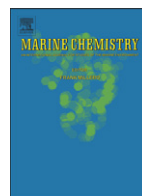




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Determination of water mass ages using radium isotopes as tracers: Implications for phytoplankton dynamics in estuaries

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ABSTRACT

Despite a relatively short residence time of water in many shallow, semi-enclosed estuaries, phytoplankton blooms in nutrient enriched systems are a common phenomenon. This poses the question how is it possible to have phytoplankton populations bloom in response to local conditions of shallow estuaries, if the water residence times are similar to cell division times? To address this paradox we used the radium quartet as a tool to measure water mass age in coastal systems (Waquoit Bay, MA, USA) subject to different degrees of land-derived nitrogen load and hence differences in phytoplankton biomass. Recently, the radium quartet has been used as geochemical tracers to determine age of water masses. Based on a number of samples collected over the course of one year, the average radium-derived age (\pm stdev) of water in three sub-estuaries of Waquoit Bay (Childs River, Quashnet River, and Sage Lot Pond) was ~ 7 (± 4.7), 11 (± 6.2), and 17 (± 7.5) days, respectively. These values are significantly longer than previous estimates based on more traditional hydrodynamic methods. Furthermore, peak chlorophyll concentrations were associated with older water masses in the heavily freshwater-influenced sub-estuaries (Childs and Quashnet). Our results suggest that water age, temperature, and nutrients all play a role in controlling phytoplankton biomass however, water age was more important at the time of the year when temperature limits phytoplankton growth (late spring, early summer). We conclude that radium-derived age models, which are similar to artificial tracer-based approaches, may be the most appropriate method for studying the role of hydrodynamics on estuarine ecology.

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1. Introduction

Limnologists and estuarine ecologists have long recognized the importance of links between water residence time and eutrophication (Schindler, 2006). The presence or absence of phytoplankton (Holmes et al., 2000; Wissel et al., 2005; Painting et al., 2007; Paerl et al., 2006) and zooplankton (Ketchum, 1954), occurrence of harmful algal blooms (Bricelj and Lonsdale, 1997), variability of dissolved nutrients (Andrews and Müller, 1983), and the percent contribution of primary production by various producers (Valiela et al., 1997a) have been associated with changes in water residence time. Residence time is an extremely important variable yet can be difficult to quantify (Alber and Sheldon, 1999; Munson et al., 2002; Sheldon and Alber, 2002). Until recently estuarine ecologists have used either simplified calculations of flushing time, residence time derived from hydrodynamic models, or age measured by dye release studies. These methods furnish estimates of freshwater renewal, the time it takes for a water parcel to leave a system through an outlet, and the time a water parcel has spent since entering the estuary through one of the boundaries,

respectively. In a system under steady state these three terms should be equal if the comparison includes the whole estuary.

1.1. Estuarine water residence time: methods and assumptions

There are inherent problems associated with each of the methods typically employed to calculate estuarine water circulation. Tidal prism models tend to be a gross over simplification of estuarine circulation (Luketina, 1998) and have extremely limited resolution in terms of time scales less than a tidal phase or spatial scales less than the size of the estuary being considered (Abdelrhman, 2007). Two- and 3-D hydrodynamic models are very complex requiring precise detail in defining spatial and temporal changes and require significant expertise and resources to develop (Abdelrhman, 2007). Additionally, biological responses (i.e. phytoplankton biomass) may or may not match the spatial and temporal scales associated with each of these methods (Munson et al., 2002; Abdelrhman, 2007).

Recently, the radium (Ra) quartet has been used as geochemical tracers to determine age of water masses and ocean circulation (Moore, 2000a, 2000b; Charette et al., 2001; Kelly and Moran, 2002; Moore et al., 2006; Dulaiova and Burnett, 2008). There are four naturally occurring radium isotopes ^{223}Ra , ^{224}Ra , ^{226}Ra , and ^{228}Ra which have half-lives of 11.4 d, 3.7 d, 1600 y, and 5.7 y, respectively. Radium is

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naturally enriched in groundwater relative to surface water and seawater and it behaves conservatively in the ocean; removal of radium from marine systems is due mainly to mixing and decay (Li et al., 1977; Li and Chan, 1979; Moore, 1996; Rama and Moore, 1996; Moore, 1997; Krest et al., 1999; Charette et al., 2001, and others). Calculation of water mass ages have undergone several iterations (Moore and Todd, 1993; Moore, 2000b; Charette et al., 2001; Moore et al., 2006), though in general the calculation of radium-derived age involved the ratio of a short-lived to a long-lived radium isotope (e.g. $^{223}\text{Ra}/^{228}\text{Ra}$), the latter isotope being used to correct for mixing effects (dilution).

Discussion of water age or residence time requires careful definition of terms (Munson et al., 2002; Sheldon and Alber, 2002). First, water mass age is not necessarily synonymous with residence time (Munson et al., 2002) unless the system is under steady state and a comparison is made across an entire estuary. Radium ages calculated using the ratio of short- to long-lived isotopes are interpretable as a tracer release, due to their input to surface water at the sediment/water interface; the short-lived isotopes act like an internal clock, since they decay as they mix away from their source along the coastline or at the estuary's boundaries (Charette et al., 2001). In this study, our radium-derived ages span entire estuaries, and assuming steady state, the terms water mass age, flushing, and residence time should be synonymous.

Early models for calculating age did not account for continuous inputs of radium from sediments and groundwater. The assumption was radium inputs only came from nearshore, or upstream in the case of estuarine systems, with no additional inputs. Since these models are essentially a closed box they have been referred to as “mummy” models (Moore, 2000b; Moore et al., 2006). Mummy models were ideally applied in the coastal ocean where the coast represented a line-source of radium and radium concentrations were controlled by mixing and decay alone within the surface mixed layer. In estuaries, where radium inputs may occur throughout the system, mummy models provide only a lower limit age estimate. To account for this shortcoming, Moore et al. (2006) formulated a more explicit “continuous input” model, which did not require closed system decay or that the specific source activity of the radium input be known (e.g. SGD), but simply the activity ratio of the input of the two isotopes.

1.2. Estuarine phytoplankton bloom dynamics: the role of water residence time

Blooms are a common phenomenon in estuaries subject to nutrient enrichment (Cloern, 1996; Andreoli et al., 1999; Lucas et al., 1999a, 1999b, and many others). For example, in Waquoit Bay (MA, USA), a typical semi-enclosed temperate coastal estuarine system, biomass levels of the various sub-estuaries are tied to land-derived nitrogen loads and to mean annual dissolved inorganic nitrogen (DIN) concentration (McClelland et al., 1997; McClelland and Valiela, 1998; Tomasky-Holmes, 2008). Previous reports of water residence time in the estuaries of Waquoit Bay range from 1.5 to 2.3 d (Geyer, 1997, WBLMER unpublished data), relatively short compared with division rates on the order of $\sim 1 \text{ d}^{-1}$ typical of estuarine phytoplankton species. Given that the residence time of water in many shallow, semi-enclosed estuaries all over the world is short (Murrell et al., 2007), Ketchum (1954), and more recently Vallino and Hopkinson (1998), among others, have pointed out that shallow estuaries hold a paradox: how can phytoplankton in estuaries bloom in response to added nutrients if the water residence times are of similar duration to the time required for phytoplankton cells to divide? Pace et al. (1992) extended this question in regard to zooplankton, whose generation times are even more prolonged.

Several studies of cell division rates demonstrate certain taxa (small diatoms, small flagellates, and certain picoplankton) may divide several times a day (Chan, 1978; Blasco et al., 1982; Waterbury et al., 1986;

Furnas, 1990; Mizuno, 1991; Fanhenstiel et al., 1995; Andreoli et al., 1999), but most other taxa have been shown to divide more slowly, less than once a day ($0.2\text{--}0.8 \text{ divisions day}^{-1}$) (Chan, 1978; Furnas, 1990; Thompson et al., 1991; Peperzak et al., 2000). Another important factor of phytoplankton growth is cell size, as phytoplankton division rates ($\text{doublings day}^{-1}$) decrease significantly as cell volume increase (Chisholm, 1992; Tang, 1995, and others). Additionally, factors such as temperature, nutrients, and light also play a role in determining phytoplankton division rates.

In this study we use the “continuous input” model for radium-derived water mass age calculations to, first, compare estimates of water age obtained previously using other methods with the Ra approach, and, second, to use the Ra-derived water age measurements to compare to phytoplankton growth dynamics, and perhaps cast light on the paradoxical situation of short residence times concurrent with phytoplankton blooms (Ketchum, 1954; Vallino and Hopkinson, 1998, among others). We applied the Ra approach to obtain new measurements of spatially explicit water mass age in several shallow estuaries and addressed whether or not phytoplankton blooms could plausibly occur within the time spent within these estuaries.

2. Methods

2.1. Site description

The sites for this study were sub-estuaries of Waquoit Bay (Childs River, Quashnet River, and Sage Lot Pond), part of the Waquoit Bay National Estuarine Research Reserve (WBNERR), located on the south shore of Cape Cod, Massachusetts, USA at approximately $-70^\circ 31' 33.30''$ $41^\circ 34' 52.44''$ (Fig. 1). The Waquoit Bay sub-estuaries are shallow (on average $<1 \text{ m}$), semi-enclosed estuaries with similar open water areas, temperature, and salinity regimes but are subject to different degrees of nitrogen loading from land (Valiela et al., 1997b; Hauxwell et al., 1998). Differences in land-derived nitrogen loads translate into differences in phytoplankton biomass. There are distinct seasonal blooms in chlorophyll *a* concentration in the Waquoit Bay sub-estuaries with highest chlorophyll *a* concentrations in the summer

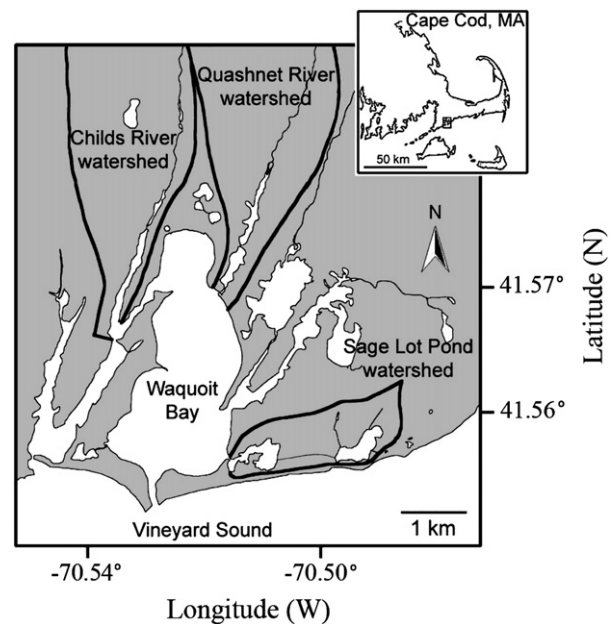


Fig. 1. Map of the Waquoit Bay sub-estuaries where surface radium samples were collected along an estuarine transect in each of the sub-estuaries. Not shown are the locations of the groundwater samples and piezometer samples from various locations in the sub-estuaries.

and lowest in the winter with magnitude of the peak depended on nutrient enrichment (Tomasky-Holmes, 2008).

The watersheds of the sub-estuaries are underlain by an unconsolidated sand and gravel aquifer (Barlow and Hess, 1993; Leblanc et al., 1986) comprised primarily of quartz and feldspar sand. Groundwater flow is almost entirely in the horizontal direction, with an approximate flow velocity of 0.4 m per day (LeBlanc et al., 1991). Because of the coarse nature of the underlying glacial sediments on Cape Cod percolation is favored over runoff (Valiela et al., 2000) and 45% of the annual precipitation is recharged to groundwater (Eichner and Cambareri, 1992; Valiela et al., 1997b). Groundwater discharge to the sub-estuaries accounts for ~89% of the total freshwater input to Waquoit Bay (Cambareri and Eichner, 1998).

2.2. Sample collection

2.2.1. Groundwater

Groundwater is defined here as the mixture of fresh groundwater and seawater that intrudes into the aquifer, otherwise known as the subterranean estuary (Moore, 1999). To quantify radium activities and activity ratios in groundwater we used two different methods. First, we used drive-point piezometers and a hand-operated vacuum pump to collect ~10–20 l of groundwater at several locations around the periphery of each estuary. Along each estuary, we selected sites just above the high tide mark and drove a piezometer to various depths (all $\sim \leq 1$ m) below the water table. Water was stored in cubitainers for processing.

Second, we collected groundwater flowing into the estuaries through the sediments by use of seepage meters. Seepage meters were constructed from the tops and bottoms of 55-gallon plastic drums. Each chamber was about 0.6 m in diameter (0.27 m^2) \times 0.3 m tall, with a quick-connect port attachment for water collection and a vent to minimize pressure within the headspace during installation. The chambers were pressed into the sediments so that only a small headspace remained. After deployment, chambers were allowed to equilibrate for 24 h with an open vent, after which each vent was closed and collection bags were attached to the quick connect port. This equilibration period allows for the benthos and groundwater flow, which were disturbed during meter installation, to return to its natural state. Collection bags consisted of pre-wetted thin-walled plastic bags connected to a quick-connect port on top of each chamber. Bags were left attached to each seepage meter for ~2–3 h after which time bags filled with groundwater were collected.

2.2.2. Estuarine/surface water

Samples were taken to measure radium activities in the estuaries along a salinity gradient (from <1 –~29‰) from Childs River, Quashnet River, and Sage Lot Pond in March, June/July, August, and October 2002. In order to maintain consistency between sampling periods in the water masses we collected, sampling stations were chosen according to salinity rather than fixed locations. A hand-held YSI (Yellow Springs Instruments Incorporated, Yellow Springs, OH) model 85 salinity probe was used to measure salinity. Filtered ($1 \mu\text{m}$ cartridge filter) water samples (~25 l) from the different estuaries were collected from the top half meter of the water column using a deck-board pump. Samples were collected into 25 l cubitainers.

2.3. Radium isotopes: sample processing and analyses

Radium isotopes were extracted from the various samples by passing the water samples through Mn-impregnated acrylic fiber packed columns (Moore and Reid, 1973). Water column samples were pumped through the column at a flow rate of $\sim 1 \text{ l min}^{-1}$. Smaller volume groundwater samples were gravity fed through the Mn fiber columns, which typically resulted in a lower flow rate ($<0.5 \text{ l min}^{-1}$).

Mn-fibers from the columns were partially dried and analyzed for ^{223}Ra and ^{224}Ra activities in a delayed coincidence counter (Moore and Arnold, 1996). After the short-lived radium isotopes were quantified, the Mn-fibers were ashed (at $820 \text{ }^\circ\text{C}$ for 16 h), homogenized, and placed in counting vials. The vials were then placed in a well-type γ spectrometer (Canberra, model GCW4023) to measure ^{226}Ra and ^{228}Ra activities (Charette et al., 2001). Detectors were calibrated using certified standards (NIST-SRM) prepared in the same fashion as samples. ^{223}Ra and ^{224}Ra activities were decay-corrected for the time of collection. Detection limits for both the long-lived and short-lived isotopes were 0.2 dpm (e.g. 0.05 dpm/l for a 4 l groundwater sample) (Gonneea et al., 2008). Uncertainties were typically $\pm 8\%$ for ^{226}Ra and ^{228}Ra and $\pm 7\%$ for ^{223}Ra and ^{224}Ra .

2.4. Size-fractionated phytoplankton

To examine the different size-fractions of phytoplankton along an estuarine gradient in each estuary, phytoplankton samples, 5-ml samples, fixed with 0.1% glutaraldehyde (final concentration), frozen in liquid nitrogen (Vaulot et al., 1989; Olson et al., 1993), were collected at fixed stations along a longitudinal axis in Childs River, Quashnet River, and Sage Lot Pond monthly from February–October 2002. An Epics V flow cytometer coupled with a Cicero acquisition system with excitation at 488 nm was used to simultaneously measure chlorophyll *a* fluorescence, cell size, and cell concentration. A modified version of CYTO-WIN software was used to analyze the data. Further data analysis was performed using the MATLAB software package (The MathWorks). To express FCM relative fluorescence as extracted chlorophyll *a* equivalence, a relationship between flow cytometric relative fluorescence and extracted chlorophyll *a* concentration was developed and applied according to the following equation: Predicted extracted chlorophyll *a* ($\mu\text{g l}^{-1}$) = $((1.0851 \times \log \text{transformed FCM relative fluorescence}) - 11.186) \times \text{cells/ml}$. For a more detailed description of instrumentation, sampling protocol, and methodological considerations see (Tomasky-Holmes, 2008).

3. Results and discussion

3.1. Groundwater and surface water radium activities

To allow comparisons, we will focus on ^{223}Ra and ^{228}Ra , the two isotopes used as the age tracer pair in a previous study of SGD and residence time in Waquoit Bay proper (Charette et al., 2001). Groundwater radium activities in Childs River, Quashnet River, and Sage Lot Pond differed substantially; Childs River groundwater ^{223}Ra and ^{228}Ra activities were ~2 times higher than in the Quashnet River groundwater, respectively (Table 1). The sample set was relatively well distributed along a salinity range from 0 to 31. While the short-lived Ra isotopes were positively correlated with sample salinity ($R^2 = 0.23$ in both cases), the long-lived Ra isotopes were not (not shown). Despite the difference in activities, there was no significant difference in the $^{223}\text{Ra}/^{228}\text{Ra}$ activity ratio nor was there a correlation with salinity. We do not have a ready explanation for the difference in radium activities between the two estuaries but suspect that it has to do with differences in subterranean estuarine chemistry. Gonneea et al. (2008) found that Fe and Mn cycling influences groundwater radium activities, which may account for the difference between the two watersheds.

Activities of the radium quartet in the estuarine surface waters of Childs River, Quashnet River, and Sage Lot Pond on the 4 different sampling dates are presented in Table 2. The range of values of radium activities we report fall within the lower part of the range found in previous studies of surface waters (Rama and Moore, 1996; Charette et al., 2001; Scott and Bradley Moran, 2001; Kelly and Moran, 2002; Moore et al., 2006; Houghman and Moran, 2007). Surface water radium activities were on average a factor of 1.5 times lower than

Table 1

Radium isotope activities (dpm l⁻¹) in the groundwater of the Waquoit Bay sub-estuaries during August 2002 using piezometers and October 2002 using seepage meters. Uncertainties were typically ± 8% for ²²⁶Ra and ²²⁸Ra and ± 7% for ²²³Ra and ²²⁴Ra.

	Salinity ‰	Date	²²⁴ Ra	²²³ Ra	²²⁶ Ra	²²⁸ Ra	²²³ Ra/ ²²⁸ Ra	
<i>Samples collected with piezometers</i>								
Childs River	0.0	27 August	0.31	0.01	0.11	0.28	0.04	
	4.8	2002	27.25	1.17	1.41	16.97	0.07	
Quashnet River	22.2		13.25	0.95	0.16	1.69	0.57	
	25.3		17.67	1.24	0.35	6.32	0.20	
	28.5	28 August	19.49	0.97	0.22	1.61	0.60	
	8.2	2002	2.76	0.31	0.22	1.63	0.19	
	25.0		5.28	0.45	0.15	0.97	0.46	
	11.2		1.39	0.14	0.09	0.23	0.60	
	8.3		1.66	0.14	0.07	0.23	0.59	
	19.4		5.20	0.26	0.16	0.98	0.26	
	18.7		5.52	0.33	0.12	0.67	0.49	
	3.4	29 August	0.62	0.03				
11.4	2002	2.41	0.15	0.06	0.26	0.57		
18.1		4.49	0.14	0.10	0.53	0.26		
22.4		5.84	0.14	0.21	1.06	0.14		
26.6		14.23	0.63	0.25	0.93	0.68		
Sage Lot Pond	25.4	29 August	3.67	0.14	0.25	2.60	0.05	
	31.0	2002	16.82	1.48	0.43	5.39	0.28	
	28.1		5.08	0.35	0.17	2.56	0.14	
	25.9		4.03	0.26	0.14	2.36	0.11	
<i>Samples collected with seepage meters</i>								
Childs River	12.8	30 October	3.88	1.07	0.12	0.80	1.34	
	15.8	2002	2.94	0.47	0.41	1.10	0.42	
	6.2		0.72	0.28	0.21	0.84	0.33	
	2.8		0.14	0.04	0.13	0.27	0.15	
	2.0		0.69	0.14	0.13	0.46	0.30	
	17.6		3.65	0.73	0.59	0.95	0.77	
	2.5		0.57	0.17	0.24	0.62	0.28	
	2.6		0.78	0.14	0.25	0.50	0.29	
	Quashnet River	7.8	30 October	1.05	0.18	0.27	0.75	0.23
		7.6	2002	1.45	0.18	0.19	1.01	0.18
12.9			7.94	0.59	0.27	4.54	0.13	
12.6			7.26	0.47	0.29	4.60	0.10	
23.5			3.31	0.94	0.59			
Piezometer average						0.34		
Seepage meter average						0.38		
Grand average						0.35		

groundwater activities (Tables 1 and 2). All radium isotope activities were correlated in surface water samples for each of the estuaries as can be seen, for example, with ²²³Ra and ²²⁸Ra ($r = 0.71$; Fig. 2). The relationship between ²²³Ra and ²²⁸Ra did not differ across the sub-estuaries (i.e. minimal difference in the slopes) however the y-intercepts differed suggesting the Childs River freshwater end-member has more radium compared to Quashnet River and Sage Lot Pond. The consistent manner in which ²²³Ra increased with ²²⁸Ra (similar for the entire quartet) suggests that the radium isotopes originated from similar sources, as was found in Waquoit Bay proper (Charette et al., 2001).

²²³Ra and ²²⁸Ra increased over the oligohaline and mesohaline reaches with salinities 0–18‰, then stayed constant or decreased slightly (more so for ²²³Ra) in the polyhaline reaches (18–30‰; Fig. 3). Radium activities increased with salinity as a result of desorption from sediment particles or increased SGD-input of radium and then decreased due to decay (²²³Ra and ²²⁴Ra) and mixing (all 4 isotopes) with radium-depleted Vineyard Sound water.

Radium activities in the oligohaline reaches were higher in Childs River than in Quashnet River (Fig. 3). Activities in the mesohaline and polyhaline reaches overlapped in Childs River, Quashnet River, and Sage Lot Pond, suggesting that radium activities at the polyhaline reaches were a result of mixed waters derived from tidal exchanges of Waquoit Bay and Vineyard Sound water.

3.2. Seasonal pattern in radium activities

Radium activities were highest in the summer (Fig. 4). Peak radium activities lagged approximately 1 month behind peak water table elevations (Fig. 4), as found in the Pettaquamscutt estuary in Rhode Island (Kelly and Moran, 2002), and several Rhode Island coastal ponds (Houghman and Moran, 2007); Michael et al. (2005) found a similar lag time between SGD and water table elevations in Waquoit Bay. The seasonality of radium activity seem therefore seems largely linked to changes in flow of groundwater from the aquifer. There may be smaller additional radium contributions from shallow sediments (Charette et al., 2001).

3.3. Water mass ages determined from radium isotopes

Water mass ages were calculated in several ways. First, ages were calculated using a variation of the radioactive decay equation adapted from Moore (2000b), which has been referred to as the “mummy” model (Moore, pers. comm.):

$$\tau = \left[\ln \left(\frac{{}^{223}\text{Ra}/{}^{228}\text{Ra}}{i} - \ln \left(\frac{{}^{223}\text{Ra}/{}^{228}\text{Ra}}{\text{exRa}} \right)_{\text{obs}} \right) \right] / \lambda_{223} \quad (1)$$

where $({}^{223}\text{Ra}/{}^{228}\text{Ra})_i$ is the ratio of ²²³Ra to ²²⁸Ra in the groundwater endmember, $({}^{223}\text{Ra}/{}^{228}\text{Ra})_{\text{obs}}$ is the ²²³Ra to ²²⁸Ra ratio observed in the estuary, and λ_{223} is the decay constant for ²²³Ra (0.0608 d⁻¹). The ${}^{228}\text{Ra}_{\text{ex}}$ in this model refers to ²²⁸Ra in excess of its open ocean value since the model assumes that both isotopes decrease to zero as the age approaches infinity (Charette et al., 2001).

Second, ages were calculated using the “continuous input model” using ²²³Ra/²²⁸Ra data and the Moore et al. (2006) Eq. (2).

$$\tau = \left[F \left(\frac{{}^{223}\text{Ra}/{}^{228}\text{Ra}}{i} \right) - I \left(\frac{{}^{223}\text{Ra}/{}^{228}\text{Ra}}{i} \right) \right] / \left[\left(\frac{{}^{223}\text{Ra}/{}^{228}\text{Ra}}{i} \right) \lambda_{223} \right] \quad (2)$$

where $F({}^{223}\text{Ra}/{}^{228}\text{Ra})_i$ is the ²²³Ra/²²⁸Ra activity ratio of the flux into the system (i.e. groundwater or equivalent to $({}^{223}\text{Ra}/{}^{228}\text{Ra})_i$ in Eq. (1) and $I({}^{223}\text{Ra}/{}^{228}\text{Ra})_i$ is the ²²³Ra/²²⁸Ra activity ratio in the system (i.e. estuarine sample, equivalent to $({}^{223}\text{Ra}/{}^{228}\text{Ra})_{\text{obs}}$ in Eq. (1)).

Assumptions for Eq. (1) were as follows: 1) the system was under steady state on the time-scale of the ²²³Ra half-life, 2) the initial ratio of short to long-lived isotope in the groundwater was temporally and spatially constant, and 3) no addition or subtraction of radium other than mixing or decay occurred once water left the sediment/water interface. Assumptions for Eq. (2) were the same as for Eq. (1), except that additional inputs of Ra throughout the estuary are accounted for. Furthermore, in Eq. (2) additions of radium include fluxes from sediment, river, and groundwater, and we further assume the flux ratios from these additional sources were similar to those found in the groundwater samples we collected.

In the case of either approach (Eqs. (1) or (2) above), the main source of uncertainty lies with variability in the end-member ratio (Charette et al., 2008). Factors such as groundwater salinity, residence time, and redox potential are generally most important for controlling variations in Ra activity (Gonneea et al., 2008). For ratios, especially those involving the short-lived Ra isotopes, flushing time and bulk sediment geochemistry (e.g. carbonate vs. aluminosilicate mineralogy) are paramount (Crotwell and Moore, 2003; Charette and Buesseler, 2004). Overall, the best way to minimize the uncertainty is to attempt to capture the range of variability through a large number of samples and, in the case of the age model, collect samples as close to the point of discharge as possible. For our study, we took multiple samples with shallow piezometer installations ($n = 19$) and seepage meters ($n = 12$), which recover groundwater as near shore as feasible, just before it transits the sediment water interface. As mentioned earlier, there was no significant difference in the ²²³Ra/²²⁸Ra ratio between Childs and Quashnet River estuaries. This

Table 2

Radium isotope activities (dpm L⁻¹) in the estuarine surface waters of the Waquoit Bay sub-estuaries during March, June/July, August, and October 2002. Water ages were calculated from the continuous input model as applied to the ²²³Ra/²²⁸Ra data. Uncertainties were typically ± 8% for ²²⁶Ra and ²²⁸Ra and ± 7% for ²²³Ra and ²²⁴Ra.

	Salinity ‰	Date	²²⁴ Ra	²²³ Ra	²²⁶ Ra	²²⁸ Ra	²²³ Ra/ ²²⁸ Ra	Age (d)
<i>March</i>								
Quashnet River	5.6	19 March 2002	0.29	0.05	0.13	0.19	0.29	3.5
	7.0		0.29	0.07	0.12	0.25	0.27	5.1
	3.9		0.19	0.04	0.12	0.15	0.29	3.5
	21.8		0.42	0.06	0.10	0.34	0.17	16.4
	22.0		0.43	0.07	0.12	0.40	0.18	15.8
Childs River	11.2	21 March 2002	0.46	0.09	0.14	0.29	0.32	1.4
	12.0		0.58	0.21	0.15	0.37	0.56	-6.2 [†]
	24.2		0.49	0.10	0.13	0.35	0.28	4.2
	26.0		0.41	0.09	0.09	0.34	0.27	4.7
	29.3		0.30	0.06	0.07	0.34	0.18	14.8
Sage Lot Pond	29.0	14 March 2002	0.29	0.05	0.09	0.29	0.16	20
	29.0		0.36	0.05	0.08	0.40	0.13	26
	29.9		0.59	0.07	0.10	0.38	0.19	13.7
	29.9		0.39	0.03	0.08	0.41	0.07	70.8 [‡]
<i>June/July</i>								
Quashnet River	0.2	27 June 2002	0.05	0.01				
	4.6		0.20	0.05	0.11	0.21	0.22	9.2
	5.0		0.24	0.04	0.09	0.19	0.21	10.4
	10.2		0.52	0.09	0.14	0.39	0.23	8.6
	10.0		0.51	0.09	0.12	0.34	0.26	5.7
	15.7		0.67	0.09	0.18	0.57	0.16	19.1
	16.2		0.62	0.12	0.18	0.49	0.24	7.4
	20.8		0.85	0.12	0.21	0.61	0.19	13.6
	20.8		0.74	0.14	0.18	0.62	0.22	9.8
	27.1		0.87	0.09	0.20	0.71	0.13	28
	26.0		0.86	0.13	0.19	0.62	0.22	10
	30.3		0.94	0.11	0.20	0.77	0.15	22.6
	29.8		0.95	0.13	0.20	0.79	0.16	18.8
Childs River	0.6	05 July 2002	0.36	0.11	0.18	0.28	0.38	-1.4 [†]
	6.0		0.49	0.18	0.21	0.52	0.33	0.7
	4.9		0.45	0.12	0.20	0.40	0.30	2.3
	15.4		0.70	0.13	0.22	0.65	0.19	13.2
	14.9		0.65	0.14	0.20	0.62	0.22	9.6
	12.4		0.71	0.20	0.21	0.62	0.32	1.5
	12.7		0.77	0.14	0.21	0.54	0.26	5.8
	20.9		0.90	0.15	0.20	0.70	0.22	10
	19.8		0.79	0.14	0.24	0.72	0.19	13.7
	24.7		1.01	0.18	0.22	0.73	0.25	6.4
	24.7		1.03	0.16	0.22	0.80	0.20	12.6
	27.7		1.02	0.14	0.22	0.72	0.20	12.8
	27.4		0.86	0.14	0.18	0.68	0.21	10.7
Sage Lot Pond	28.2	05 July 2002	1.12	0.14	0.17	0.76	0.18	15.3
	28.0		1.05	0.13	0.20	0.80	0.16	19.9
	31.5		1.45	0.15	0.21	0.95	0.16	20
	31.5		1.52	0.14	0.23	1.00	0.14	25.6
<i>August</i>								
Quashnet River	9.6	27 August 2002	0.41	0.08	0.15	0.29	0.27	4.8
	17.1		0.76	0.12	0.22	0.60	0.20	12.8
	20.8		0.76	0.11	0.15	0.47	0.22	9.3
	25.5		0.95	0.12	0.15	0.60	0.19	13
	30.3		0.98	0.14	0.17	0.52	0.26	5.4
Childs River	1.1	27 August 2002	0.41	0.08	0.12	0.41	0.20	11.8 [‡]
	22.3		0.78	0.12	0.14	0.54	0.23	8.7
	25.3		0.98	0.16	0.20	0.58	0.27	4.6
	28.7		0.72	0.11	0.14	0.57	0.20	12.7
	10.9		0.59	0.12	0.16	0.40	0.30	2.6
	15.1		0.82	0.17	0.19	0.54	0.31	2.3
Sage Lot Pond	31.5	29 August 2002	1.25	0.16	0.19	0.84	0.19	13.2
	31.6		1.37	0.16	0.21	0.73	0.22	9.7
	31.7		1.20	0.11	0.17	0.75	0.15	22.6
	31.7		1.15	0.14	0.09	0.42	0.34	0.5
<i>October</i>								
Childs River	14.0	23 October 2002	0.56	0.11	0.13	0.38	0.29	3.2
	20.5		0.68	0.13	0.16	0.48	0.27	5
	0.7		0.40	0.09	0.14	0.21	0.41	-2.5 [†]
	5.5		0.53	0.11	0.17	0.32	0.34	0.5
	8.1		0.61	0.12	0.18	0.46	0.26	5.3

Table 2 (continued)

	Salinity ‰	Date	²²⁴ Ra	²²³ Ra	²²⁶ Ra	²²⁸ Ra	²²³ Ra/ ²²⁸ Ra	Age (d)
<i>October</i>								
Childs River	27.0		0.75	0.09	0.11	0.44	0.20	12.3
	29.6		0.61	0.06	0.13	0.53	0.12	31.4 [‡]
Quashnet River	22.2	24 October 2002	0.66	0.12	0.12	0.41	0.28	3.8
	24.1		0.88	0.15	0.13	0.50	0.30	2.7
	9.8		0.33	0.06	0.11	0.31	0.20	12.7
	13.8		0.31	0.03	0.11	0.28	0.12	32.6 [‡]
	4.0		0.17	0.03	0.08	0.16	0.18	15
	0.4		0.06	0.02	0.04	0.08	0.25	6.8
	29.0		0.74	0.08	0.14	0.42	0.20	11.7

[†] Negative ages were not included in plots.

[‡] Indicates statistical outliers, mean residual is 2 standard deviations larger than what would be expected from fitting the correct model, and were not included in plots.

was also true for average ratios from piezometers (²²³Ra/²²⁸Ra = 0.34) and seepage meters (²²³Ra/²²⁸Ra = 0.38). Therefore, we used a grand mean ²²³Ra/²²⁸Ra activity ratio of 0.35 (Table 1) for determining model ages in our estuary samples.

3.4. Application of Age Models to Waquoit Bay sub-estuaries

Water mass ²²³Ra/²²⁸Ra ages calculated from Eqs. (1) and (2) and using an endmember activity ratio of 0.35 show: (1) age increased with salinity and (2) “mummy” model ages that were younger than those calculated using the “continuous input” model (Fig. 5). Since the “continuous input” model was more appropriate for these shallow systems, it is likely that the difference in ages between the two models is due to additional inputs after the water mass has left the sediment/water interface. This is based on the knowledge that there are significant groundwater inputs along the periphery of the sub-estuaries (Valiela et al., 1997a, 1997b, 2000) and the fact that sediments most likely provide additional sources of radium along the length of the estuaries. Both factors are likely exaggerated by the relatively small volume of the estuaries relative to the potential source fluxes.

To assess whether or not there was sufficient time available for blooms to occur, we compare previously reported estimates of residence time and flushing (Table 3) along with water mass ages calculated with the continuous input model, using ²²³Ra/²²⁸Ra. The mean age (± stdev) of water in Childs River, Quashnet River, and Sage Lot Pond was ~7 ± 4.7, 11 ± 6.2, and 17 ± 7.5 days, respectively. These are considerably longer timescales than what hydrodynamic and tidal prism models suggested (Table 3). Published values for flushing and residence time in Childs River and Quashnet River estuaries might be impaired because bathymetric data used were limited to the lower 2/3 and 1/3 portions of the estuaries, respectively, and so

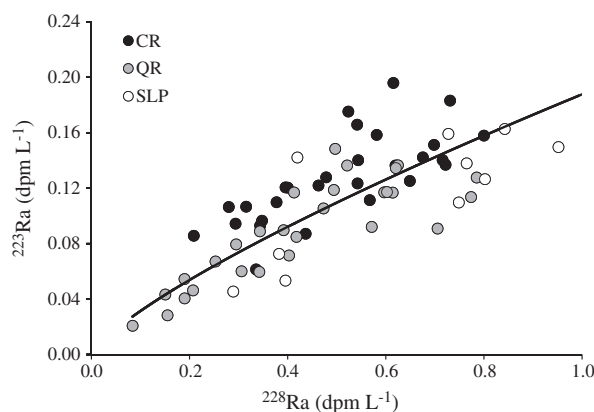


Fig. 2. Relationship between ²²³Ra and ²²⁸Ra in estuarine surface water samples. *R* = 0.71 for the regression of all surface samples (power curve fit).

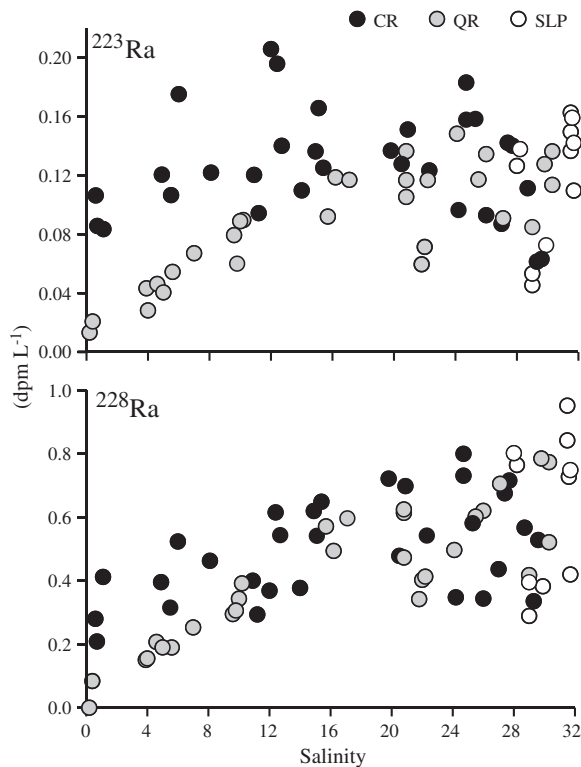


Fig. 3. Relationship between ²²³Ra and ²²⁸Ra and salinity in each of the sub-estuaries.

did not include upper portions of the estuaries. Additionally, return flow, which is accounted for with the Ra approach, is not always implicit in certain model formulations such as those reported by Geyer (1997).

It is interesting that Childs River and Quashnet River had similar average ages because the Quashnet River watershed is ~2 times larger than that of Childs River, which roughly translates into more groundwater delivery. Even though the Quashnet River watershed is larger there are several major constrictions in flow (Geyer, 1997) that, in theory, could inhibit exchange rates. Additionally, the average width and depth of Childs River in the polyhaline reaches is significantly wider and deeper than in Quashnet River, which could account for more rapid exchange in the Childs River. Therefore, we suspect the range of ages in Quashnet River are older than Childs River most likely because there is considerably more freshwater delivery by

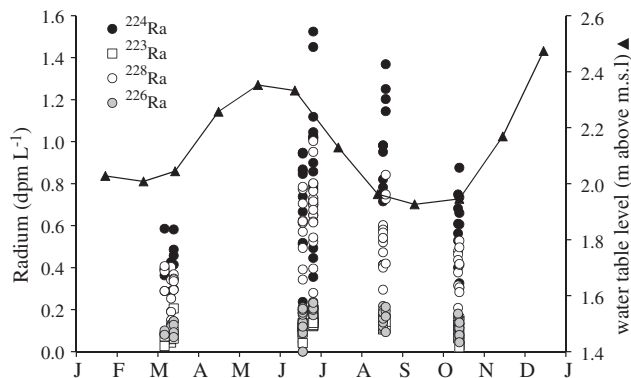


Fig. 4. Seasonal distribution of ²²⁴Ra, ²²³Ra, ²²⁸Ra, and ²²⁶Ra in estuarine surface water compared to water table elevations and bottom water temperatures. Water table height (m) relative to mean sea level, data from USGS site number 413525070291904, site name MA-MIW 29 Mashpee, MA, location Latitude 41°35'25", Longitude 70°29'19". This is the closest USGS monitoring well located near the sampling locations. Data can be found at <http://waterdata.usgs.gov/nwis/inventory>.

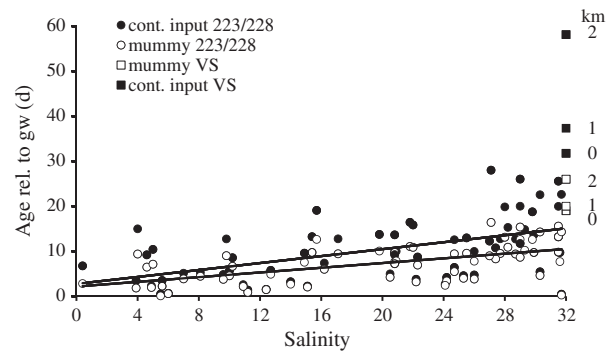


Fig. 5. Comparison of water mass age relative to groundwater and salinity using the 2 different models to calculate age. Open and closed circles are for surface waters in the sub-estuaries and open and closed squares are for samples collected in Vineyard Sound (VS) by Charette et al. (2001) 0, 1, and 2 km offshore. The continuous input model $R = 0.53$; the mummy model $R = 0.58$.

both groundwater (Cambareri and Eichner, 1998) and river input to the system and there is more travel distance in the upper reaches of the Quashnet compared to Childs River. The average age of Sage Lot Pond water is older because: 1) there is considerably less groundwater input to the system and 2) there is more exchange with adjacent older Waquoit Bay and Vineyard Sound water masses (Charette et al., 2001).

3.5. Application of age models to phytoplankton distribution and growth rates

Phytoplankton concentrations peaked within an age range of 8 to 12 days in Childs River and Quashnet River, respectively irrespective of phytoplankton size-fraction (Fig. 6). The concomitant decrease in chlorophyll and increase in age > 12 days is brought on by the mixing of adjacent Vineyard Sound water that is 1) older, 2) lower in nutrient concentrations, and 3) relatively depleted in chlorophyll relative to the sub-estuaries (Lawrence et al., 2004). Furthermore, the expression of biomass is most likely dependent on the combined effect of how long the phytoplankton have been in estuaries, nutrient concentration in the water, and lack of grazing pressure on the phytoplankton community.

Eppley (1972) described a model of phytoplankton growth based on temperature and a basic exponential growth equation, $P_t = P_0 e^{(\mu * t \text{ day})}$ (J. Kremer, WBLMER unpublished data), where P_t is phytoplankton population remaining after time (1 day), P_0 is the initial phytoplankton population, and μ is the phytoplankton growth rate ($\mu = 0.81e^{0.0633 * T}$ where $T = \text{temperature}$). With this equation we evaluated the expected growth rate for different flushing scenarios (30%, 50%, and 75%; equivalent to 3.3, 2.0, and 1.3 day residence times, respectively) to determine if a population

Table 3
Estimates of flushing times and residence times in the Waquoit Bay sub-estuaries and water mass ages measured in this study.

Location	Time (d)	Method	Reference
Childs River	0.8–2.7	Flushing time	Geyer (1997)
Quashnet River	0.6–1.0	"	"
Childs River	2.04–4.09	Tidal prism	Valiela et al. (2004)
Quashnet River	1.31–2.61	"	"
Sage Lot Pond	1.98–3.96	"	"
Childs River	2.3	2-D Hydrodynamic model	Tatsu Isaji, unpublished data
Quashnet River	1.7	"	"
Sage Lot Pond	1.5	"	"
Childs River	6.3–9.6 (7.8)	Water mass age	This study
Quashnet River	8.9–14 (11)		
Sage Lot Pond	12–20 (17)		

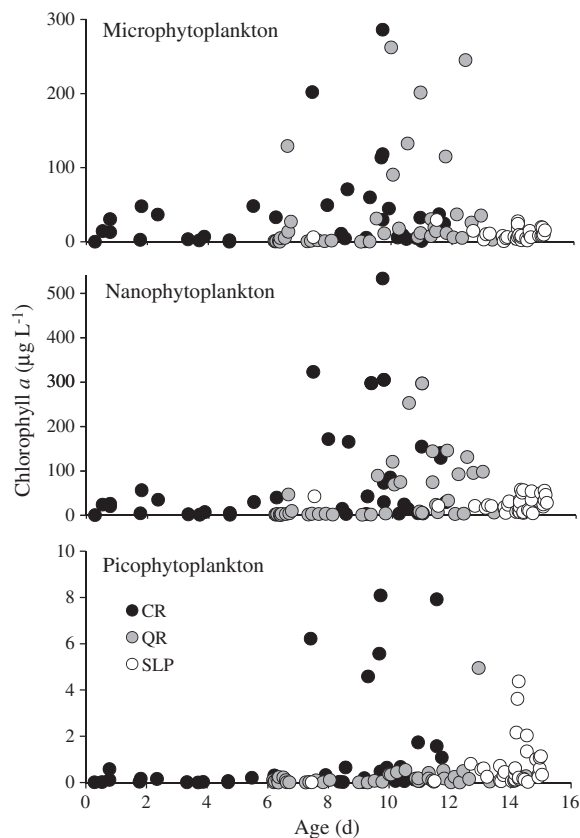


Fig. 6. Relationship between size-fractionated chlorophyll *a* concentrations and water mass age. Chlorophyll *a* was measured from February–October 2002 by flow cytometry. For detailed description of methods and sampling protocol see (Tomasky-Holmes, 2008).

could persist and accumulate under the specified flushing scenarios. Model results suggest that a population could withstand 75% daily loss (1.3 day residence time) when doubling times are $\sim 2 \text{ day}^{-1}$ (Fig. 7a); according to the Eppley curve, doublings of 2 day^{-1} occur at 24°C (Fig. 7a), the temperature associated with late summer (August) in the Waquoit Bay sub-estuaries. Conversely, for March, when growth rates are predicted to be $\sim 0.5 \text{ day}^{-1}$ (2°C), providing residence times are greater than 3.3 days (30% flushing), the radium-derived ages are still sufficiently long enough to maintain a phytoplankton bloom. While this model would have predicted non-optimal phytoplankton growth conditions within the Childs and Quashnet River sub-estuaries for the relatively low physical model-based estimates of residence time (Table 3), the radium based estimates are sufficiently high implying that a process other than estuarine mixing limits primary productivity in these systems.

To apply this to actual data from the sub-estuaries we used measured average monthly temperatures and predicted growth rates (doublings day^{-1}) from Fig. 7a, and then applied the different doubling times for each month to the measured concentrations of chlorophyll starting in February 2002. These predicted concentrations compared to measured concentrations were similar in Childs and Quashnet River, the more enriched estuaries (Fig. 7b), suggesting phytoplankton blooms may be driven primarily by temperature. Nutrients were also important, as can be seen by the lack of agreement between predicted chlorophyll and measured chlorophyll in Sage Lot Pond (Fig. 7b) where dissolved inorganic nutrient concentrations and N to P ratios suggested phytoplankton were nitrogen-limited during summer (Tomasky-Holmes, 2008). Additionally, grazers are also likely to play a role in mediating the response of phytoplankton to nutrient supply and circulation time but their role was not addressed in this work. Temperature and nutrients seem to be major

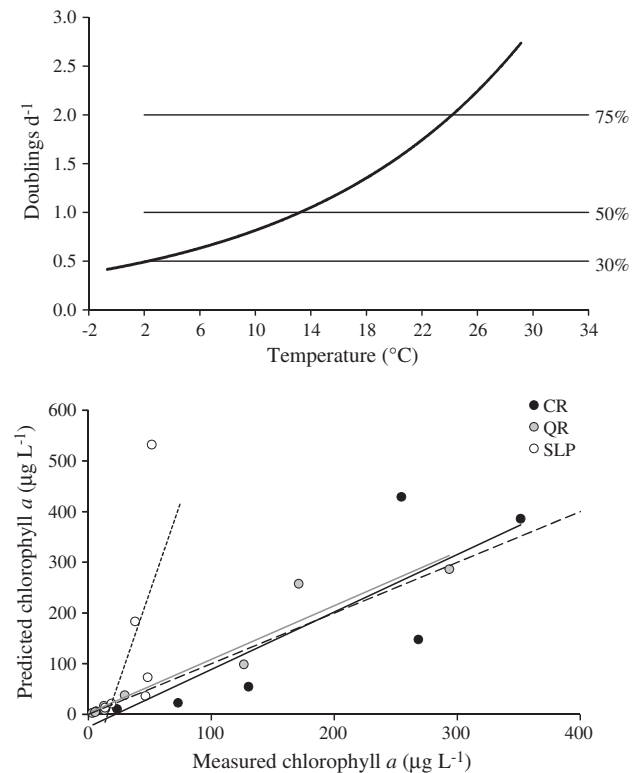


Fig. 7. A: Eppley (1972) curve of phytoplankton growth and temperature. Horizontal lines indicate growth rate at which populations can withstand 75%, 50% and 30% loss daily (J. Kremer WBLMER unpublished data). B: Comparison of extrapolated and measured concentrations of chlorophyll *a* in Childs River, Quashnet River, and Sage Lot Pond. Large dashed line, black line, gray line, and small dashed line are the 1:1 and regression lines for Childs River, Quashnet River, and Sage Lot Pond respectively.

controls setting the stage for phytoplankton blooms, but their effects were modified to some degree by rapidity of water flows through the Waquoit Bay estuaries.

Using the continuous Ra input model to calculate age provided estimates that consider nearly all sources of radium entering the estuarine system. The resulting estimates are of integrated age, since any one parcel of water along a salinity gradient can be a mixture of older and younger water. Desorption of Ra isotopes from fresh particles (not previously exposed to brackish water) may over-estimate age in the oligo- and mesohaline portions of the estuary; ages determined using ^{223}Ra do not seem to be significantly affected by this process, though future studies should experimentally test its relative effect on model ages.

Using radium to measure water mass age provided estimates that were longer than those obtained with other methods, long enough to allow phytoplankton to grow within estuaries such as those in Waquoit Bay during late spring, early summer. At other times of year temperature, nutrient supply, light availability (and perhaps grazing) limited primary production, even though there was enough time for phytoplankton to grow. These results suggest that radium-derived age models, which are similar to artificial tracer-based approaches, may be a very useful method for studying the role of hydrodynamics on estuarine ecology.

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