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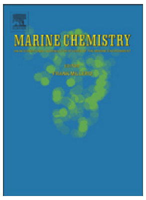

Determination of water mass ages using radium isotopes as tracers: Implications for phytoplankton dynamics in estuaries

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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 (±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.

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}Ra/^{228}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 ~1 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 (0.2–0.8 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 (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 W 31′ 33.30″ 41 N 34′ 52.44″ (Fig. 1). The Waquoit Bay sub-estuaries are shallow (on average <1 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

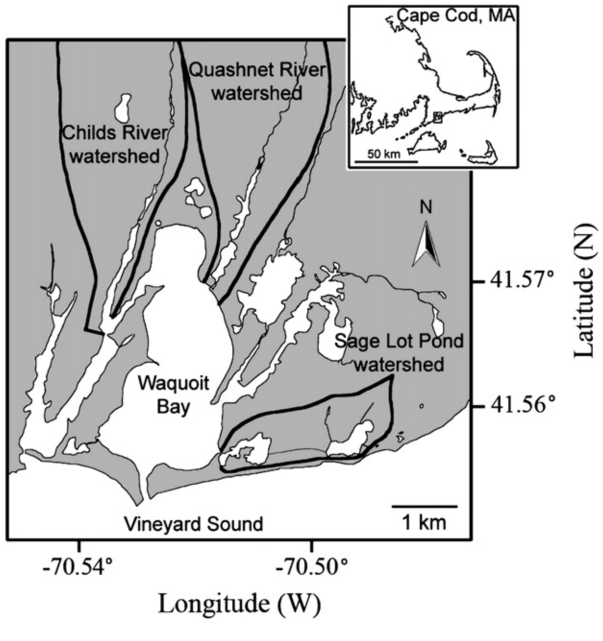

Fig. 1. Map of the Waquoit Bay sub-estuaries where surface radium samples were collected along an estuarine transect in each of the sub-estuaries. Not shown are the locations of the groundwater samples and piezometer samples from various locations in the sub-estuaries.