Elsevier Editorial System(tm) for Journal of Environmental Radioactivity
Manuscript Draft

Manuscript Number:

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

Article Type: Special Issue: Radium and Radon Isotopes

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

Corresponding Author: Dr. Henrieta Dulaiova, Ph.D.

Corresponding Author's Institution: University of Hawaii

First Author: Henrieta Dulaiova

Order of Authors: Henrieta Dulaiova; Richard Camilli; Paul B Henderson; Matthew A Charette

Abstract: We constructed a survey system of radon/methane/nitrate/salinity to map submarine groundwater discharge (SGD) and corresponding nitrate fluxes. 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.

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

Henrieta Dulaiova[1a], Richard Camilli[2], Paul B. Henderson[1], and Matthew A. Charette[1]

[1]Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543

[2]Applied Ocean Physics and Engineering, Woods Hole Oceanographic Institution, Woods Hole, MA 02543

Submitted to: Journal of Environmental Radioactivity

Ra-Rn special issue

March 16, 2009

[a]Corresponding author: hdulaiov@hawaii.edu, current address: Department of Geology and Geophysics, University of Hawaii, Honolulu, HI 96822

Abstract

We constructed a survey system of radon/methane/nitrate/salinity to map submarine groundwater discharge (SGD) and corresponding nitrate fluxes. 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 (Johannes, 1980; Valiela et al., 1990; 1992; Slomp and Van Cappellen, 2004; Umezawa et al., 2008).

Current methods to directly measure submarine groundwater discharge (SGD) and corresponding nitrogen fluxes are inadequate because groundwater discharge is heterogeneous in location and composition, and occurs over large areas. 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. 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.

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

41 concentrations of these tracers in coastal waters indicate areas where groundwater
42 outcrops to the surface.

43 The utility of ^{222}Rn as a tracer of SGD has been demonstrated in a wide range of
44 environments from coastal embayments to the coastal ocean (Charette et al., 2008). Rn-
45 222 is a naturally occurring radioactive element with a half-life of 3.8 days. As a non-
46 reactive noble gas its only losses from the water column are due to radioactive decay and
47 evasion to the atmosphere. Because groundwater is in contact with radon emanating
48 aquifer material, ^{222}Rn concentrations in groundwater are often about two to three orders
49 of magnitude higher than most surface waters. Groundwater becomes enriched in radon
50 independently of its composition (fresh water or seawater) so radon is a tracer of total
51 SGD driven by both terrestrial and marine forces. If a groundwater source is present in a
52 coastal environment it is likely to be the only radon input of significant magnitude to
53 surface water, which makes this tracer very useful for identifying areas of groundwater
54 input into lakes, rivers and the coastal ocean (Cable et al., 1996; Burnett et al., 2002;
55 Burnett and Dulaiova, 2003).

56 Methane has successfully been employed as a tracer of groundwater inputs into
57 near-shore waters along the coast of the northeastern Gulf of Mexico (Bugna et al., 1996
58 and Cable et al., 1996), Florida Bay (Corbett at al., 2000), Long Island (Dulaiova et al.,
59 2006), and Korea (Kim and Hwang, 2002). Being subject to biological processing,
60 methane is not a conservative tracer though it has proven to be useful where its
61 concentration in groundwater highly exceeds methane inventories in the water column.

62 Recent technological advancements have enabled high resolution, continuous
63 measurement of these tracers for large-scale mapping of coastlines. Such measurements

64 using radon monitors have been previously applied (Burnett and Dulaiova, 2003) but
65 only as qualitative surveys to identify SGD hot-spots; none of these studies derived
66 quantitative SGD rates – a major goal of the research described herein. The objectives of
67 our study were to: 1) construct a radon/methane/nitrate mapping system that measures the
68 concentrations of these components in the surface water in-situ with an increased
69 resolution over conventional systems, 2) use tracer data to identify SGD hot-spots and
70 develop a model for its quantitative determination, and 3) assess the importance of SGD
71 with regards to coastal nitrogen budgets and non-point source pollution.
72
73 **2. Methods**
74 Our mapping system consists of several component instruments. Among these
75 component instruments is a modified radon surveying system (Dulaiova et al., 2005),
76 which consists of 3 commercially available radon-in-air analyzers (RAD7, manufactured
77 by Durridge, Inc., Massachusetts) employed to measure ^{222}Rn from a continuous stream
78 of water passing through an air-water exchanger that distributes radon from the running
79 water to a closed air loop. The exchanger, which takes about 15 minutes to reach full
80 equilibrium in the loop, causes a relatively slow response to changes in radon
81 concentrations in water. The other disadvantage of the exchanger is that it has a memory-
82 effect due to inefficient flushing of radon from the closed loop. To improve the response
83 time of the system we replaced the air-water exchanger with a membrane contactor
84 (Liquicel, manufactured by Membrana), which is a set of hollow fibers made of a
85 hydrophobic membrane that allow radon and other gases to pass from water into the air

86 phase. The cell is used as a single-pass open system which has a much shorter memory-
87 effect and requires no wait time for equilibrium.

88 Methane was measured using a TETHYS in-situ underwater mass spectrometer
89 that was operated on a towed platform from a small coastal boat, providing real-time data
90 to a top-side computer. The TETHYS instrument is capable of measuring dissolved gases
91 and volatile light hydrocarbons at sub ppb levels, with sampling intervals on the order of
92 5 seconds for most gases. This technique has been used for ocean floor methane seep
93 mapping in marine environments (Camilli and Duryea, 2007; Mau et al., 2007). For these
94 investigations the mass spectrometer was equipped with an integrated CTD (model
95 SBE49 FastCAT, SeaBird Electronics Inc., Bellevue, Washington, USA) provided
96 continuous flow sample introduction at a rate of approximately 3 ml s^{-1}, along with
97 external salinity, temperature and pressure data.

98 The towed survey was carried out with the mass spectrometer operating at depths
99 between one and three meters. During the survey deployment over 500 discrete sample
100 measurements of ion peak heights were recorded at m/z 15 as an indicator of relative
101 methane intensity. In addition to the methane time series data, ion peaks at m/z 17, 28, 32,
102 40, and 44 were recorded to identify relative changes in gases corresponding, respectively,
103 to water vapor, di-nitrogen, oxygen, argon and carbon dioxide. The methane ion peak
104 intensity (m/z 15) was then normalized to water vapor intensity (m/z 17) in order to
105 generate a temperature normalized methane intensity estimate. Spectral sweeps across
106 the instrument's full mass range (2-200 AMU) were performed at selected sites to
107 identify any potential contributions from anomalous gases or volatile hydrocarbons.

The survey system is 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 about 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 latentcy 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. At this site, 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 (~25 m wide) band (Michael et al., 2005). Radon is more than two orders of magnitude enriched in groundwater relative to surface water (Dulaiova et al., 2008) and the estimated seepage flux determined by a continuous radon model ranges between 0.6 to 5.6 $m^3\ m^{-1}\ d^{-1}$ (Mulligan and Charette, 2006) and is 5.3 $m^3\ m^{-1}\ d^{-1}$ based on a ^{226}Ra box model (Charette et al.,2001). The presence of high SGD enriched in both radon and nitrate makes Waquoit Bay an ideal testing site for the mapping system. Using this information about the spatial distribution of SGD we were able ground-truth the sensitivity and resolution of our instruments.

In order to contrast seasonal changes in SGD and nutrient inputs, we deployed the complete system to survey Waquoit Bay on two occasions (August 2006 and December 2006) and we also did a time series stationary monitoring over a 13-hour period simultaneously in two locations: in Childs- and Quashnet Rivers (September 2007).

151 Following the Waquoit Bay studies we surveyed Boston Harbor, MA and its
152 estuaries (June 2008). This included a stationary long-term monitoring at the University
153 of Massachusetts, Boston dock near Savin Hill Cove for the period between May 2 and
154 June 4, 2008 (Fig. 1). In these Boston Harbor studies the mass spectrometer was not
155 available and the radon monitor was operated with the traditional air-sea exchanger
156 because the water contained significant amounts of suspended matter that clogged the
157 membrane contactor. The harbor is relatively shallow with an average depth of
158 approximately 5 m, and is well flushed by strong tides, with an average water residence
159 time of five to seven days (Jiang and Zhou, 2008).
160 Boston Harbor was chosen as a more complex environment to demonstrate that
161 the mapping technique is applicable to both surficial and groundwater nitrogen inputs.
162 Furthermore, despite of the recent improvements in water quality (relocation of the city's
163 sewage outfall offshore), non-point source pollution from SGD and potential relic sewers
164 or combined sewer overflow (CSO) systems are poorly characterized. Greater
165 understanding of submarine groundwater discharge and its spatial distribution throughout
166 the harbor is useful because of the potential for mobilization of contaminants from the
167 highly contaminated (lead, mercury, silver, anthropogenic organic pollutants) bottom
168 sediments (McGroddy and Farrington, 1995; Stolzenbach and Adams, 1998; Eganhouse
169 and Sherblom, 2001), which are the conduit for SGD. Therefore even small fluxes of
170 SGD may be biogeochemically significant if contaminant concentrations are enhanced in
171 groundwater.
172

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 measurement 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 sample 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 concentrations (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 the air-water exchanger (Fig. 2).

Similar results were demonstrated during 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 and decreases 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

196 environments with lower fine particulate concentration. During times of high seasonal
197 productivity the membrane often clogs quickly during the survey and therefore requires
198 constant maintenance.
199
200 *4.2 SGD rates derived from tracers*
201 Unlike radon, methane is a non-conservative gas and its concentration may be
202 influenced by microbial and biochemical processes during which it can be produced or
203 consumed in the sediments and water column. It is therefore only useful in areas where a
204 significant concentration gradient exists between groundwater and surface water, in
205 principle, when there is enough anaerobic organic matter decomposition in the aquifer.
206 Groundwater methane concentrations measured in the subterranean estuary at the head of
207 Waquoit Bay in 2004 were up to 65 μM (Charette and Camilli, unpublished results). We
208 tested the applicability of methane as SGD tracer in Waquoit Bay by measuring water
209 column radon and methane simultaneously. We expected that the tracers would have
210 similar spatial distribution if the source of methane was the same as of radon, i.e.
211 groundwater discharge. Indeed, as demonstrated in Figure 3b that is the case, but with
212 the methane data providing a better spatial resolution than radon due to the more frequent
213 methane sampling rate. Differences between the two tracer patterns are likely due to the
214 different sampling intervals (radon being smoothed out spatially) and the non-
215 conservative nature of methane (biochemical sources and sinks in the water column and
216 sediments). Our results from Waquoit Bay demonstrate that in this environment the two
217 tracers complement each other in that methane enables a very fine spatial resolution and

218 radon provides positive identification of SGD origin, confirming SGD as the source of
219 methane.
220 We next evaluate the usefulness of these tracers in assessing the spatial
221 distribution of SGD. The concentration of radon/methane in the water column will
222 depend on several factors (Fig. 4):
223 1) in-situ production by ingrowth from ^{226}Ra, radon's radioactive parent dissolved
224 in water/ biogeochemical reactions; 2) inputs by diffusion, sediment resuspension,
225 bioturbation, or gas ebullition from sediments; 3) input by groundwater discharge; 4)
226 removal by exchange with open ocean water (i.e., dilution with low radon/methane
227 offshore water); 5) removal by evasion from water to the atmosphere; 6) losses by
228 radioactive decay/biogeochemical reactions.
229 If there is a significant difference between groundwater and surface water tracer
230 concentrations and SGD is present we may neglect 1) in-situ tracer production in the
231 water column; and 2) non-SGD inputs from sediments as these processes will not be
232 major contributors to the final tracer inventories. This is usually true for radon but with
233 methane biogeochemical production in the sediments and consequent ebullition must be
234 considered as a potential source. Hence, we only use this tracer in this study as a
235 qualitative indicator of SGD.
236 Continuous SGD tracer records (Rn, Ra, methane, Si and many others) show that
237 the highest tracer concentrations can usually be observed at or around low tides. At flood
238 tide the high-tracer coastal waters are diluted by offshore low tracer water (process 4).
239 Because of this dilution process we observe low tracer concentrations at high tide. This
240 pattern is also driven by a change in the hydraulic gradient in the coastal aquifer in

response to the tidal fluctuation that causes lower hydrostatic pressure at low tides resulting in increased seepage and thus higher tracer fluxes. To measure the best representative non-diluted coastal tracer inventories we survey during low and ebbing tide.

We convert all radon and salinity measurements from our surveys into SGD fluxes based on the following equations (Moore, 1996):

$$Q_{SGD_{tot}} = \frac{A_{Rn_{cw}} * V}{\tau * A_{Rn_{gw}}}, \quad (1)$$

and

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

where $Q_{SGD_{tot}}$ and $Q_{SGD_{fresh}}$ are total (fresh and saline) and fresh submarine groundwater discharge ($m^3\ d^{-1}$), $A_{Rn_{cw}}$ and $A_{Rn_{gw}}$ are radon activities in the coastal water 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. Each radon and salinity measurement in the survey in this calculation is considered as an individual value that is a representative of a part of the coastline. For each measurement the volume of the coastal water box is calculated from the half distance between the previous and following measurements (variable depending on the boat speed, WB~ 10-300 m; BH~100-300 m), water column or mixed layer depth, and the width of the seepage face, which in Waquoit Bay was 30 m (Michael et al., 2005) and in the absence of better estimates we assumed the same for Boston Harbor. Another option is to express SGD 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

263 divided by the coastline length (half distance from the previous plus half distance from
264 the following measurement). Since radon is measured as an integrated value over this
265 distance, it truly represents the above described section of the coastline. Assumptions are
266 necessary when using Eq. (1) and (2) for radon and salinity balance. Among them, the
267 flushing rate of the coastal box is considered one tidal cycle (11.4 hours), and any radon
268 that is brought to the coast by incoming tides or upstream locations is neglected. Errors
269 associated with these assumptions can be minimized if the mapping is done at low tide.
270 Figure 5, illustrates a time series radon measurement in Boston Harbor and shows that
271 radon concentrations at high tide are ten times lower than at low tide and follow a
272 baseline open bay concentration. Therefore the assumption of mixing on the tidal time
273 scale is more appropriate for our calculation than using the flushing rate of the whole
274 harbor (~5-9 days). Due to the short time scale of coastal mixing, we neglect any
275 radioactive decay of radon (loss of only 9% over tidal cycle) and atmospheric losses
276 represent only a few to few tens of % from total radon inventory. Losses by evasion are
277 calculated from measured wind speeds and tracer concentration gradients between water
278 and air (Burnett and Dulaiova, 2003).

279 Another assumption invoked for Waquoit Bay and Boston Harbor is the
280 groundwater radon concentration. At these sites it was impractical measure the
281 representative groundwater activity for each segment along the coastline, however at
282 study sites where one expects large variability groundwater radon should be measured for
283 each coastal segment in order to lower the uncertainties of the final SGD calculation.
284 One has to consider the benefits of such effort, because an order of magnitude variation
285 in groundwater radon is required to generate an order of magnitude difference in SGD

286 rates. Here we used radon activities derived during a concurrent study of the
287 subterranean estuary in Waquoit Bay (150 dpm L^{-1}; Dulaiova et al., 2008).
288 Radon provides an estimate of total SGD but it cannot be used to determine the
289 fraction of fresh vs. saline groundwater discharge. In systems with little or no surface
290 runoff it is possible to use salinity and Eq. (2) to calculate fresh SGD. Although there are
291 two rivers in Waquoit Bay, they are groundwater fed (Valiela et al., 1990) and we used
292 salinity in this system to calculate a rough estimate of fresh SGD. We could not make the
293 same assumption for Boston Harbor because several rivers and streams deliver significant
294 quantities of freshwater into the harbor.
295 Tracer distributions in Waquoit Bay in Aug 06 and Dec 06 are plotted on Figure
296 6. The bay water was much fresher in Dec 06 than Aug 06 and the corresponding radon
297 and methane levels also support the idea of much higher SGD in the winter. Based on
298 these tracers, the major sources of groundwater are in the Childs and Quashnet Rivers,
299 and at the head of the bay. Methane and salinity provide the best resolution and in some
300 regions they exhibit strong negative correlation suggesting the presence of fresh
301 groundwater discharge (Childs River). Radon provides assurance that the observed
302 methane profiles are of groundwater origin. As expected, the magnitude of SGD follows
303 the radon and methane distributions. Using equations (1) and (2) and the corresponding
304 coastline length for each value we derived that maximum SGD rates occur in Childs
305 River (5 m^3 m^{-1} day^{-1} of total SGD in summer and some sections as high as 30 m^3 m^{-1}
306 day^{-1} in winter), followed by the head of the bay (2 and 3 m^3 m^{-1} day^{-1} in the summer and
307 winter, respectively). We expected elevated SGD in Quashnet River, but due to low
308 water levels we were not able to survey in such detail as the other parts of the bay. Total

309 SGD fluxes for the whole bay are $11x10^3$ m^3 day^{-1} in the summer and $56x10^3$ m^3 day^{-1} in
310 winter. From that, fresh SGD rates are approximately $5x10^3$ m^3 day^{-1} in the summer and
311 $8x10^3$ m^3 day^{-1} in winter, again these estimates are skewed by the presence of surface
312 runoff. Our calculation of total SGD may also carry an uncertainty related to the change
313 of flushing rate of the near-shore zones for the two different seasons (τ in Eq. (1) and
314 (2)).

315 There have been several SGD studies in Waquoit Bay (Mulligan and Charette,
316 2006; Michael et al., 2003; Michael, 2004; Cambareri and Eichner, 1998) with which we
317 can compare our results (Table 1). Our estimates for fresh (920 (Aug 06) and 2050 (Dec
318 06) m^3 d^{-1}) and total (2845 and 4292 m^3 d^{-1}) SGD for the head of the bay agreed very
319 well with all previous studies (950 to 2419 m^3 d^{-1}). In Childs River our fresh SGD (2680
320 and 6159 m^3 d^{-1}) was very close to Cambareri and Eichner's (1998) estimate which is a
321 representative of a yearly average (2740 m^3 d^{-1}). Our results for fresh SGD for the whole
322 bay are lower than Cambareri and Eichner's (1998) and we believe that is because we
323 could not properly survey Quashnet River and hence our estimates are missing a
324 relatively large fresh SGD component.

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

331 salinity and radon indicates the presence of mostly brackish/saline groundwater
332 discharge.
333 SGD rates varied from 1.5 to 10 m^3 m^{-1} day^{-1}. The highest fluxes occurred in the
334 northern sectors of the harbor. This survey covered approximately 50% of the coastline
335 in North Harbor and 10% in South Harbor. The corresponding SGD rates were $90x10^3$
336 m^3 day^{-1} and $20x10^3$ m^3 day^{-1} in the surveyed sections. If extrapolated to represent
337 discharge from the total length of coastline would be 11 and 39% of river discharge in the
338 North and South Harbors, respectively. These fluxes include the discharge of fresh and
339 marine groundwater components. In comparison, total groundwater discharge determined
340 from an earlier study in Quincy Bay (Wollaston Beach) ranged from 1.3 to $2.2x10^3$ m^3
341 day^{-1} on a coast-perpendicular transect that was scaled up to represent a 4.6 km length of
342 coastline. This flux was calculated to be equivalent to 7-12% of surface discharge
343 (Poppe and Moffett, 1993). Our survey results at the Wollaston Beach suggest rates from
344 1.4 to $2.2x10^3$ m^3 day^{-1} but our study also indicates that SGD is variable and the rate
345 doubles in the southeast section of the beach. We expect that this spatial variability in
346 SGD (Fig. 7) may explain the difference in calculated groundwater to surface discharge
347 ratios (i.e., our 39% estimate as opposed to the 12% estimated by Poppe and Moffett,
348 1993).
349 Fresh SGD calculated based on the National Urban Runoff Program model
350 (Menzie et al., 1991) for the whole South Harbor is $41x10^3$ m^3 day^{-1} and the North
351 Harbor is $43x10^3$ m^3 day^{-1}, representing 8 and 3% of river discharge, respectively
352 (Menzie et al., 1991). These fluxes cannot be directly compared to our estimates because
353 these are only fresh groundwater discharge rates. Instead, we used these numbers to

354 calculate the ratio of fresh to total SGD from our survey. The modeled fresh SGD
355 represents 23% of total SGD in the North Harbor and 2% in South Harbor. We
356 acknowledge that we did not survey Hingham Bay where we expect an increase in SGD
357 due to the presence of marshes that focus groundwater discharge and are sites of intense
358 tidally induced groundwater circulation. Our total SGD estimate for South Harbor based
359 on the survey in Quincy Harbor (only 10% of total coastline length) is therefore probably
360 underestimated.
361
362 *4.3 Groundwater nitrogen inputs*
363 Considering that groundwater nutrient concentrations are usually elevated in
364 comparison to surface water it is important to examine SGD as source of nitrogen to
365 coastal waters. Our survey provides indirect evidence of these sources based on the co-
366 occurrence of elevated levels of nitrogen species and SGD hot-spots. The method proves
367 to be very effective in distinguishing groundwater nitrogen fluxes from inputs from
368 surface runoff or other sources, because only the groundwater nitrate/ammonia is
369 accompanied by radon.
370 Simultaneous radon and dissolved inorganic nitrogen (DIN) measurements in the surface
371 water can be simplified to the following scenarios:
372 1) *High radon - high nitrate* are an indication of significant SGD with possible
373 elevated groundwater nitrogen inputs;
374 2) *High radon – low nitrate** are an indication of significant SGD with insignificant
375 nitrogen inputs;

3) *Low radon – low nitrate** are an indication of insignificant SGD and nitrogen inputs;

4) *Low radon – high nitrate* 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 watercolumn 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 nitrate concentrations in correlation with SGD.

Nitrate+nitrite inventory in Waquoit Bay was much higher in the winter than summer. In the summer, nitrate concentrations are very well correlated with SGD throughout the bay (Fig. 8) and peak at 6 μM in the Childs River. Moderate groundwater fluxes in Quashnet River are not accompanied by significant nitrate flux. 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 new source would be apparent in excess of a low background concentration. In contrast the 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).

To test the correlation of SGD and nitrate inputs in detail, the two sites in Waquoit Bay with the highest SGD rates (Childs River and Quashnet River) were continuously monitored for radon, salinity and nutrients during a period of one low tide-

399 high tide cycle (Fig. 1 and Fig. 9). We found that in the Childs River radon
400 concentrations (4-12 dpm L^{-1}) were very well correlated with nitrate (and DIN) and
401 negatively correlated with salinity indicating a fresh groundwater source. This supports
402 our findings from the survey that there is high SGD and groundwater derived nitrate in
403 the Childs River. Other nutrients such as phosphate and silicate exhibited no clear
404 correlation with radon or salinity suggesting that SGD is not their primary source (Fig. 9).
405 Ammonia was constant throughout the measurement period at ~5 μM. In contrast, in
406 Quashnet River radon levels were comparable to those in the Childs River but nitrate
407 concentrations were negligible and DIN consisted almost exclusively of ammonia.
408 Ammonia was at the same level as in Childs River (1-5 μM). DIN was not correlated
409 with radon and therefore its source could not be SGD. Phosphate and silicate were
410 positively correlated with radon and negatively correlated with salinity.
411 The differences between the two sites can be explained by land-use practices in
412 their watersheds as these influence groundwater composition. The Childs River
413 watershed is more urbanized with septic tanks and fertilizers as major nitrogen sources
414 than the Quashnet River watershed. Valiela et al. (1992) found that these urbanized
415 watershed areas significantly influence groundwater DIN concentrations – most
416 significantly nitrate. Our results are in accordance with these findings.

417 Water quality in Boston Harbor improved after the Deer Island wastewater
418 treatment facility discharge was moved offshore in 2000 (Taylor, 2006). DIN
419 concentrations in the harbor dropped by 50% over the following five years. Currently, the
420 major sources of nitrogen into the harbor are atmospheric deposition, rivers, groundwater
421 discharge, stormwater discharge, combined sewer outflows, and coastal disposal sites

422 (Menzie et al., 1991, MWRA, 2008). During our survey ammonia concentrations ranged
423 from 1.6 to 41 μM (median 20 μM) and nitrate+nitrite concentrations were an order of
424 magnitude lower, between 0.1 and 5.8 μM (median 0.7 μM). Due to the complexity of
425 point and non-point nitrogen sources in the harbor no clear correlation between
426 ammonia/nitrate and radon can be expected for the harbor as a whole. Areas in Inner
427 Harbor, Dorchester Bay, and Quincy Bay show high SGD and surface water DIN (Fig. 7).
428 This correlation implies that the source of these nutrients may be groundwater discharge.
429 Sites with moderate SGD rates (i.e. western Dorchester Bay) are also potential sources of
430 groundwater derived nitrogen. Sites that had elevated SGD but low DIN are SE Quincy
431 Bay and Pleasure Bay. At these sites groundwater is not a significant source of DIN into
432 the surface water, despite high discharge rates. These findings illustrate the high
433 variability of SGD in the harbor and its possible effects on surface water DIN
434 concentration. Sites with potential significant groundwater derived nitrogen that
435 necessitate further investigation are the Inner Harbor and parts of Dorchester Bay and
436 Quincy Bay. Although SGD is an obvious source of nutrients here, its significance may
437 be diminished by point releases of effluents into surface waters throughout the harbor
438 (http://www.mwra.state.ma.us/harbor/graphic/4-1.gif).

439

440 *4.4 Groundwater DIN fluxes*

441 There is ongoing debate as to how best derive groundwater nutrient fluxes from
442 known groundwater discharge rates and groundwater nutrient concentration measured in
443 wells and piezometers. Valiela et al., (1992) illustrated that nitrogen attenuation by
444 denitrification, sorption of ammonia, and other microbial processes may decrease

445 nitrogen levels in groundwater along its flow path. Additional biochemical processes in
446 the subterranean estuary (Kroeger and Charette, 2008) and at the sediment water interface
447 (Seitzinger, 1988) further modify the groundwater composition and make it difficult to
448 estimate groundwater nitrogen concentrations at the point of discharge. A simple
449 multiplication of groundwater discharge and nutrient concentrations therefore provide
450 only a rough estimation of nutrient fluxes.

451 In Waquoit Bay groundwater nitrate concentrations measured in coastal wells in
452 the Childs River watershed averaged 133 μM and 4.2 μM in the Quashnet River
453 watershed (Valiela et al., 1992). The simplistic approach of multiplying these
454 concentrations with groundwater fluxes from our survey, result in groundwater derived
455 nitrogen fluxes of 68 kg N d^{-1} in the winter and 13 kg N d^{-1} in the summer. Valiela at al.
456 (1992) also estimated that approximately 60% of the nitrate is denitrified within a thin
457 layer at the sediment-water interface, so the net fluxes may be 60% lower than our
458 estimates.

459 For the survey in Quincy Bay (South Boston Harbor) we can use nitrogen
460 concentrations measured by Poppe and Moffett (1993) who found DIN concentrations
461 ranging from 20 μM (nearshore) to 140 μM (50 m inland). They contend nitrogen
462 concentrations decrease due to denitrification that within their shallow coastal well
463 transect. Based on these activities we calculate DIN fluxes of 7-51 kg N d^{-1} for that part
464 of the harbor. North Harbor is even more complex as there are sites with elevated SGD
465 but low nitrogen and also sites with elevated nitrogen and SGD. This suggests that
466 groundwater DIN is highly variable. Menzie et al. (1991) determined representative
467 groundwater DIN concentrations throughout the harbor of 7 to 710 μM. Using their

468 average value of 71 μM we get a DIN flux of 81 kg N d^{-1}. But these results need further
469 improvement with more detailed groundwater DIN determination. Nevertheless our SGD
470 survey already provides reliable groundwater discharge rates and a good basis for future
471 groundwater DIN flux investigations.
472
473 **5. Conclusions**
474 By combining radon/methane/nitrate into a survey system we are able quickly and
475 efficiently create detailed maps of submarine groundwater discharge in coastal
476 embayments. The new methane analyzer provided excellent resolution and response to
477 varying methane concentrations in Waquoit Bay. The enhanced radon monitoring system
478 had improved resolution though use of the membrane contactor interface can become
479 clogged in high particulate environments. We developed a model for converting mapped
480 radon into total SGD fluxes in Waquoit Bay and Boston Harbor and determined areas of
481 significant groundwater fluxes. These data were combined with surface water nitrogen
482 concentrations to identify areas of potential non-point source pollution. Two sites in
483 Waquoit Bay were studied in detail for correlation between nitrate and radon over a tidal
484 cycle and the results confirmed that in Childs River there is high groundwater derived
485 nitrate, whereas Quashnet River has SGD which is not a considerable source of nitrate.
486 All of our results were in good agreement with earlier findings of SGD and nitrogen
487 sources in Waquoit Bay.
488 We identified several sites in Boston Harbor that had significant SGD coincident
489 with elevated surface water nitrogen concentrations, but more detailed investigations are
490 needed to confirm SGD as a nitrogen source. However, our survey results provide basis

for further studies. We are confident that the survey system is very effective in revealing areas of non-point source pollution and that this system is suitable for larger scale regional SGD mapping projects.

Acknowledgements

The authors wish to thank the Waquoit Bay National Estuarine Research Reserve for their continued support of our research efforts in Waquoit Bay and Francesco Peri and the crew of the Landing craft from the Environmental, Earth & Ocean Sciences Department at the University of Massachusetts in Boston for their assistance with the survey of Boston Harbor. R. Camilli acknowledges the National Ocean Partnership Program (NOPP) for supporting the development of the TETHYS mass spectrometer through research grant #OCE-0537173. H. Dulaiova, M. A. Charette and R. Camilli acknowledge funding support from the WHOI Coastal Institute and MIT Sea Grant College Program. H. Dulaiova was funded by the WHOI Academic Program's postdoctoral scholarship.

510 **References**

511 Bugna, G. C., J. P. Chanton, J. E. Cable, W. C. Burnett, and P. H. Cable, 1996. The
512 importance of groundwater discharge to the methane budgets of nearshore and
513 continental shelf waters of the northeastern Gulf of Mexico. *Geochimica et*
514 *Cosmochimica Acta* 60 (23): 4735-4746.

515 Burnett, W.C., J. P. Chanton, J. Christoff, E. Kontar, M. Lambert, W. S. Moore, D.
516 O'Rourke, C. Smith, L. Smith, and M. Taniguchi, 2002. Assessing methodologies for
517 measuring groundwater discharge to the ocean. *EOS* 83: 117-123.

518 Burnett, W. C., and H. Dulaiova, 2003. Estimating the dynamics of groundwater input
519 into the coastal zone via continuous radon-222 measurements. *Journal of*
520 *Environmental Radioactivity* 69: 21-35.

521 Burnett, W.C., P.K. Aggarwal, A. Aureli, H. Bokuniewicz, J.E. Cable, M.A. Charette, E.
522 Kontar, S. Krupa, K.M. Kulkarni, A. Loveless, W.S. Moore, J.A. Oberdorfer, J.
523 Oliveira, N. Ozyurt, P. Povinec, A.M.G. Privitera, R. Rajar, R.T. Ramessur, J.
524 Scholten, T. Stieglitz, M. Taniguchi, J.V. Turner, 2006. Quantifying submarine
525 groundwater discharge in the coastal zone via multiple methods. *Science of the Total*
526 *Environment* 367: 498–543

527 Cable, J.E. G. C. Bugna, W. C. Burnett, and J. P. Chanton, 1996. Application of ^{222}Rn
528 and CH_4 for assessment of groundwater discharge to the coastal ocean. *Limnology &*
529 *Oceanography* 41: 1347-1353.

530 Cambareri, T. C., and E.M. Eichner. 1998. Watershed Delineation and Ground Water
531 Discharge to a Coastal Embayment. *Ground Water* 36: 626-634.

532 Camilli, R., Duryea, A., 2007. Characterizing marine hydrocarbons with *in-situ* mass
533 spectrometry, IEEE/MTS OCEANS '07 On the Edge of Tomorrow Vancouver,
534 Canada, pp. 1-7.

535 Charette, M.A., K. O. Buesseler, and J. E. Andrews, 2001. Utility of radium isotopes for
536 evaluating the input and transport of groundwater-derived nitrogen to a Cape Cod
537 estuary. *Limnology and Oceanography* 46(2): 465-470.

538 Charette, M.A.,W.S. Moore and W.C. Burnett, 2008. Uranium- and thorium-series
539 nuclides as tracers of submarine groundwater discharge. *Radioactivity in the*
540 *Environment*, ed. S. Krishnaswami, J.K. Cochran, vol: "U-Th Series Nuclides in
541 Aquatic Systems" 13: 155-191.

542 Corbett, D. R., K. Dillon, W. C. Burnett, and J. P. Chanton, 2000. Estimating the
543 groundwater contribution into Florida Bay via natural tracers, ^{222}Rn and CH_4.
544 *Limnology & Oceanography* 45: 1546-1557

545 Dulaiova, H., R. Peterson, W. C. Burnett, and D. Lane-Smith. 2005. A multidetector
546 continuous monitor for assessment of ^{222}Rn in the coastal ocean. *J. Radioan. and Nucl.*
547 *Chem.* 263(25): 361-365.

548 Dulaiova W. C. Burnett, J. P. Chanton, W. S. Moore. H. J. Bokuniewicz, M. A. Charette,
549 and E. Sholkovitz, 2006. Assessment of groundwater discharge into West Neck Bay,
550 New York, via natural tracers. *Continental Shelf Research* 26(16): 1971-1983.

551 Dulaiova, H., Gonneea, M. E., P. B. Henderson, and M. A. Charette, 2008. Geochemical
552 and physical sources of radon variation in a subterranean estuary - Implications for

553 radon groundwater end-member activities in submarine groundwater discharge studies,
554 *Marine Chemistry* 110(1-2): 120-127.

555 Eganhouse, R.P., Sherblom, P.M., 2001. Anthropogenic organic contaminants in the
556 effluent of a combined sewer overflow: impact on Boston Harbor. Marine
557 Environmental Research 51, 51-74.

558 Jiang M. S. and M. Zhou, 2008. The Massachusetts Bay Hydrodynamic Model: 2005
559 Simulation. Boston: Massachusetts Water Resources Authority. Report 2008-12. 58
560 pp.

561 Johannes R. E., 1980. The ecological significance of the submarine discharge of
562 groundwater. *Mar. Ecol. Prog. Ser*. 3: 365-373.

563 Kim, G. and D.-W. Hwang, 2002. Tidal pumping of groundwater into the coastal ocean
564 revealed from submarine ^{222}Rn and CH_4 monitoring. *Geophysical Research Letters* 29
565 (14): 23-27.

566 Kroeger, K.D., and M.A. Charette, 2008. Nitrogen biogeochemistry of submarine
567 groundwater discharge. *Limnology and Oceanography* 53: 1025-1039.

568 Mau, S., Valentine, D.L., Clark, J.F., Reed, J., Camilli, R., Washburn, L., 2007.
569 Dissolved methane distributions and air-sea flux in the plume of a massive seep field,
570 Coal Oil Point, California. Geophysical Research Letters 34.

571 McGroddy, S. E., and J.W. Farrington, 1995. Sediment porewater partitioning of
572 polycyclic aromatic hydrocarbons in three cores from Boston Harbor, Massachusetts.
573 *Environmental Science & Technology*, 29: 1542-1550.

574 Menzie, C. A., J. J. Cura, J. S. Freshman, and B. Potocki, 1991. Boston Harbor: Estimates
575 of loadings. Report 91-4, Massachusetts Water Resources Authority, Harbor Studies
576 Group. pp. 122.

577 Michael, H. A. 2004. Seasonal dynamics in coastal aquifers: investigation of submarine
578 groundwater discharge through field measurements and numerical models. PhD
579 dissertation, MIT.

580 Michael, H. A., Lubetsky, J. S., Harvey, C. F., 2003. Characterizing submarine
581 groundwater discharge: a seepage meter study in Waquoit Bay, Massachusetts.
582 Geophysical Research Letters 30. Doi:10.1029/2002GL0160000.

583 Michael, H. A., A. E. Mulligan, and C. F. Harvey, 2005. Seasonal oscillations in water
584 exchange between aquifers and the coastal ocean. *Nature* 436(7054): 77-87.

585 Moore, W. S., 1996. Large groundwater inputs to coastal waters revealed by ^{226}Ra
586 enrichments. *Nature* 380: 612-614.

587 Mulligan, A. E. and M. A. Charette, 2006. Intercomparison of submarine groundwater
588 discharge estimates from a sandy unconfined aquifer. *Journal of Hydrology*, 327: 411-
589 425.

590 MWRA, 2008, The state of Boston harbor. The harbor and river monitoring program:
591 http://www.mwra.state.ma.us/harbor/html/bhmonitoring.htm

592 Poppe, L. J. and A. M. Moffett, 1993. Ground water discharge and the related nutrient
593 and trace metal fluxes into Quincy Bay, Massachusetts. *Environmental Monitoring*
594 *and Assessment*, 25: 15-27.

595 Seitzinger, S. P., 1988. Denitrification in freshwater and coastal marine ecosystems:
596 Ecological and geochemical significance. *Limnology and Oceanography* 33: 702-724.

597 Slomp, C. P. and P. Van Cappellen, 2004. Nutrient inputs to the coastal ocean through
598 submarine groundwater discharge: controls and potential impact. *Journal of*
599 *Hydrology* 295: 64-86.

600 Stolzenbach, K. D., and E.E. Adams, 1998. Contaminated sediments in Boston Harbor.
601 Cambridge, MA: MIT Sea Grant College Program.

602 Taylor D. I., 2006. 5 years after transfer of Deer Island flows offshore: an update of
603 water-quality improvements in Boston Harbor. Boston: Massachusetts Water
604 Resources Authority. Report ENQUAD 2006-16. 77 p.

605 Umezawa Y., I. Herzfeld, C. Colgrove, and C.M. Smith, 2008. Impact of terrestrial
606 nutrients through submarine groundwater discharge (SGD) on macroalgal bloom at
607 fringing reef ecosystem "(In) From Headwaters to the Ocean: Hydrological Change
608 and Watershed Management," M. Taniguchi, Y. Fukushima, W.C. Burnett, M. Haigh
609 and Y. Umezawa, Eds. Rotterdam, Balkema.

610 Valiela, I., J. Costa, K. Foreman, J. M. Teal, B. Howes, D. Aubrey, 1990. Transport of
611 groundwater-borne nutrients from watersheds and their effects on coastal waters.
612 *Biogeochemistry* 10: 177-197.

613 Valiela I., K. Foreman, M. LaMontagne, D. Hersh, J. Costa, P. Peckol, B. DeMeo-
614 Andreson, C. D'Avanzo, M. Babione, C.-H. Sham, J. Brawley, K. Lajtha, 1992.
615 Couplings of watersheds and coastal waters- sources and consequences of nutrient
616 enrichment in Waquoit Bay, Massachusetts, *Estuaries* 15(4): 443-457.

617 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
618 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		916						
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

619

620 Figure captions:

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

625 Fig. 2: Response time of Liquicel and the air-water gas exchanger to changes in radon
626 concentrations in water. First, radon-free water was passing through both systems,
627 after 20 minutes the water intake was switched to high radon concentration water, and
628 after 55 minutes the water intake was switched back to radon-free water. Ten
629 minutes after switching from high radon to radon-free water intake 10% of the radon
630 remains in the Liquicel system. The same 10 % level is reached in the air-water gas
631 exchanger after 45 minutes.

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

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

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

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

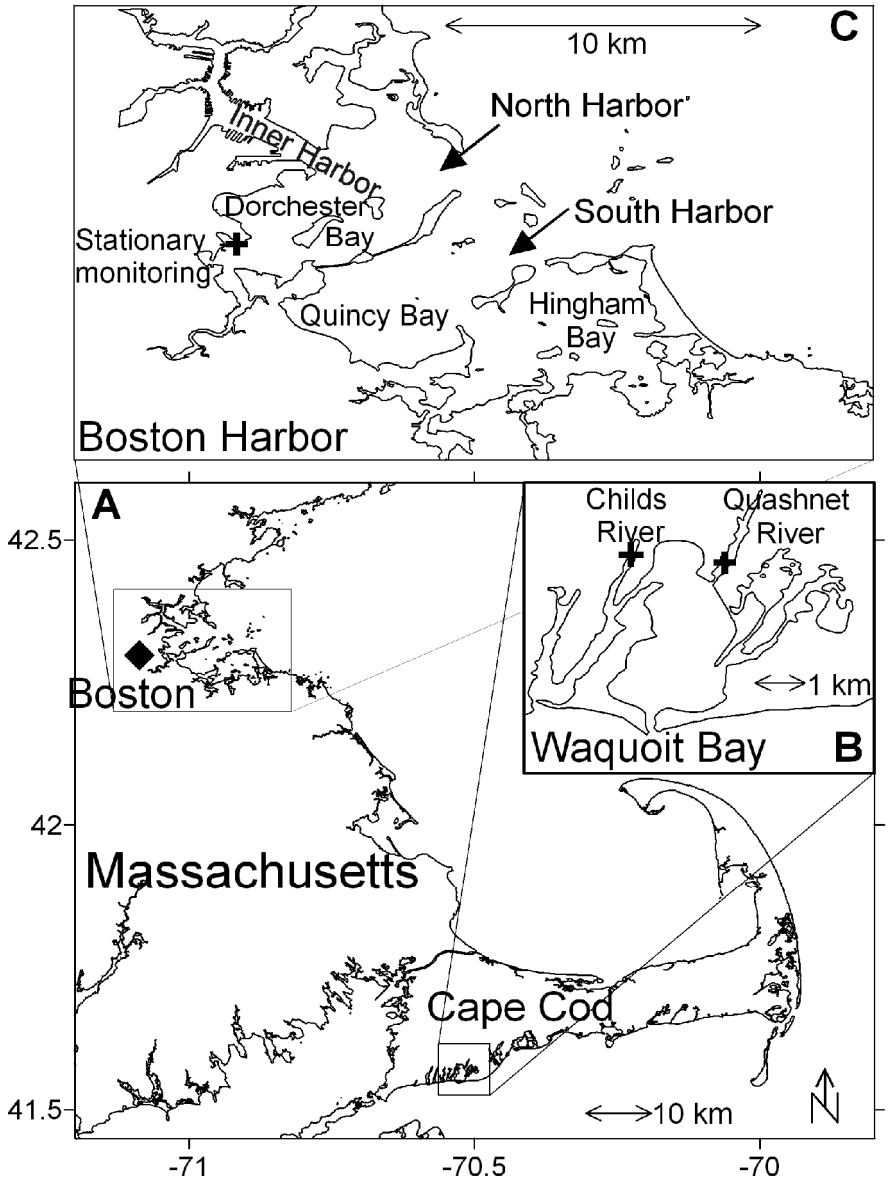
651 Fig. 6: Summer (A, B, C) and winter (D, E, F, G) coastal surface water survey results
652 from Waquoit Bay showing salinity (A, D); radon in dpm L^{-1} (B, E); nitrate+nitrite in
653 μM (C, F); and methane in relative units (G, winter only). Warm colors are high and
654 cold colors are low values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

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

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

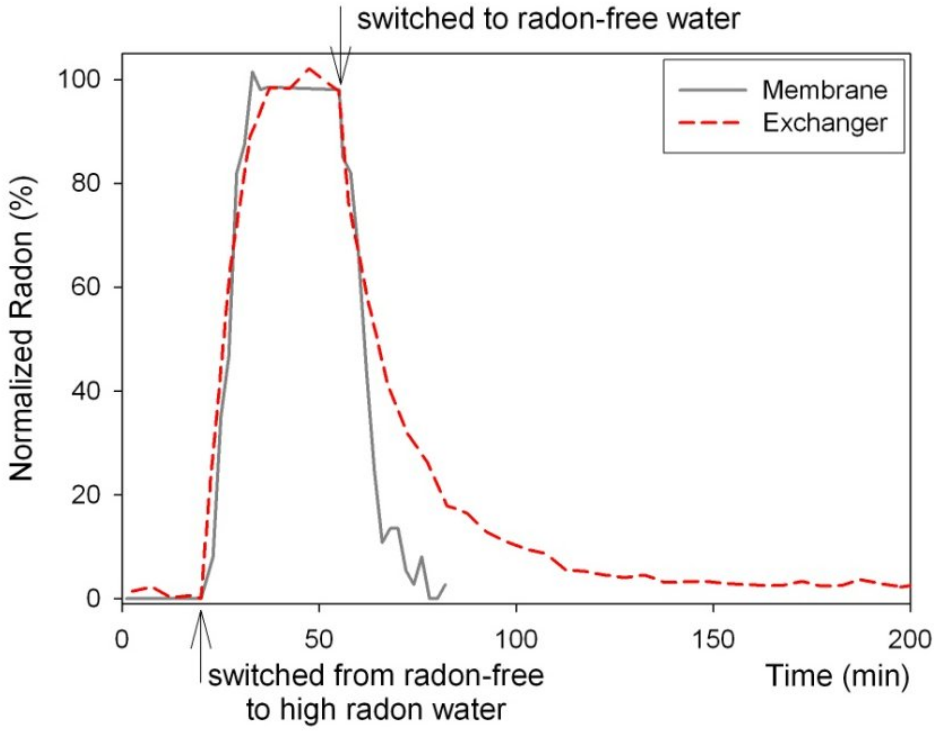
668 Fig. 9: Time series measurements of radon, salinity and nutrients for a period of a change
669 of low tide to high tide in A: Childs River and B: Quashnet River on Dec 5, 2007.
670 Water level, nitrate+nitrite, ammonium, phosphate, silicate, DIN, radon and salinity
671 parameters are indicated over an 8-hour period.
672
673
674
675

676
677



678
679
680
681

Fig. 1



682
683
684
685
686

Fig. 2

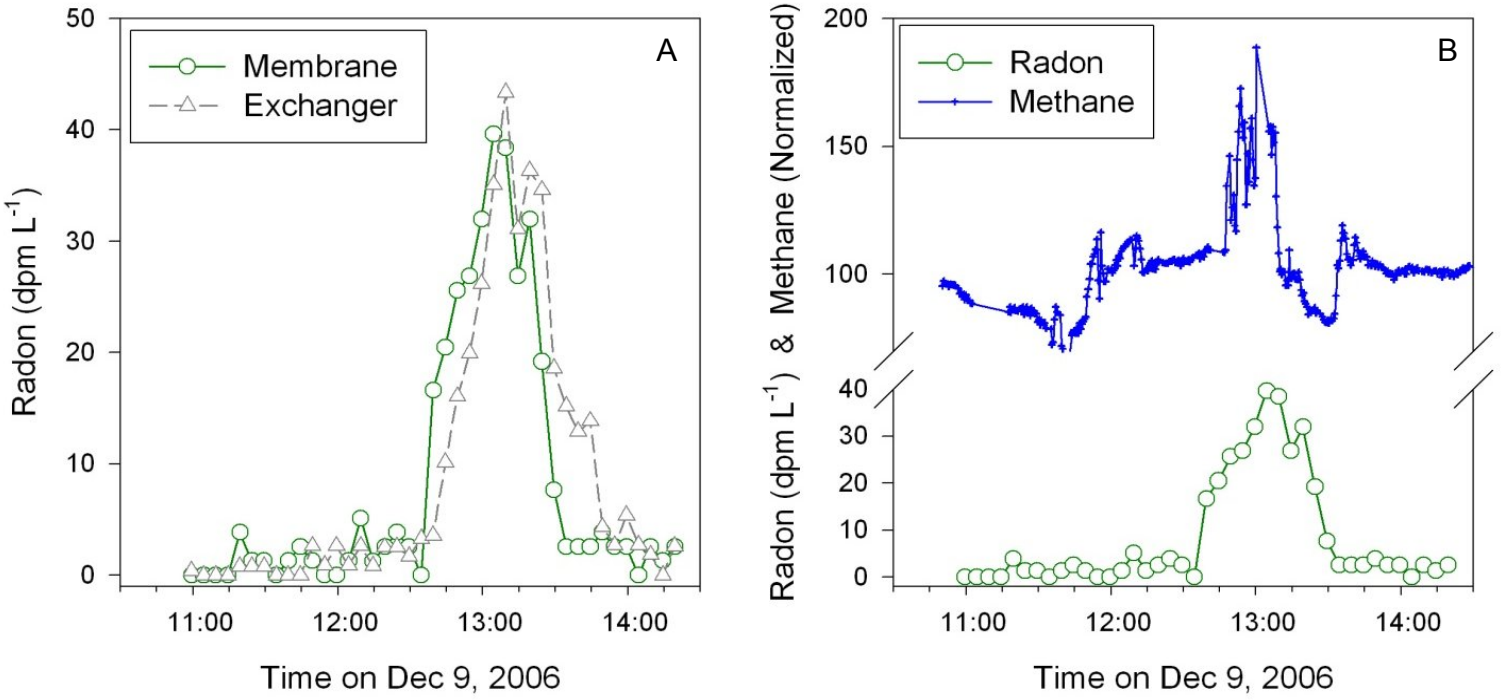
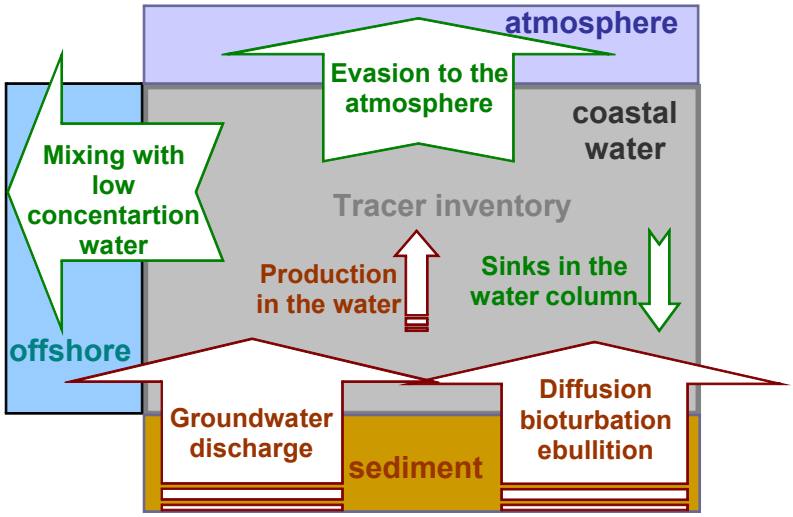

A
Membrane
Exchanger
Radon (dpm L-1)
Time on Dec 9, 2006
B
Radon
Methane
Radon (dpm L-1) & Methane (Normalized)
Time on Dec 9, 2006

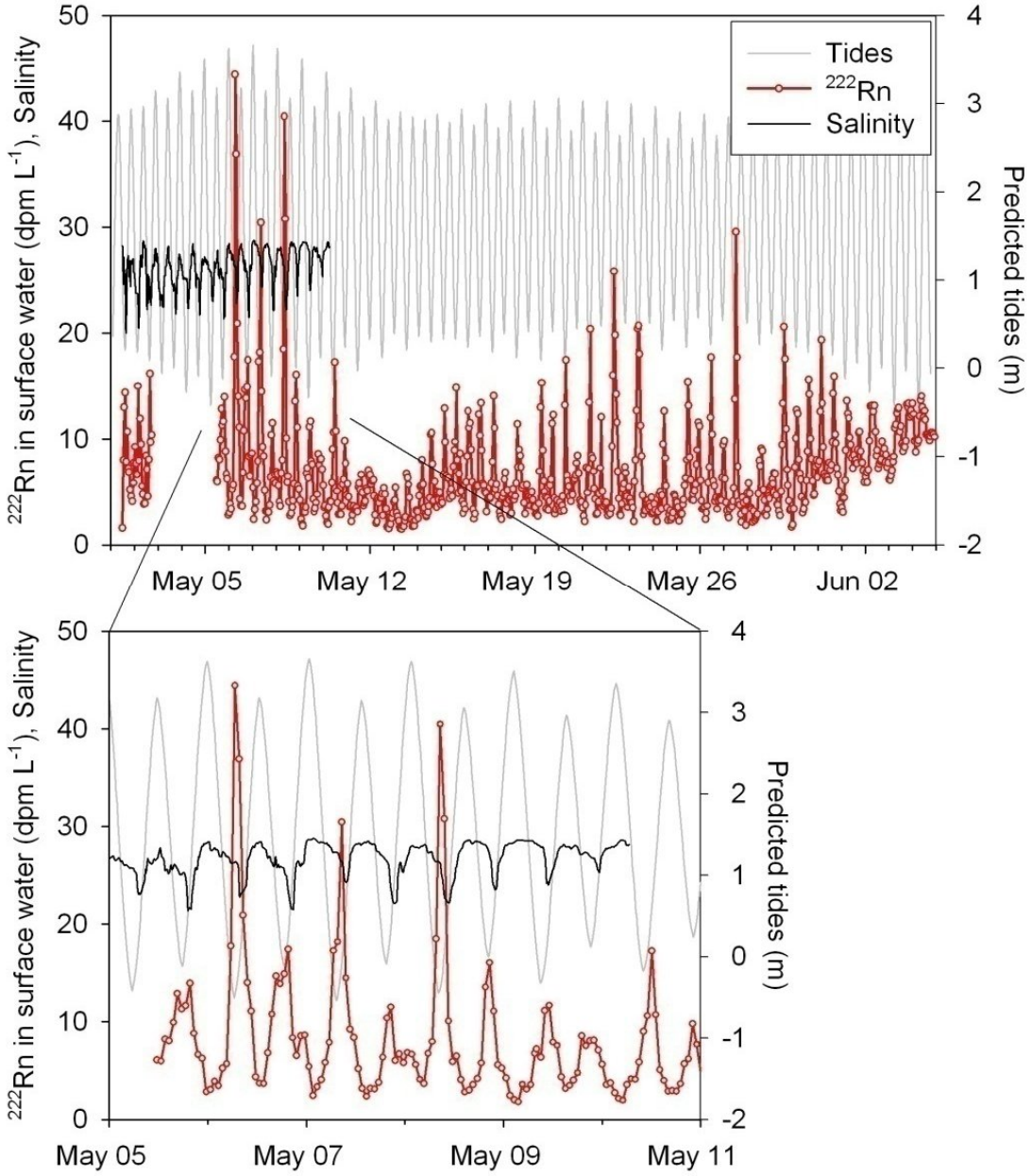
Fig. 3

693
694



695
696
697 Fig. 4
698

699



700
701
702

Fig. 5

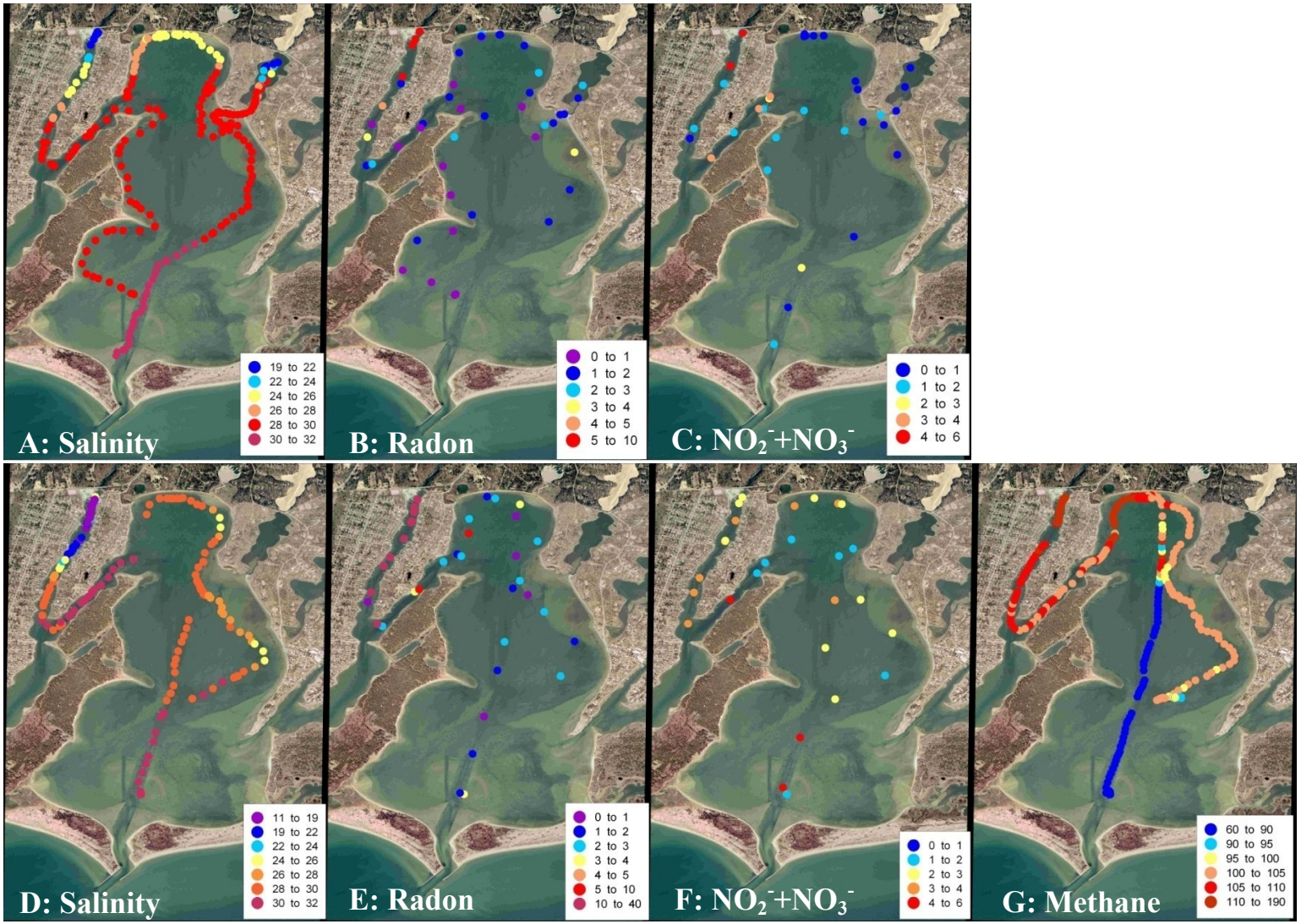

A: Salinity
19 to 22
22 to 24
24 to 26
26 to 28
28 to 30
30 to 32
B: Radon
0 to 1
1 to 2
2 to 3
3 to 4
4 to 5
5 to 10
C: NO_2^-+NO_3^-
0 to 1
1 to 2
2 to 3
3 to 4
4 to 6
D: Salinity
11 to 19
19 to 22
22 to 24
24 to 26
26 to 28
28 to 30
30 to 32
E: Radon
0 to 1
1 to 2
2 to 3
3 to 4
4 to 5
5 to 10
10 to 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

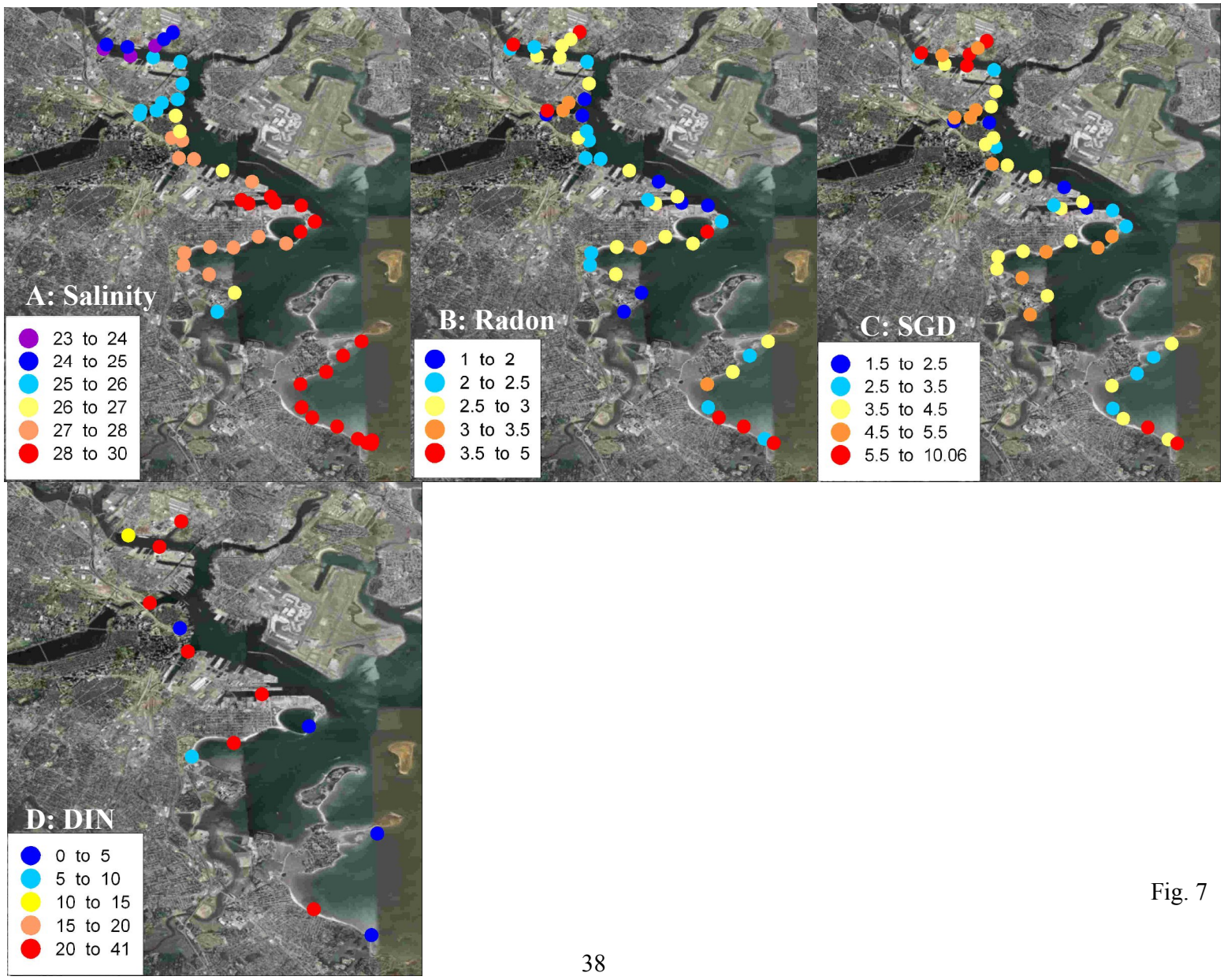

A: Salinity
23 to 24
24 to 25
25 to 26
26 to 27
27 to 28
28 to 30
B: Radon
1 to 2
2 to 2.5
2.5 to 3
3 to 3.5
3.5 to 5
C: SGD
1.5 to 2.5
2.5 to 3.5
3.5 to 4.5
4.5 to 5.5
5.5 to 10.06
D: DIN
0 to 5
5 to 10
10 to 15
15 to 20
20 to 41

Fig. 7

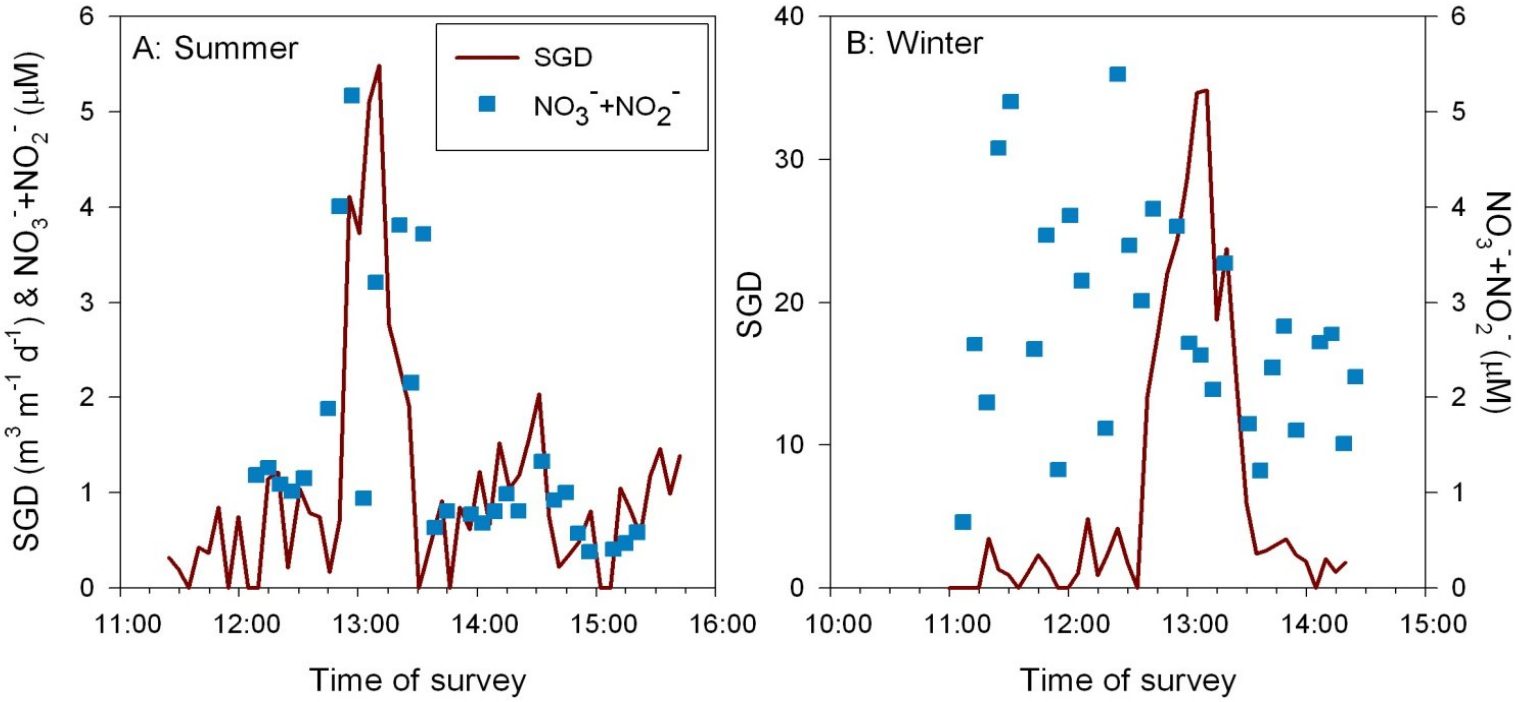

A: Summer
SGD
$NO_3^-+NO_2^-$
SGD (m^3 m^{-1} d^{-1}) & $NO_3^-+NO_2^-$ (μM)
Time of survey
B: Winter
SGD
$NO_3^-+NO_2^-$ (μM)
Time of survey

Fig. 8

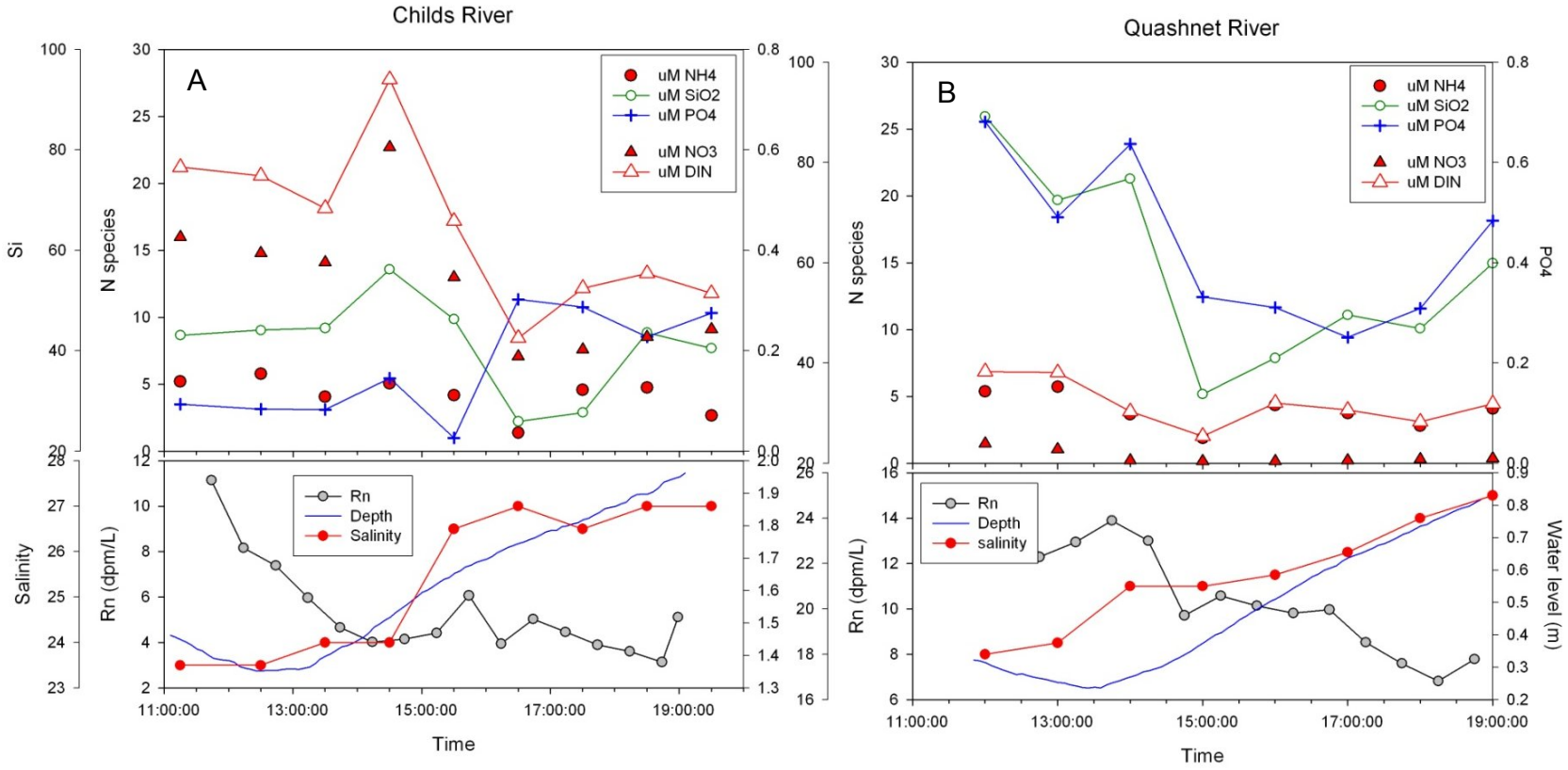

Childs River
A
uM NH4
uM SiO2
uM PO4
uM NO3
uM DIN
Si
N species
Rn
Depth
Salinity
Rn (dpm/L)
Salinity
Time
11:00:00
13:00:00
15:00:00
17:00:00
19:00:00
Quashnet River
B
uM NH4
uM SiO2
uM PO4
uM NO3
uM DIN
N species
PO4
Rn
Depth
salinity
Rn (dpm/L)
Water level (m)
Time
11:00:00
13:00:00
15:00:00
17:00:00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

Fig. 9