}$  becomes attached to particulate material and is carried down as the material settles. The special advantage of this method is that the half-life of  $^{90}\text{Y}$  allows the measurement of fast particle dynamics that might be found in small lakes, in rivers, at the mouths of rivers, and in near-shore marine systems. We used this approach to examine particle behavior in the water column of a freshwater lake throughout an annual cycle and found the estimates of particle fluxes, based on the  $^{90}\text{Y}$ – $^{90}\text{Sr}$  disequilibrium, to be in agreement with results obtained by the more traditional gravimetric method using sediment traps.

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