Coupled radon, methane and nitrate sensors for large-scale assessment of groundwater discharge and non-point source pollution to coastal waters

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Abstract

We constructed a survey system of radon/methane/nitrate/salinity to find sites of submarine groundwater discharge (SGD) and groundwater nitrate input. We deployed the system in Waquoit Bay and Boston Harbor, MA where we derived SGD rates using a mass balance of radon with methane serving as a fine resolution qualitative indicator of groundwater. In Waquoit Bay we identified several locations of enhanced groundwater discharge, out of which two (Childs and Quashnet Rivers) were studied in more detail. The Childs River was characterized by high nitrate input via groundwater discharge, while the Quashnet River SGD was notable but not a significant source of nitrate. Our radon survey of Boston Harbor revealed several sites with significant SGD, out of these Inner Harbor and parts of Dorchester Bay and Quincy Bay had groundwater fluxes accompanied by significant water column nitrogen concentrations. The survey system has proven effective in revealing areas of SGD and non-point source pollution.

Keywords: non-point source pollution, submarine groundwater discharge, methane, radon, nitrate, Waquoit Bay, Boston Harbor

1. Introduction

Recent estimates suggest that groundwater discharge into coastal waters worldwide represents up to one tenth of the total river flow, in some areas it might be as high as one third of the river discharge (Moore, 1996; Dulaiova et al, 2006). Expanding residential and commercial near-shore development is leading to increased nutrient inputs to groundwater that eventually migrate into to coastal waters. Several-decades long research shows that nitrogen inputs via non-point sources over large coastline areas cause decline of ecological health and may support harmful algal blooms (Valiela et al., 1990; 1992; Slomp and Van Cappellen, 2004; Lee and Kim, 2007; Umezawa et al., 2008).

Current methods to directly measure submarine groundwater discharge (SGD) and corresponding nitrogen fluxes (benthic chambers, seepage meters) are inadequate because groundwater discharge is heterogeneous in location and composition, and occurs over large areas (Burnett et al., 2006). The flow is spatially variable, with water preferentially discharging through conduits in sediments or rocks. Its magnitude is also influenced by temporal variability on tidal and seasonal time scales (Dulaiova et al., 2006, Kim and Hwang, 2002). Marine processes like tides and waves, seasonal declines in hydrologic head in coastal aquifers, and dispersion drive seawater into these aquifers. This water eventually discharges back to the surface creating a second, saline component of submarine groundwater discharge that enhances nutrient transport from the land to the coastal zone (Robinson et al., 2003).

Our previous research showed that quantitative estimates of the magnitude of submarine groundwater discharge on a local scale can be obtained from tracer studies (Burnett and Dulaiova, 2003; Burnett et al., 2006). Due to their enrichment in

groundwater relative to surface water, radon and methane serve as universal indicators of both fresh groundwater and recirculated seawater inputs into the coastal zone. Elevated concentrations of these tracers in coastal waters indicate areas where groundwater outcrops to the surface.

The utility of ^{222}Rn as a tracer of total SGD has been demonstrated in a wide range of environments from coastal embayments to the coastal ocean (Charette et al., 2008). Rn-222 is a naturally occurring radioactive element with a half-life of 3.8 days. As a non-reactive noble gas its only losses from the water column are due to radioactive decay and evasion to the atmosphere. Because groundwater is in contact with radon emanating aquifer material, ^{222}Rn activities in groundwater are often about two to three orders of magnitude higher than most surface waters. Groundwater becomes enriched in radon independently of its composition (fresh water or seawater) so radon is a tracer of total SGD driven by both terrestrial and marine forces (Dulaiova et al., 2008). If a groundwater source is present in a coastal environment it is likely to be the only radon input of significant magnitude to surface water, which makes this tracer very useful for identifying areas of groundwater input into lakes, rivers and the coastal ocean (Cable et al., 1996; Burnett et al., 2002; Burnett and Dulaiova, 2003).

Methane has successfully been employed as a tracer of groundwater inputs into near-shore waters along the coast of the northeastern Gulf of Mexico (Bugna et al., 1996 and Cable et al., 1996), Florida Bay (Corbett at al., 2000), Long Island (Dulaiova et al., 2006), and Korea (Kim and Hwang, 2002). Being subject to biological processing, methane is not a conservative tracer though it has proven to be useful where its concentration in groundwater highly exceeds methane inventories in the water column.

Recent technological advancements have enabled high resolution, continuous measurement of these tracers for large-scale mapping of coastlines. Such measurements using radon monitors have been previously applied (Burnett and Dulaiova, 2003) but only as qualitative surveys to identify SGD hot-spots; none of these studies derived quantitative SGD rates – a major goal of the research described herein. The objectives of our study were to: 1) construct a radon/methane/nitrate mapping system that measures the concentrations of these components in the surface water in-situ with an increased resolution over conventional systems, 2) use tracer data to identify SGD hot-spots and develop a model for its quantitative determination, and 3) assess the importance of SGD with regards to coastal nitrogen budgets and non-point source pollution.

2. Methods

Our mapping system consists of several component instruments. One of these instruments is a modified radon surveying system (Dulaiova et al., 2005), which consists of 3 commercially available radon-in-air analyzers (RAD7, manufactured by Durridge, Inc., Massachusetts) employed to measure ^{222}Rn from a continuous stream of water passing through an air-water exchanger that distributes radon from the running water to a closed air loop. The exchanger, which takes about 15 minutes to reach full equilibrium in the loop, causes a relatively slow response to changes in radon activities in water. The other disadvantage of the exchanger is that it has a memory-effect due to sluggish flushing of radon from the closed loop. To improve the response time of the system we replaced the air-water exchanger with a membrane contactor (Liquicel, manufactured by Membrana), which is a set of hollow fibers made of a hydrophobic membrane that allow

87 radon and other gases to pass from water into the air phase. The cell is used as a single-
88 pass open system which has a much shorter memory-effect and requires no wait time for
89 equilibrium. We calibrated the membrane radon stripping efficiency at variable water
90 flow rates though the membrane (1-15 L min^{-1}) and also by varying the water temperature
91 by heating the water to different temperatures between 5 and 30 ^{o}C. For these tests we
92 used groundwater sampled from a well containing 300 dpm L^{-1} radon. We constructed
93 calibration curves of stripping efficiency against water flow-rate and temperature and
94 these curves were used to calculate field data during the surveys. The water flow-rate
95 through the membrane and water temperature in the field were constantly monitored
96 during the survey. During our surveys in Waquoit Bay we included a 10 μm and 1 μm
97 cartridge filter (Osmonics) upstream of the membrane.
98 Methane was measured using a TETHYS in-situ underwater mass spectrometer
99 that was operated on a towed platform from a small coastal boat, providing real-time data
100 to a top-side computer. The TETHYS instrument is capable of measuring dissolved gases
101 and volatile light hydrocarbons at sub ppb levels, with sampling intervals on the order of
102 5 seconds for most gases. This technique has been used for ocean floor methane seep
103 mapping in marine environments (Camilli and Duryea, 2007; Mau et al., 2007). For these
104 investigations the mass spectrometer was equipped with an integrated CTD (model
105 SBE49 FastCAT, SeaBird Electronics Inc., Bellevue, Washington, USA) provided
106 continuous flow sample introduction at a rate of approximately 3 ml s^{-1}, along with
107 external salinity, temperature and pressure data.
108 The towed survey was carried out with the mass spectrometer operating at depths
109 between one and three meters. During the survey deployment over 500 discrete sample

measurements of ion peak heights were recorded at m/z 15 as an indicator of relative methane intensity. In addition to the methane time series data, ion peaks at m/z 17, 28, 32, 40, and 44 were recorded to identify relative changes in gases corresponding, respectively, to water vapor, di-nitrogen, oxygen, argon and carbon dioxide. The methane ion peak intensity (m/z 15) was then normalized to water vapor intensity (m/z 17) in order to generate a temperature normalized methane intensity estimate. Spectral sweeps across the instrument's full mass range (2-200 AMU) were performed at selected sites to identify any potential contributions from anomalous gases or volatile hydrocarbons.

The survey system is also complemented by a commercially available automated nutrient analyzer (W. S. Envirotech Ecolab) to measure water column nitrate + nitrite concentrations. Other auxiliary measurements include salinity and temperature, which may aid in identifying the nature of groundwater discharge (fresh meteoric water or recirculated seawater). During the surveys the instrument cluster was positioned on a small coastal vessel. Each instrument had an independent water intake pump located at 1 m below the surface. The vessel's track was logged using a Garmin global positioning system in 10 second intervals. Post processing of data involved synchronous merging of TETHYS data, radon, salinity, temperature, and nitrate values with GPS tracklog files. Due to varying latency of the instruments, each parameter was measured in different logging intervals. Radon was usually measured in 5 minute integrated intervals, methane including salinity and temperature every 30 seconds, and nitrate was sampled once every 6 minutes. Therefore in the final results the radon profile is spatially smoothed in comparison to the methane and salinity data that were sampled in much shorter time increments.

In stationary mode we only deployed the radon, salinity and temperature logging systems. In these studies nutrients samples were hand-collected, filtered and kept frozen until analysis. Concentrations of phosphate, nitrate, ammonium, and silicate in hand-collected samples were measured colorimetrically, using a Lachat nutrient auto-analyzer (Hach, Quickchem© 8000 Series).

3. Study sites

We deployed the mapping system in Waquoit Bay, MA (Fig. 1), an area with extensive prior hydrological and geochemical SGD data sets. Waquoit Bay is a shallow estuary on the south shoreline of Cape Cod, MA. The geologic deposits on Cape Cod consist of outwash gravel, sand, and silt with occurrences of lacustrine deposits of silts and clays (Cambareri and Eichner, 1998). Waquoit Bay receives groundwater from the Cape Cod aquifer, which is an unconfined aquifer, approximately 100 to 120 m thick and it is bounded by marine water at its margins and less permeable deposits of till and bedrock below. The bay is located along the southern margin of the Sagamore Lens, which is part of the Cape Cod Aquifer. A significant portion of the freshwater input into Waquoit Bay occurs as submarine groundwater discharge (Valiela et al., 1990; Cambareri and Eichner, 1998; Charette et al., 2001). False color imagery of surface temperatures recorded during September 2002 indicate several locations of groundwater discharge into the bay (Mulligan and Charette, 2006). Zones of high groundwater discharge are known to be present in Childs River and down gradient of bluffs along the head of the bay (Mulligan and Charette, 2006). Seepage meter studies indicate that in this area SGD occurs in a narrow (~30 m wide) band (Michael et al., 2005). Radon is more than two

156 orders of magnitude enriched in fresh and saline groundwater relative to surface water
157 (Dulaiova et al., 2008) and the estimated seepage flux determined by a continuous radon
158 model ranges between 0.6 to 5.6 m^3 m^{-1} d^{-1} (Mulligan and Charette, 2006) and is 5.3 m^3
159 m^{-1} d^{-1} based on a ^{226}Ra box model (Charette et al.,2001). The presence of high SGD
160 enriched in both radon and nitrate makes Waquoit Bay an ideal testing site for the
161 mapping system. Using this information about the spatial distribution of SGD we were
162 able ground-truth the sensitivity and resolution of our instruments.
163 In order to contrast seasonal changes in SGD and nutrient inputs, we deployed the
164 complete system to survey the whole periphery of Waquoit Bay on two occasions
165 (August 2006 and December 2006) and we also did a time series stationary monitoring
166 over a 13-hour period simultaneously in two locations as indicated on Figure 1: in Childs-
167 and Quashnet Rivers (September 2007).
168 Following the Waquoit Bay studies we surveyed Boston Harbor, MA and its
169 estuaries (June 2008). The harbor is relatively shallow with an average depth of
170 approximately 5 m, and is well flushed by strong tides, with an average water residence
171 time of five to seven days (Jiang and Zhou, 2008). Our sampling included a stationary
172 long-term monitoring at the University of Massachusetts, Boston dock near Savin Hill
173 Cove for the period between May 2 and June 4, 2008 (Fig. 1). In these Boston Harbor
174 studies the mass spectrometer was not available and the radon monitor was operated with
175 the traditional air-sea exchanger because the water contained significant amounts of
176 suspended matter that clogged the membrane contactor.
177 Boston Harbor was chosen as a more complex environment to demonstrate that
178 the mapping technique is applicable to both surficial and groundwater nitrogen inputs.

Furthermore, despite of the recent improvements in water quality (relocation of the city's sewage outfall offshore), non-point source pollution from SGD and potential relict sewers or combined sewer overflow (CSO) systems are poorly characterized. Greater understanding of submarine groundwater discharge and its spatial distribution throughout the harbor is useful because of the potential for mobilization of contaminants from the highly contaminated (lead, mercury, silver, anthropogenic organic pollutants) bottom sediments (McGroddy and Farrington, 1995; Stolzenbach and Adams, 1998; Eganhouse and Sherblom, 2001), which are the conduit for SGD. Therefore even small fluxes of SGD may be biogeochemically significant if contaminant concentrations are enhanced in groundwater.

4. Results and Discussion

4.1 Resolution of tracer surveys

The mapping system provides in-situ estimates of radon and methane concentrations in real-time during mapping. This makes it possible to efficiently identify and focus measurements at sites where SGD is occurring, thereby providing better estimates of tracer distributions and the spatial extent of groundwater discharge. This new system has the advantage of a better spatial resolution due to the high resolution methane sampling (every 30 seconds) and an improved radon mapping system. Ultimately the spatial resolution for each of the system's component technologies is a function of sampling interval and survey velocity.

We demonstrated that the continuous radon monitor equipped with the membrane contactor has quicker response and less memory effect than the traditional system,

providing better sensitivity to changes in surface water radon activities (Fig. 2). In laboratory conditions the new Liquicel-RAD7 design minimizes response latency because radon is flushed from the system about 4 times faster than from the air-water exchanger (Fig. 2).

Similar results were demonstrated during a field survey in Waquoit Bay where we deployed the two radon measurement systems simultaneously. Figure 3a shows that the system equipped with the membrane responded to radon increases by 5 minutes, and decreases about 15 minutes quicker than the system attached to the air-water exchanger. Despite the Liquicel membrane's advantages for high-resolution radon sampling, it is disadvantageous in that it requires a much more rigorous calibration of radon stripping efficiency with temperature and water flow-rate than the air-water exchanger. Furthermore, the membrane only works in environments with lower fine particulate concentration. During times of high seasonal productivity the membrane clogs quickly, the water flow is restricted and this results in lower radon stripping efficiency.

4.2 SGD rates derived from tracers

Unlike radon, methane is a non-conservative gas and its concentration may be influenced by microbial and biochemical processes during which it can be produced or consumed in the sediments and water column. It is therefore only useful in areas where a significant concentration gradient exists between groundwater and surface water, in principle, when there is enough anaerobic organic matter decomposition in the aquifer. Correspondingly, groundwater redox pε measured in the subterranean estuary at the head of Waquoit Bay in June 2004 was 1.4 to 7.5, and methane concentrations were 20 to 300

225 nM (Charette and Camilli, unpublished results). The samples were collected across the
226 whole salinity gradient (0 to 27) and methane was found in both fresh and saline
227 groundwaters supporting the assumption that methane is a useful tracer for fresh
228 groundwater and recircuated seawater discharge. We tested the applicability of methane
229 as SGD tracer in Waquoit Bay by measuring water column radon and methane
230 simultaneously. We expected that the tracers would have similar spatial distribution if the
231 source of methane was the same as of radon, i.e. groundwater discharge. Indeed, as
232 demonstrated in Figure 3b that is the case, but with the methane data providing a better
233 spatial resolution than radon due to the more frequent methane sampling rate.
234 Differences between the two tracer patterns are likely due to the different sampling
235 intervals (radon being smoothed out spatially) and the non-conservative nature of
236 methane (biochemical sources and sinks in the water column and sediments). Our results
237 from Waquoit Bay demonstrate that in this environment the two tracers complement each
238 other in that methane enables a very fine spatial resolution and radon provides positive
239 identification of SGD origin, confirming SGD as the source of methane.
240 We next evaluate the usefulness of these tracers in assessing the spatial
241 distribution of SGD. The concentration of radon/methane in the water column will
242 depend on several factors (Fig. 4):
243 1) in-situ production by ingrowth from ^{226}Ra, radon's radioactive parent dissolved in
244 water/ biogeochemical reactions; 2) inputs by diffusion, sediment resuspension,
245 bioturbation, or gas ebullition from sediments; 3) input by groundwater discharge; 4)
246 removal by exchange with open ocean water (i.e., dilution with low radon/methane
247 offshore water); 5) removal by evasion from water to the atmosphere; 6) losses by

248 radioactive decay/biogeochemical reactions. Methane biogeochemical production in the
249 sediments and consequent ebullition and methane oxidation in the water column must be
250 considered as a potential source/sink. Hence, we only use this tracer in this study as a
251 qualitative indicator of SGD.

252 Continuous SGD tracer records (Rn, Ra, methane, Si and many others) show that
253 the highest tracer concentrations in the water column can usually be observed at or
254 around low tides (this study Fig. 5 for BH and Fig. 9 for WB; see also Dulaiova et al.
255 2006; Burnett and Dulaiova, 2003) . At flood tide the high-tracer coastal waters are
256 diluted by offshore low tracer water (process 4). Because of this dilution process we
257 observe low tracer concentrations at high tide. This pattern is also driven by a change in
258 the hydraulic gradient in the coastal aquifer in response to the tidal fluctuation that causes
259 lower hydrostatic pressure at low tides resulting in increased seepage and thus higher
260 tracer fluxes. To measure the best representative non-diluted coastal tracer inventories
261 we survey during low and ebbing tide.

262 We convert all radon and salinity measurements from our surveys into SGD
263 fluxes based on the following equations:

264 $$Q_{SGD_{tot}} = \frac{A_{Rn\_cw} * V}{\tau * A_{Rn\_gw}}, \quad (1)$$

265 and

266 $$Q_{SGD_{fresh}} = \frac{(S_o - S_{cw}) * V}{\tau * S_o}, \quad (2)$$

267 where $Q_{SGD_{tot}}$ and $Q_{SGD_{fresh}}$ are total (fresh and saline) and fresh submarine groundwater
268 discharge ($m^3\ d^{-1}$), A_{Rn_cw} and A_{Rn_gw} are radon activities in the coastal water corrected
269 for non-SGD sources and losses and groundwater (dpm m^{-3}). S_{cw} and S_o are coastal water

and offshore salinity. V is the volume of the coastal water box that the measurement represents (m^3) and τ is the flushing rate of the volume of water considered in the calculation.

Based on equation (1) the conversion of surveyed radon activity to groundwater fluxes into the coastal zone may be summarized by the following:

1) Radon activity in the coastal water (A_{cw}): Each radon measurement in the survey in this calculation is considered individually and is a representative of a segment of the coastline. This activity is corrected for the following non-SGD related sources and sinks of radon in the water column:

   a. We correct for in-situ production from dissolved ^{226}Ra by calculating excess radon as:

      Excess ^{222}Rn = total ^{222}Rn - ^{226}Ra (3)

   b. The amount of radon diffusing from the bottom sediments can be estimated from an experimentally defined relationship between ^{226}Ra content of sediments and the corresponding measured ^{222}Rn flux by diffusion (Burnett et al., 2003). That empirical relationship was derived from experimental data from several different environments (both marine and fresh), where

      Radon flux by diffusion (dpm m^{-2} day^{-1}) = 495 x ^{226}Ra activity + 18.2. (4)

      Bottom sediment ^{226}Ra activity in Waquoit Bay is <0.5 dpm g^{-1} (Gonneea et al., 2008) and the radon diffusion calculated from Eq. 4 is 125 dpm m^{-2} $tide^{-1}$. Diffusion therefore supports less than 3%

of the average measured radon inventory. We assume the same input for Boston Harbor.

c. Radon that is brought to the coast by incoming tides or upstream locations is eliminated from the radon balance by subtracting offshore or upstream radon activities from in-situ radon. This influence can be minimized or even neglected if the mapping is done at low tide and if the study site is well flushed with low-radon offshore waters at high tide.

d. Radon losses due to radioactive decay are calculated using the coastal water residence time (τ; defined below). Due to the short time scale of coastal mixing (here assumed to be tidal) the radioactive decay of radon represents a loss of only 9% over tidal cycle.

e. Atmospheric losses are calculated from measured wind speeds, water temperature and tracer concentration gradients between water and air (Burnett and Dulaiova, 2003):

$$F_{atm}=k(C_w-\alpha C_{atm}) \quad (5)$$

where C_w and C_{atm} are the radon activities in water and air, respectively; α is Ostwald's solubility coefficient; and k is the gas transfer velocity, a function of kinematic viscosity, molecular diffusion, and turbulence. In Waquoit Bay and Boston Harbor

atmospheric losses are responsible for 1-10 % of radon lost per tidal cycle from the total radon inventory.

2) For each measurement the volume of the coastal water box (V) is calculated from the length of the coastal segment, average water column or mixed layer depth, and the width of the seepage face. The length of the coastal segment is the half distance between the previous and following measurements of the survey and it is variable depending on the boat speed, for the surveys in WB it ranged between 10-300 m and in BH 100-300 m. Since radon is measured as an integrated value over this distance, it truly represents this section of the coastline. The width of the seepage face in Waquoit Bay was 30 m (Michael et al., 2005) and in the absence of better estimates we assumed the same for Boston Harbor. SGD can also be expressed as discharge per meter of coastline ($m^3\ m^{-1}\ d^{-1}$) in which case the volume of the coastal box in Eq. (1) and (2) is divided by the coastline length (half distance from the previous plus half distance from the following measurement).
3) The flushing rate (τ) of the coastal box is considered one tidal cycle (12.25 hours). This is based on our observation from a time series radon measurement in Boston Harbor (Fig. 5) that at high tide the radon values follow a baseline open bay activities indicating that the coastal box is flushed with every tidal cycle. We assume the same for Waquoit Bay. In case the mixing regime is significantly faster then tidal (i.e. due

to winds and currents) our SGD estimate will be conservative. For these reasons our assumption of mixing on the tidal time scale is more appropriate for our calculation than using the flushing rate of the whole harbor/bay which may be ~5-9 days for Waquoit Bay and 5-7 days Boston Harbor (Jiang and Zhou, 2008), respectively.

4) Groundwater Radon (A_{gw}): We used a groundwater end-member radon activity that was derived during a concurrent study of the subterranean estuary (STE) at the head of Waquoit Bay (Dulaiova et al., 2008) which was dedicated to the description of radon activity across the whole salinity gradient in the STE over 3 years. In this study we concluded that fresh groundwater has 120±40 dpm L^{-1} radon year round, while the recirculated seawater has 410±190 dpm L^{-1}. Based on the seasonal changes occurring in the STE 150 to 320 dpm L^{-1} was the most probable groundwater end-member radon activity range for total SGD. We arrived at this value from the expected fresh to saline groundwater ratio in discharging groundwater (Michael et al., 2005). This study has been the most comprehensive in terms of investigation of groundwater end-member activities to date in SGD studies in the literature and includes fresh and brackish to salty groundwater analysis. Hence we are confident that we use the best available radon value in our tracer survey SGD calculations. Still, our assumption here is that there is no large variability in end-member radon activities in the aquifer along the coastline. At study sites where one expects large geological

heterogeneity, groundwater radon should be measured for each coastal segment in order to lower the uncertainties of the final SGD calculation. One has to consider the benefits of such effort, because an order of magnitude variation in groundwater radon is required to generate an order of magnitude difference in SGD rates.

As mentioned earlier we surveyed for SGD tracers at low tide in order to have the least diluted water column by offshore waters during flood tide. At two sites in Waquoit Bay (Childs River and Quashnet River) we tested how the water radon inventory (radon activity[dpm m^{-3}] x depth[m]) changes over a tidal cycle. Theoretically, if there was no SGD and there were no currents and losses by mixing flood tide should dilute the radon but the water column inventory should stay the same. However, variable SGD, currents and mixing cause fluctuations in radon activity and we found that the radon inventories were 3,000 and 13,000 dpm m^{-2} at low tide and 4,700 and 8,500 dpm m^{-2} at high tide in Quashnet and Childs Rivers respectively. The observed 50% change in inventories is equivalent to 50% difference in the calculated SGD. These findings support that the most sensitive survey can be done at low tide when waters are least diluted and least influenced by mixing losses and we expect the highest SGD.

Radon provides an estimate of total SGD but it cannot be used to determine the fraction of fresh vs. saline groundwater discharge. In systems with little or no surface runoff it is possible to use salinity and Eq. (2) to calculate fresh SGD. This calculation uses some of the same terms (τ, V) and is based on similar assumptions as the radon approach described above. Additional assumptions in Eq(2) are that we neglect salinity changes due evaporation and rain. The salinity increasing effect of evaporative distilling

384 varies due to changes in water temperature, solar radiation, air humidity and wind speed.
385 It potentially influenced the salinity of the surface water in our summer season surveys
386 during which the water temperature was warmer (Waquoit Bay Sep06 average water
387 temperature was 24.5 ^{o}C and Boston Harbor Jul08 average temperature was 17.3 ^{o}C) than
388 during the winter survey (Waquoit Bay Dec06 average water temperature was 3.8 ^{o}C).
389 Still, we expect the influence of evaporation to be negligible (<0.1 ppt per tidal cycle;
390 Sumner and Belaineh, 2005) and in the salt balance calculation in Eq(3) we neglect
391 evaporation.

392 Although there are two rivers in Waquoit Bay, they are groundwater fed (Valiela
393 et al., 1990) and we used salinity in this system to calculate a rough estimate of fresh
394 SGD. We could not make the same assumption for Boston Harbor because several rivers
395 and streams deliver significant quantities of freshwater into the harbor. At both sites our
396 SGD estimates also include groundwater delivered to the bay/harbor by gaining streams
397 as these will have higher radon activities and our methods cannot differentiate radon from
398 local and upstream locations.

399 Tracer distributions in Waquoit Bay in Aug 06 and Dec 06 are plotted on Figure
400 6. The bay water was much fresher in Dec 06 than Aug 06 and the corresponding radon
401 and methane levels also suggest higher SGD in the winter. Based on these tracers, the
402 major sources of groundwater are in the Childs and Quashnet Rivers, and at the head of
403 the bay. Methane and salinity provide the best resolution and in some regions they
404 exhibit negative correlation suggesting the presence of fresh groundwater discharge
405 (Childs River). Radon provides assurance that the observed methane profiles are of
406 groundwater origin. As expected, the magnitude of SGD follows the radon and methane

distributions. Using equations (1) and (2) and the corresponding coastline length for each value we derived that maximum SGD rates occur in Childs River (5.5 $m^3 m^{-1} d^{-1}$ of total SGD in summer and some sections as high as 30 $m^3 m^{-1} d^{-1}$ in winter), followed by the head of the bay (2 and 3 $m^3 m^{-1} d^{-1}$ in the summer and winter, respectively). We expected elevated SGD in Quashnet River, but due to low water levels we were not able to survey it in such detail as the other parts of the bay. Total SGD fluxes for the whole bay based on radon groundwater activities of 120-310 dpm L^{-1} are 5.5-11x10^3 $m^3 d^{-1}$ in the summer and 28-56x10^3 $m^3 d^{-1}$ in winter. From that, fresh SGD rates are approximately 5x10^3 $m^3 d^{-1}$ in the summer and 8x10^3 $m^3 d^{-1}$ in winter, again these estimates are skewed by the presence of surface runoff. Our calculation of total SGD may also carry an uncertainty related to the change of flushing rate of the near-shore zones for the two different seasons (τ in Eq. (1) and (2)).

There have been several SGD studies in Waquoit Bay (Mulligan and Charette, 2006; Michael et al., 2003; Michael, 2004; Cambareri and Eichner, 1998) with which we can compare our results (Table 1). Our estimates for fresh (920 (Aug 06) and 2050 (Dec 06) $m^3 d^{-1}$) and total (2845 and 4292 $m^3 d^{-1}$) SGD for the head of the bay agreed very well with all previous studies (950 to 2419 $m^3 d^{-1}$). In Childs River our fresh SGD (2680 and 6159 $m^3 d^{-1}$) was very close to Cambareri and Eichner's (1998) estimate which is a representative of a yearly average (2740 $m^3 d^{-1}$). Our results for fresh SGD for the whole bay are lower than Cambareri and Eichner's (1998) and we believe that is because we could not properly survey Quashnet River and hence our estimates are missing a relatively large fresh SGD component.

Radon is used in the calculation of total SGD in Boston Harbor surveyed in Sep 08 (Fig. 7). In general, radon levels were elevated throughout the bay with several SGD hot-spots indicated by high radon in the Inner Harbor and Quincy Bay (red circles on Fig. 7). In some parts of the harbor radon and salinity showed a strong negative correlation suggesting the discharge of low salinity high radon groundwater (Inner Harbor), in the southern part of our survey (Quincy Bay) the lack of negative correlation between salinity and radon indicates the presence of mostly brackish/saline groundwater discharge.

SGD rates varied from 1.5 to 10 $m^3\ m^{-1}\ d^{-1}$. The highest fluxes occurred in the northern sectors of the harbor. This survey covered approximately 50% of the coastline in North Harbor and 10% in South Harbor. The corresponding SGD rates were $90x10^3$ $m^3\ d^{-1}$ and $20x10^3\ m^3\ d^{-1}$ in the surveyed sections. If extrapolated to represent discharge from the total length of coastline would be 11 and 39% of river discharge in the North and South Harbors, respectively (http://waterdata.usgs.gov/nwis/rt). These fluxes include the discharge of fresh and marine groundwater components. In comparison, total groundwater discharge determined from an earlier study in Quincy Bay (Wollaston Beach) ranged from 1.3 to $2.2x10^3\ m^3\ d^{-1}$ on a coast-perpendicular transect that was scaled up to represent a 4.6 km length of coastline. This flux was calculated to be equivalent to 7-12% of surface discharge (Poppe and Moffett, 1993). Our survey results at the Wollaston Beach suggest rates from 1.4 to $2.2x10^3\ m^3\ d^{-1}$ but our study also indicates that SGD is variable and the rate doubles in the southeast section of the beach. We expect that this spatial variability in SGD (Fig. 7) may explain the difference in

451 calculated groundwater to surface discharge ratios (i.e., our 39% estimate as opposed to
452 the 12% estimated by Poppe and Moffett, 1993).
453 Fresh SGD calculated based on the National Urban Runoff Program model
454 (Menzie et al., 1991) for the whole South Harbor is $41x10^3$ m^3 d^{-1} and the North Harbor
455 is $43x10^3$ m^3 d^{-1}, representing 8 and 3% of river discharge, respectively (Menzie et al.,
456 1991). These fluxes cannot be directly compared to our estimates because these are only
457 fresh groundwater discharge rates. Instead, we used these numbers to calculate the ratio
458 of fresh to total SGD from our survey. The modeled fresh SGD represents 23% of total
459 SGD in the North Harbor and 2% in South Harbor. We acknowledge that we did not
460 survey Hingham Bay where we expect an increase in SGD due to the presence of
461 marshes that focus groundwater discharge and are sites of intense tidally induced
462 groundwater circulation. Our total SGD estimate for South Harbor based on the survey
463 in Quincy Harbor (only 10% of total coastline length) is therefore probably
464 underestimated.
465
466 *4.3 Groundwater-derived nitrogen*
467 Considering that groundwater nutrient concentrations are usually elevated in
468 comparison to surface water it is important to examine SGD as source of nitrogen to
469 coastal waters. Our survey provides indirect evidence of these sources based on the co-
470 occurrence of elevated levels of nitrogen species and SGD hot-spots. The method proves
471 to be effective in distinguishing groundwater nitrogen fluxes from inputs from surface
472 runoff or other sources, because only the groundwater nitrate/ammonia is accompanied
473 by radon.

Simultaneous radon and dissolved inorganic nitrogen (DIN) measurements in the surface water can be simplified to the following scenarios:

1) *High radon - high DIN* are an indication of significant SGD with possible elevated groundwater nitrogen inputs;
2) *High radon – low DIN** are an indication of significant SGD with insignificant nitrogen inputs;
3) *Low radon – low DIN** are an indication of insignificant SGD and nitrogen inputs;
4) *Low radon – high DIN* are an indication of insignificant SGD and elevated nitrogen inputs from sources other than groundwater, i.e. surface water runoff and precipitation.

*Because nitrogen species water column residence time is highly dependent on seasonality (due to biological uptake), high surface water DIN can be observed before the spring bloom starts when nitrogen is not consumed quickly, and preferably at or around low tide when the groundwater signal is most evident. Therefore rather than comparing absolute concentration differences in coastal waters between summer and winter seasons, one should examine trends in DIN concentrations in correlation with SGD.

DIN concentration in Waquoit Bay was much higher in the winter than summer. In the summer, nitrate (the only measured N species) concentrations correspond nicely to variations in SGD throughout the bay (Fig. 8) and peak at 6 μM in the Childs River where total SGD rates also peak at 5.5 $m^3 m^{-1} d^{-1}$. Moderate groundwater fluxes in Quashnet River (2 $m^3 m^{-1} d^{-1}$) are not accompanied by significant nitrate concentrations. Winter nitrate concentrations are more evenly distributed with no apparent correlation with SGD. This may be due to rapid biological nitrogen uptake in the summer when any

497 new source would be apparent in excess of a low background concentration. In contrast
498 the winter nitrogen residence time in the surface water is much longer, allowing build-up
499 and more even distribution within the bay (Valiela et al., 1992). Another explanation is
500 that the nitrate+nitrite concentration is different in fresh and recirculated groundwater and
501 when the relative magnitude of fresh and recirulated groundwater discharge changes so
502 does the nitrate+nitrite concentration of the surface water (Kroeger and Charette, 2008).
503 To test the association of SGD and DIN inputs in detail, the two sites in Waquoit
504 Bay with the highest SGD rates (Childs River and Quashnet River) were continuously
505 monitored for radon, salinity and nutrients during a period of one low tide-high tide cycle
506 (Fig. 1 and Fig. 9). We found that in the Childs River radon activities (4-12 dpm L^{-1})
507 were associated with elevated DIN and low salinity suggesting a fresh groundwater
508 source. This supports our findings from the survey that there is high SGD and
509 groundwater derived nitrate in the Childs River. Other nutrients such as phosphate and
510 silicate exhibited no clear association with radon or salinity so we could not conclude that
511 SGD is their primary source (Fig. 9). Ammonia was constant throughout the
512 measurement period at ~5 μM. In contrast, in Quashnet River radon levels were
513 comparable to those in the Childs River but nitrate concentrations were negligible and
514 DIN consisted almost exclusively of ammonia. Ammonia was at the same level as in
515 Childs River (1-5 μM). DIN was not correlated with radon and therefore its source could
516 not be SGD. Phosphate and silicate had the same decreasing trend as radon.
517 The differences between the two sites can be explained by land-use practices in
518 their watersheds as these influence groundwater composition. The Childs River
519 watershed is more urbanized with septic tanks and fertilizers as major nitrogen sources

520 than the Quashnet River watershed. Valiela et al. (1992) found that these urbanized
521 watershed areas significantly influence groundwater DIN concentrations – most
522 significantly nitrate. Our results are in accordance with these findings.

523 Water quality in Boston Harbor improved after the Deer Island wastewater
524 treatment facility discharge was moved offshore in 2000 (Taylor, 2006). DIN
525 concentrations in the harbor dropped by 50% over the following five years. Currently, the
526 major sources of nitrogen into the harbor are atmospheric deposition, rivers, groundwater
527 discharge, stormwater discharge, combined sewer outflows, and coastal disposal sites
528 (Menzie et al., 1991, MWRA, 2008). During our survey ammonia concentrations ranged
529 from 1.6 to 41 μM (median 20 μM) and nitrate+nitrite concentrations were an order of
530 magnitude lower, between 0.1 and 5.8 μM (median 0.7 μM). Due to the complexity of
531 point and non-point nitrogen sources in the harbor no clear correlation between
532 ammonia/nitrate and radon can be expected for the harbor as a whole. Areas in Inner
533 Harbor, Dorchester Bay, and Quincy Bay show high SGD and surface water DIN (Fig. 7).
534 This implies that the source of these nutrients may be groundwater discharge. Sites with
535 moderate SGD rates (i.e. western Dorchester Bay) are also potential sources of
536 groundwater derived nitrogen. Sites that had elevated SGD but low DIN are SE Quincy
537 Bay and Pleasure Bay. At these sites groundwater is not a significant source of DIN into
538 the surface water, despite high discharge rates. These findings illustrate the high
539 variability of SGD in the harbor and its possible effects on surface water DIN
540 concentration. Sites with potential significant groundwater derived nitrogen that
541 necessitate further investigation are the Inner Harbor and parts of Dorchester Bay and
542 Quincy Bay. Although SGD is an obvious potential source of nutrients here, its

543 significance may be diminished by point releases of effluents into surface waters
544 throughout the harbor (Fig. 1 based on http://www.mwra.state.ma.us/harbor/graphic/4-
545 1.gif).

546

547 *4.4 Groundwater DIN fluxes*

548 There is ongoing debate as to how best derive groundwater nutrient fluxes from
549 known groundwater discharge rates and groundwater nutrient concentration measured in
550 wells and piezometers. Valiela et al., (1992) illustrated that nitrogen attenuation by
551 denitrification, sorption of ammonia, and other microbial processes may decrease
552 nitrogen levels in groundwater along its flow path. Additional biochemical processes in
553 the subterranean estuary (Kroeger and Charette, 2008) and at the sediment water interface
554 (Seitzinger, 1988) further modify the groundwater composition and make it difficult to
555 estimate groundwater nitrogen concentrations at the point of discharge. A simple
556 multiplication of groundwater discharge and nutrient concentrations in the groundwater
557 therefore provide only a rough estimation of nutrient fluxes.

558 In Waquoit Bay groundwater DIN concentrations measured in coastal wells in the
559 Childs River watershed averaged 133 μM and 4.2 μM in the Quashnet River watershed
560 (Valiela et al., 1992), and at the head of the bay the best representative DIN values were
561 94 and 27 μM for fresh groundwater and recirculated seawater, respectively. The latter
562 values were derived by Kroeger and Charette (2008) from Jun, Jul 2002, Mar, Apr, Jun,
563 July 2003 and from a 3-year long monthly monitoring of the subterranean estuary at the
564 head of Waquoit Bay concurrent with our surveys (unpublished results). The simplistic
565 approach of multiplying these concentrations with groundwater fluxes from our survey,

result in groundwater derived nitrogen fluxes of 68-87 kg N d^{-1} in the winter and 9.5-13 kg N d^{-1} in the summer. Valiela et al. (1992) and Kroeger and Charette (2008) also estimated that in Waquoit Bay approximately 60-75% of the DIN is removed within a thin layer at the sediment-water interface, so the net fluxes may be as much as 60-75% lower than our estimates.

For the survey in Quincy Bay (South Boston Harbor) we can use nitrogen concentrations measured by Poppe and Moffett (1993) who found DIN concentrations ranging from 20 μM (nearshore) to 140 μM (50 m inland). They contend that nitrogen concentrations decrease within their shallow coastal well transect due to denitrification. Based on these concentrations we calculate DIN fluxes of 7-51 kg N d^{-1} for that part of the harbor. North Harbor is even more complex as there are sites with elevated SGD but low nitrogen and also sites with elevated nitrogen and SGD. This suggests that groundwater DIN is highly variable. Menzie et al. (1991) determined representative groundwater DIN concentrations throughout the harbor of 7 to 710 μM. Using their average value of 71 μM we get a DIN flux of 81 kg N d^{-1}. But these results need further improvement with more detailed groundwater DIN determination. Nevertheless our SGD survey already provides reliable groundwater discharge rates and a good basis for future groundwater DIN flux investigations.

5. Conclusions

By combining radon/methane/nitrate into a survey system we are able to quickly and efficiently create detailed maps of submarine groundwater discharge in coastal embayments. The new methane analyzer provided excellent resolution and response to

589 varying methane concentrations in Waquoit Bay. The enhanced radon monitoring system
590 had improved resolution though use of the membrane contactor interface can become
591 clogged in high particulate environments. We developed a model for converting mapped
592 radon into total SGD fluxes in Waquoit Bay and Boston Harbor and determined areas of
593 significant groundwater fluxes. These data were combined with surface water nitrogen
594 concentrations to identify areas of potential non-point source pollution. Two sites in
595 Waquoit Bay were studied in detail for correlation between nitrate and radon over a tidal
596 cycle and the results confirmed that in Childs River there is high groundwater derived
597 nitrate, whereas Quashnet River has SGD which is not a considerable source of nitrate.
598 All of our results were in good agreement with earlier findings of SGD and the location
599 of nitrogen sources in Waquoit Bay.
600 We identified several sites in Boston Harbor that had significant SGD coincident
601 with elevated surface water nitrogen concentrations, but more detailed investigations are
602 needed to confirm SGD as a nitrogen source. However, our survey results provide basis
603 for further studies. We are confident that the survey system is very effective in revealing
604 areas of non-point source pollution and that this system is suitable for larger scale
605 regional SGD mapping projects.
606

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734 Couplings of watersheds and coastal waters- sources and consequences of nutrient
735 enrichment in Waquoit Bay, Massachusetts, *Estuaries* 15(4): 443-457.

736 Table 1: Fresh, saline and total submarine groundwater discharge rates (m^3 d^{-1}) in Waquoit Bay, MA, at the head of the bay, in Childs River and
737 for the whole bay estimated in previous studies and in this study in August 2006 and December 2006.

	Head of bay			Childs River			Whole bay		
SGD (m^3 d^{-1})	Fresh	Saline	Total	Fresh	Saline	Total	Fresh	Saline	Total
Cambareri and Eichner (1998)	1,037			2,740			27,648		
Michael et al. (2003)	950		9,160						
Michael (2004)	2,160	4,234	6,394						
Mulligan and Charette (2006)	2,419								
Charette et al. (2001)								37,152	
This study Aug06	2,050		2,845	2,680		6,880	5,367		11,212
This study Dec06	920		4,292	6,159		51,587	7,588		56,862

738

739 Figure captions:

740 Fig. 1 A: Map of Massachusetts with insets of B: Waquoit Bay, the crosses indicate the
741 Childs River and Quashnet River time series monitoring sites; C: Boston Harbor with
742 its bays, the cross indicates the Savin Hill Cove time series measurement site, also
743 indicated are North Harbor and South Harbor.

744 Fig. 2: Response time of Liquicel and the air-water gas exchanger to changes in radon
745 activities in water. First, radon-free water was passing through both systems, after 20
746 minutes the water intake was switched to high radon activity water, and after 55
747 minutes the water intake was switched back to radon-free water. Ten minutes after
748 switching from high radon to radon-free water intake 10% of the radon remains in
749 the Liquicel system. The same 10 % level is reached in the air-water gas exchanger
750 after 45 minutes.

751 Fig. 3 A: Radon measured during a survey in Waquoit Bay, MA with two different radon
752 mapping systems, one system used a classic air-water exchanger and the other the
753 newly tested membrane. Both systems were run in 5 minute integrated intervals and
754 their water intakes were positioned to sample the same water parcel. For easier
755 comparison, radon values are plotted against time instead of geographical reference
756 points. B: Simultaneous radon and methane survey in Waquoit Bay, MA. Radon is
757 smoothed out spatially because it has been measured in a continuous 5-minute
758 integrated measurement intervals, whereas methane values were recorded every 30
759 seconds. Values are plotted against time of sample collection.

760 Fig. 4: Sources and removal processes that influence radon/methane inventory in the
761 coastal water. The input terms are indicated by brown arrows and loss terms by green
762 arrows, and the tracer fluxes represent the interactions between sediments, coastal
763 water, atmosphere, and offshore water.

764 Fig. 5: Long-term monitoring of radon, water level, and salinity in Savin Hill Cove in
765 Boston Harbor. The inset is zoomed in on a selected time period that shows a clear
766 negative correlation between salinity/tides and radon. At high tide the water is
767 diluted by low radon high salinity offshore water, at low tides fresh/brackish SGD

lowers salinity and brings in new radon that is then mixed away with the next flood tide.

Fig. 6: Summer (A, B, C) and winter (D, E, F, G) coastal surface water survey results from Waquoit Bay showing salinity (A, D); radon in dpm L^{-1} (B, E); nitrate+nitrite in μM (C, F); and methane in relative units (G, winter only). Warm colors are high and cold colors are low values as indicated on each legend. Due to low water levels we were not able to survey Quashnet River in such detail as the other parts of the bay.

Fig. 7: Coastal surface water survey results from Boston Harbor showing A: salinity; B: radon in dpm L^{-1}; C: submarine groundwater discharge in $m^3\ m^{-1}\ d^{-1}$; and D: ammonia + nitrate + nitrite in μM.

Fig. 8: Nitrate+nitrite concentrations in surface water and radon derived SGD in Waquoit Bay in A: Aug 2006 and B: Dec 2006. In the summer, nitrate concentrations are very well correlated with SGD throughout the bay and peak at 6 mM in the Childs River. Winter concentrations are more evenly distributed, exhibiting no apparent correlation with SGD. This may be due to a quick biological nitrogen uptake in summer when any new source would be apparent over a low background concentration, whereas in winter nitrogen residence time in the surface water is much longer allowing build-up and more even distribution within the bay (Valiela et al., 1992). Values are plotted against time of sample collection.

Fig. 9: Time series measurements of radon, salinity and nutrients for a period of a change of low tide to high tide in A: Childs River and B: Quashnet River on Dec 5, 2007. Water level, nitrate+nitrite, ammonium, phosphate, silicate, DIN, radon and salinity parameters are indicated over an 8-hour period.

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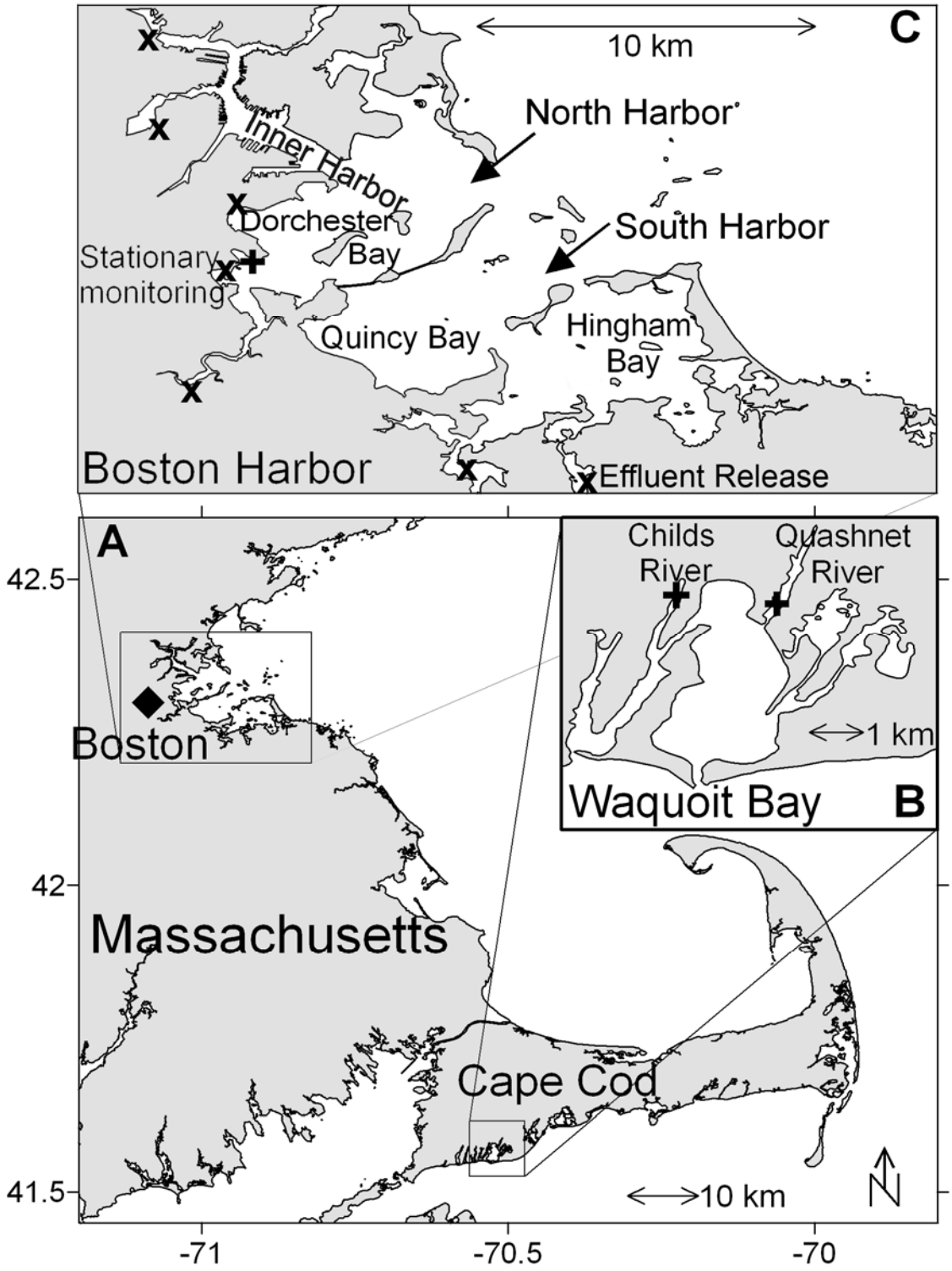

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Fig. 1

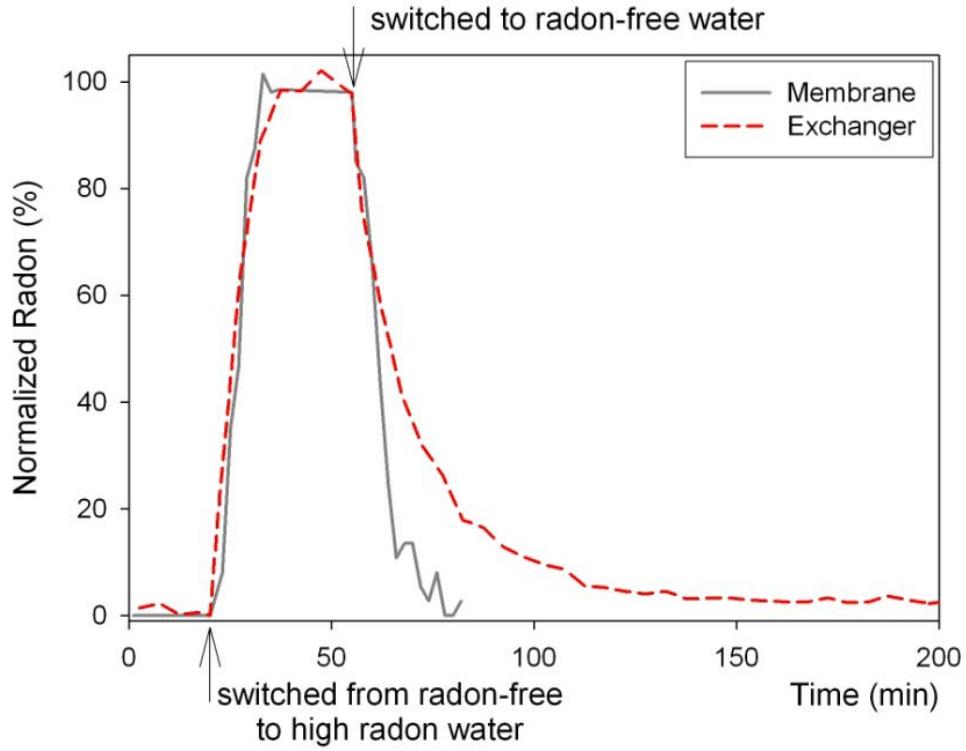

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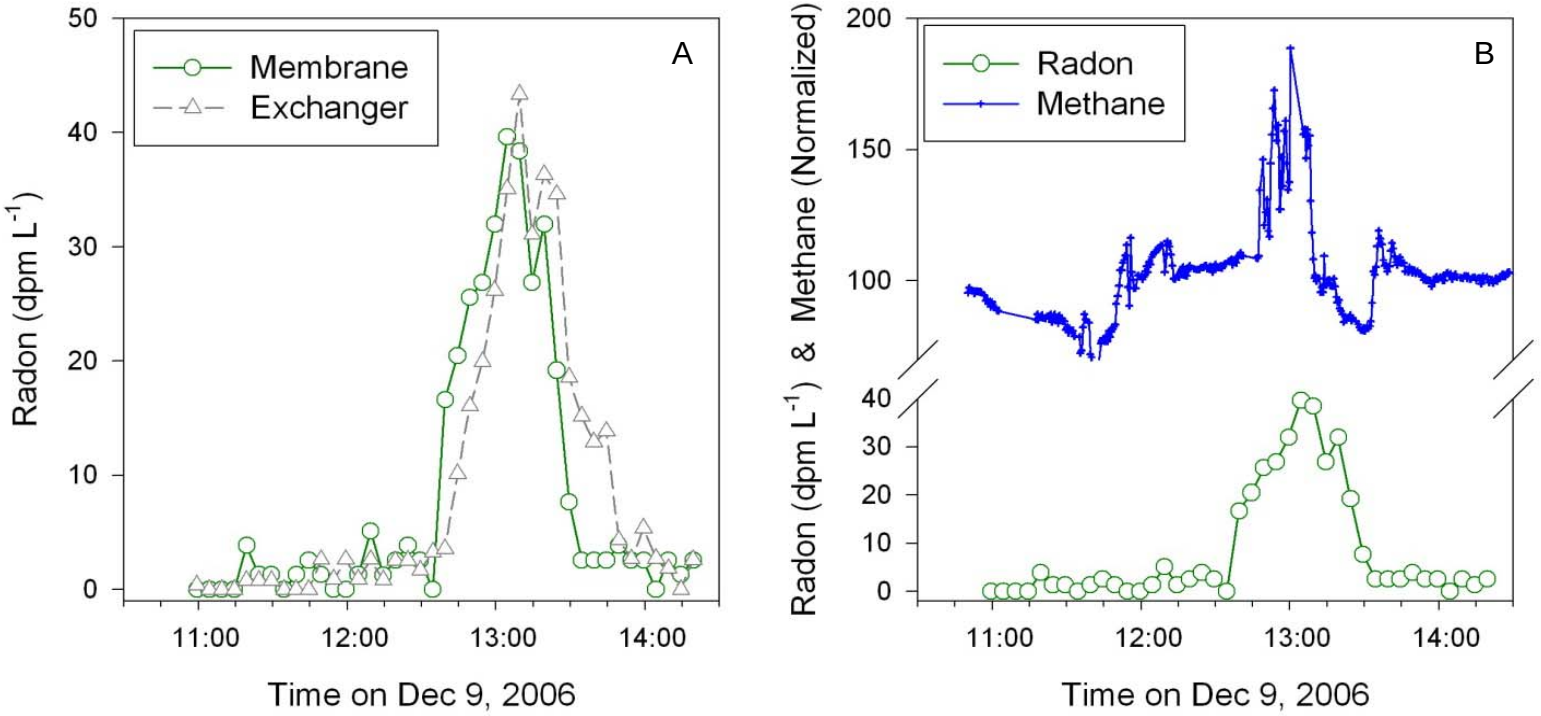
Fig. 2


A
Membrane
Exchanger
Radon (dpm L-1)
50
40
30
20
10
0
11:00
12:00
13:00
14:00
Time on Dec 9, 2006
B
Radon
Methane
Radon (dpm L-1) & Methane (Normalized)
200
150
100
40
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20
10
0
11:00
12:00
13:00
14:00
Time on Dec 9, 2006

Fig. 3

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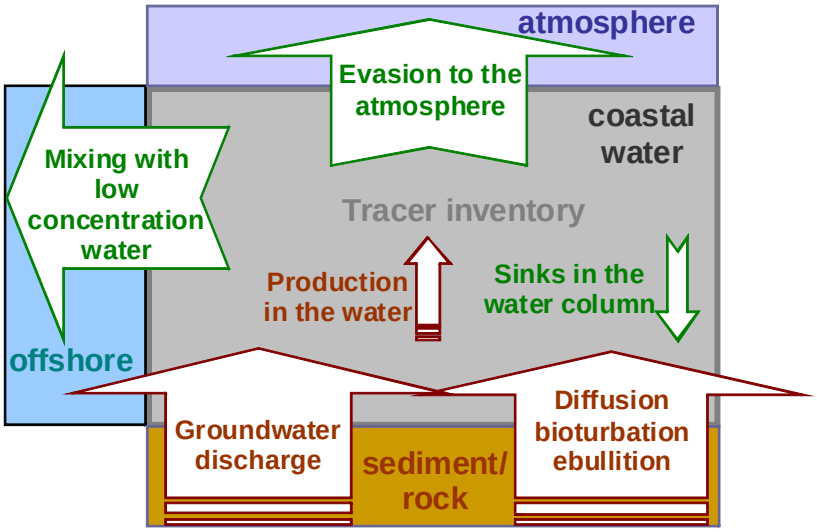

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815 Fig. 4
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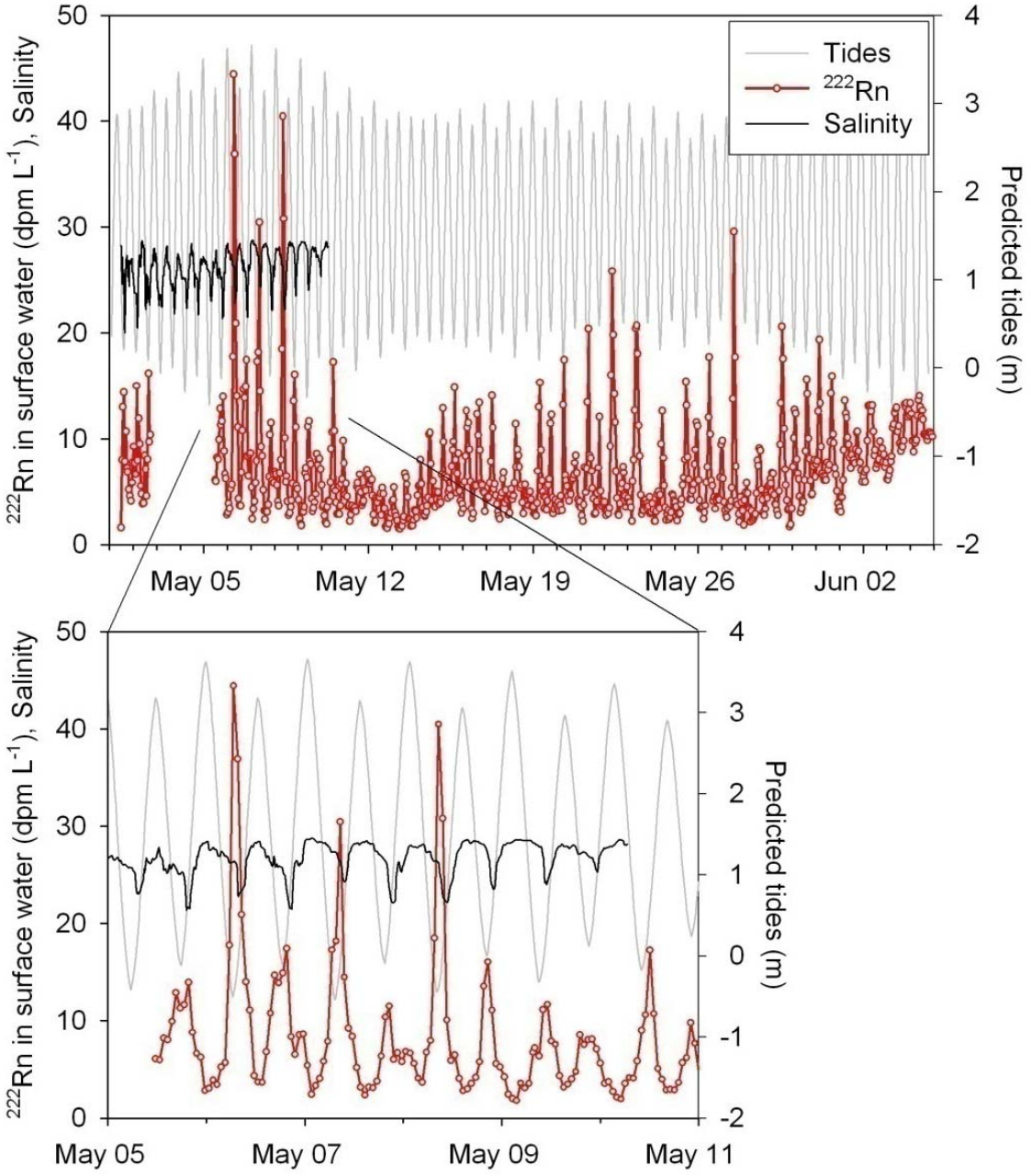

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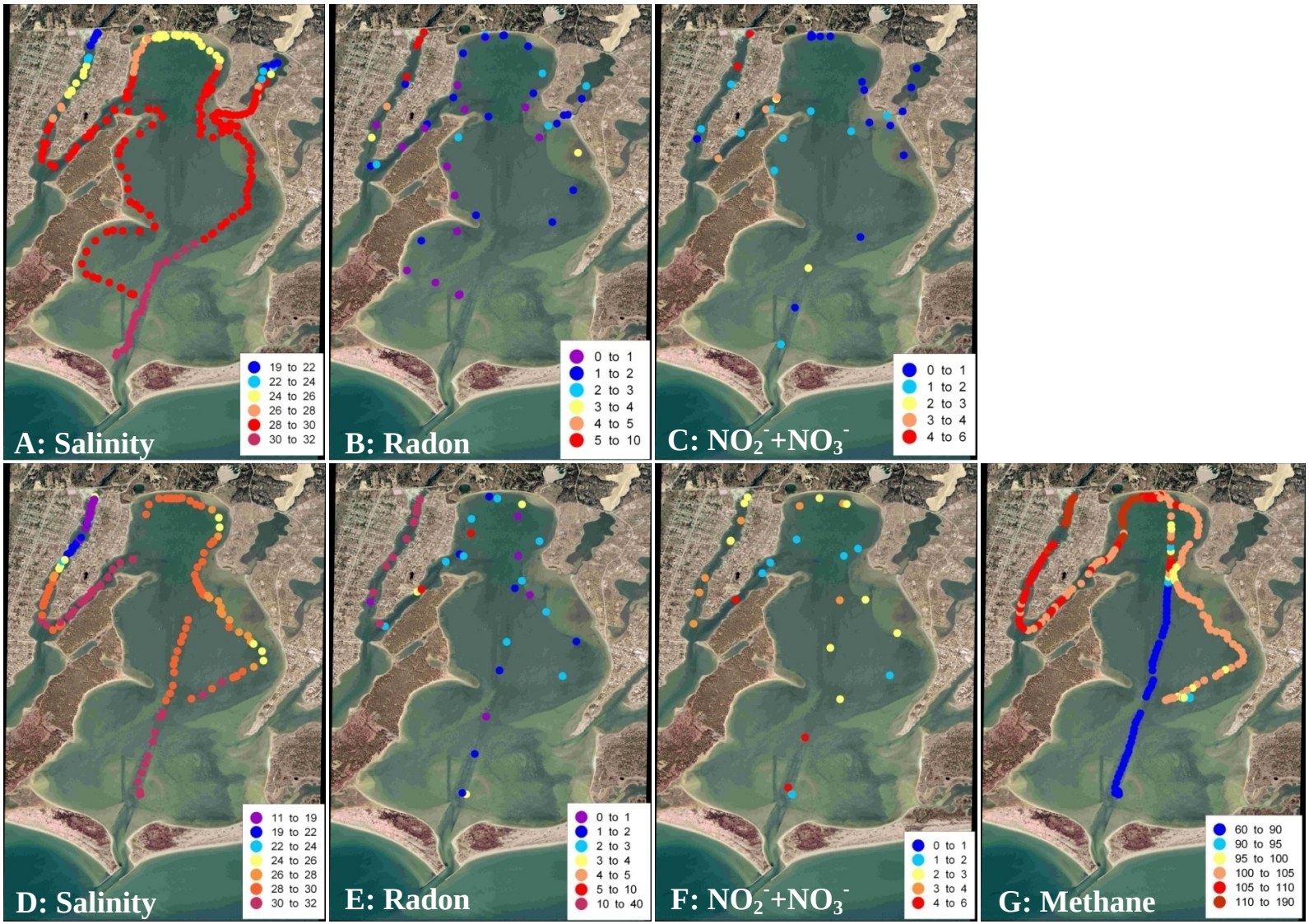
A: Salinity
19 to 22
22 to 24
24 to 26
26 to 28
28 to 30
30 to 32
B: Radon
0 to 1
1 to 2
2 to 3
3 to 4
4 to 5
5 to 10
C: NO_2^-+NO_3^-
0 to 1
1 to 2
2 to 3
3 to 4
4 to 6
D: Salinity
11 to 19
19 to 22
22 to 24
24 to 26
26 to 28
28 to 30
30 to 32
E: Radon
0 to 1
1 to 2
2 to 3
3 to 4
4 to 5
5 to 10
10 to 40
F: NO_2^-+NO_3^-
0 to 1
1 to 2
2 to 3
3 to 4
4 to 6
G: Methane
60 to 90
90 to 95
95 to 100
100 to 105
105 to 110
110 to 190

Fig. 6

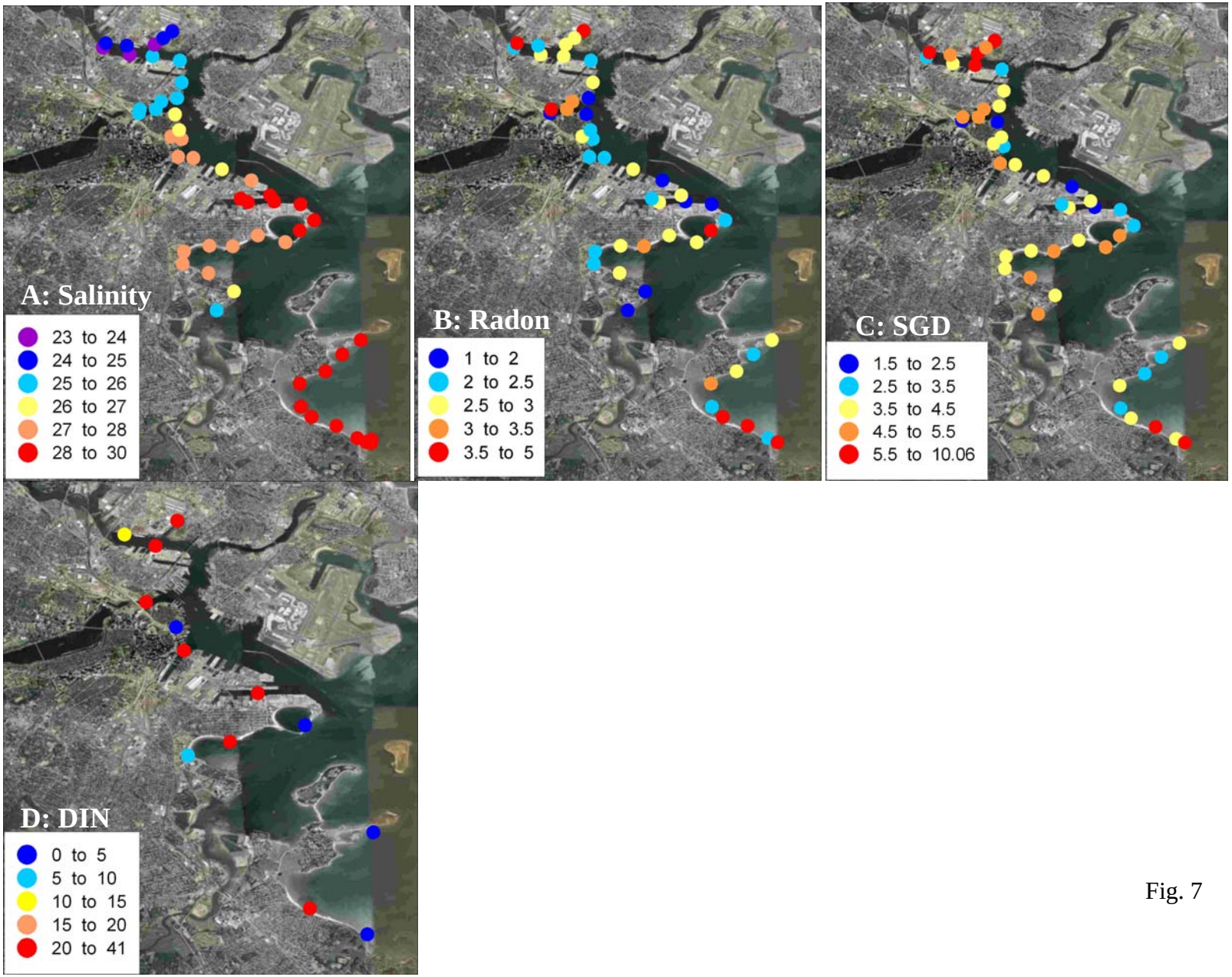
A: Salinity
23 to 24
24 to 25
25 to 26
26 to 27
27 to 28
28 to 30
B: Radon
1 to 2
2 to 2.5
2.5 to 3
3 to 3.5
3.5 to 5
C: SGD
1.5 to 2.5
2.5 to 3.5
3.5 to 4.5
4.5 to 5.5
5.5 to 10.06
D: DIN
0 to 5
5 to 10
10 to 15
15 to 20
20 to 41

Fig. 7

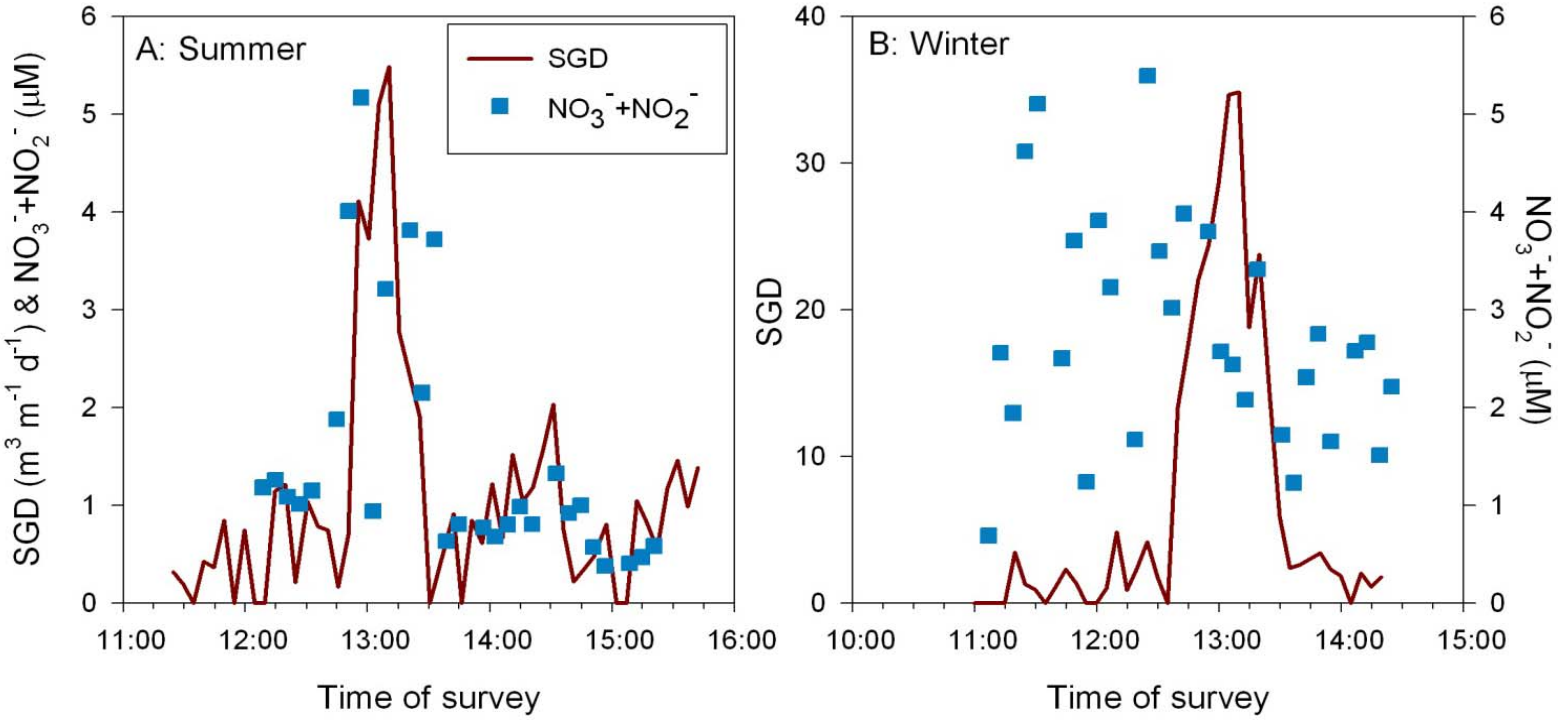
A: Summer
SGD
NO3-+NO2-
SGD (m3 m-1 d-1) & NO3-+NO2- (μM)
Time of survey
B: Winter
SGD
NO3-+NO2- (μM)
Time of survey

Fig. 8

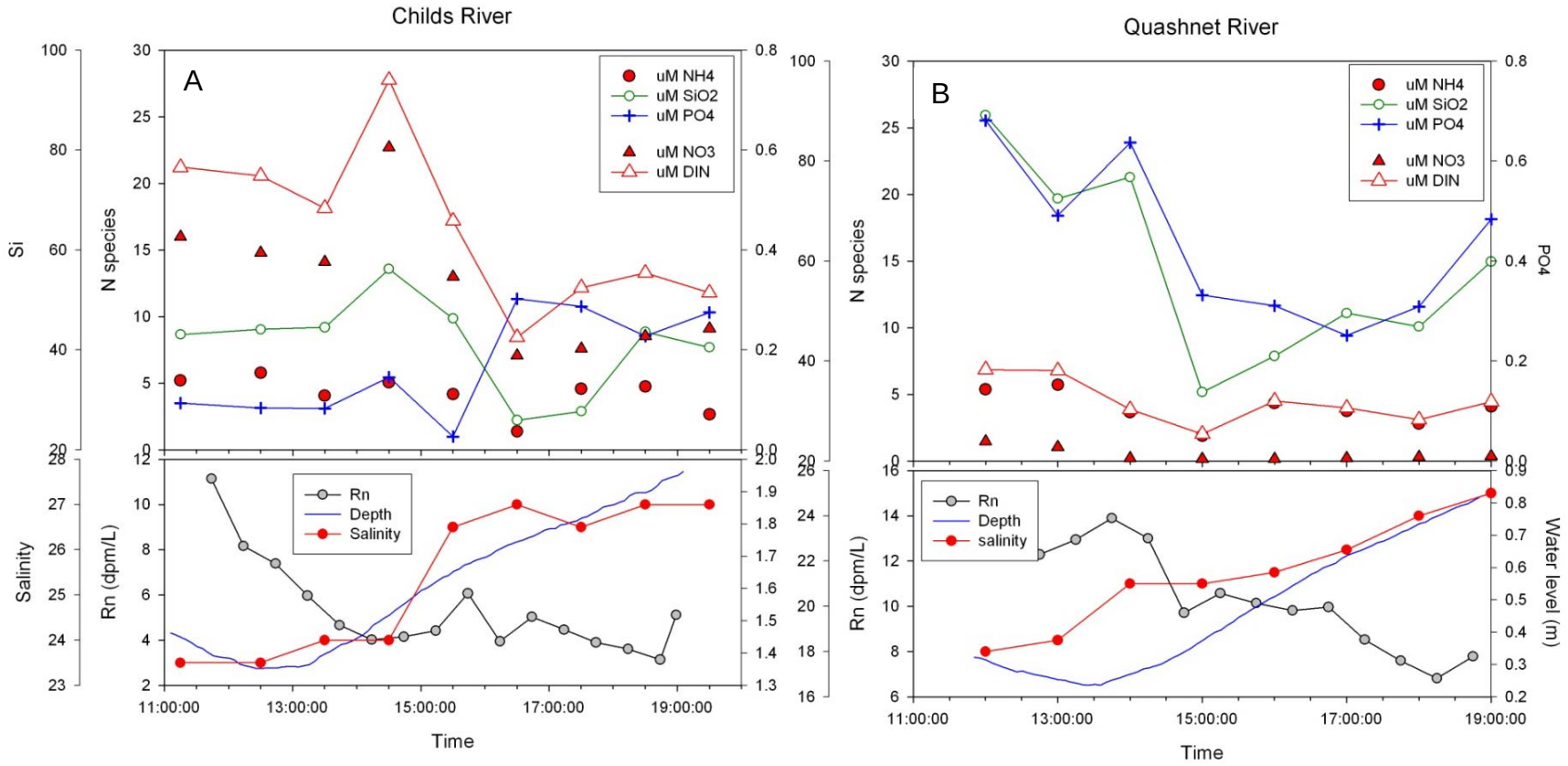
Childs River
A
uM NH4
uM SiO2
uM PO4
uM NO3
uM DIN
Si
N species
Rn
Depth
Salinity
Rn (dpm/L)
Time
11:00:00
13:00:00
15:00:00
17:00:00
19:00:00
Quashnet River
B
PO4
salinity
Water level (m)

Fig. 9