

**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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1 **Abstract**

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

14

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

17

18 **1. Introduction**

19 Recent estimates suggest that groundwater discharge into coastal waters
20 worldwide represents up to one tenth of the total river flow, in some areas it might be as
21 high as one third of the river discharge (Moore, 1996; Dulaiova et al, 2006). Expanding
22 residential and commercial near-shore development is leading to increased nutrient inputs
23 to groundwater that eventually migrate into to coastal waters. Several-decades long
24 research shows that nitrogen inputs via non-point sources over large coastline areas cause
25 decline of ecological health and may support harmful algal blooms (Valiela et al., 1990;
26 1992; Slomp and Van Cappellen, 2004; Lee and Kim, 2007; Umezawa et al., 2008).

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

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

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

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

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

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

74

75 **2. Methods**

76 Our mapping system consists of several component instruments. One of these
77 instruments is a modified radon surveying system (Dulaiova et al., 2005), which consists
78 of 3 commercially available radon-in-air analyzers (RAD7, manufactured by Durrige,
79 Inc., Massachusetts) employed to measure ^{222}Rn from a continuous stream of water
80 passing through an air-water exchanger that distributes radon from the running water to a
81 closed air loop. The exchanger, which takes about 15 minutes to reach full equilibrium in
82 the loop, causes a relatively slow response to changes in radon activities in water. The
83 other disadvantage of the exchanger is that it has a memory-effect due to sluggish
84 flushing of radon from the closed loop. To improve the response time of the system we
85 replaced the air-water exchanger with a membrane contactor (Liquicel, manufactured by
86 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 through the membrane ($1-15 \text{ L min}^{-1}$) and also by varying the water temperature
91 by heating the water to different temperatures between 5 and 30 °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

110 measurements of ion peak heights were recorded at m/z 15 as an indicator of relative
111 methane intensity. In addition to the methane time series data, ion peaks at m/z 17, 28, 32,
112 40, and 44 were recorded to identify relative changes in gases corresponding, respectively,
113 to water vapor, di-nitrogen, oxygen, argon and carbon dioxide. The methane ion peak
114 intensity (m/z 15) was then normalized to water vapor intensity (m/z 17) in order to
115 generate a temperature normalized methane intensity estimate. Spectral sweeps across
116 the instrument's full mass range (2-200 AMU) were performed at selected sites to
117 identify any potential contributions from anomalous gases or volatile hydrocarbons.

118 The survey system is also complemented by a commercially available automated
119 nutrient analyzer (W. S. Envirotech Ecolab) to measure water column nitrate + nitrite
120 concentrations. Other auxiliary measurements include salinity and temperature, which
121 may aid in identifying the nature of groundwater discharge (fresh meteoric water or
122 recirculated seawater). During the surveys the instrument cluster was positioned on a
123 small coastal vessel. Each instrument had an independent water intake pump located at 1
124 m below the surface. The vessel's track was logged using a Garmin global positioning
125 system in 10 second intervals. Post processing of data involved synchronous merging of
126 TETHYS data, radon, salinity, temperature, and nitrate values with GPS tracklog files.
127 Due to varying latency of the instruments, each parameter was measured in different
128 logging intervals. Radon was usually measured in 5 minute integrated intervals, methane
129 including salinity and temperature every 30 seconds, and nitrate was sampled once every
130 6 minutes. Therefore in the final results the radon profile is spatially smoothed in
131 comparison to the methane and salinity data that were sampled in much shorter time
132 increments.

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

138

139 **3. Study sites**

140 We deployed the mapping system in Waquoit Bay, MA (Fig. 1), an area with
141 extensive prior hydrological and geochemical SGD data sets. Waquoit Bay is a shallow
142 estuary on the south shoreline of Cape Cod, MA. The geologic deposits on Cape Cod
143 consist of outwash gravel, sand, and silt with occurrences of lacustrine deposits of silts
144 and clays (Cambareri and Eichner, 1998). Waquoit Bay receives groundwater from the
145 Cape Cod aquifer, which is an unconfined aquifer, approximately 100 to 120 m thick and
146 it is bounded by marine water at its margins and less permeable deposits of till and
147 bedrock below. The bay is located along the southern margin of the Sagamore Lens,
148 which is part of the Cape Cod Aquifer. A significant portion of the freshwater input into
149 Waquoit Bay occurs as submarine groundwater discharge (Valiela et al., 1990; Cambareri
150 and Eichner, 1998; Charette et al., 2001). False color imagery of surface temperatures
151 recorded during September 2002 indicate several locations of groundwater discharge into
152 the bay (Mulligan and Charette, 2006). Zones of high groundwater discharge are known
153 to be present in Childs River and down gradient of bluffs along the head of the bay
154 (Mulligan and Charette, 2006). Seepage meter studies indicate that in this area SGD
155 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 m³ m⁻¹ d⁻¹ (Mulligan and Charette, 2006) and is 5.3 m³
159 m⁻¹ d⁻¹ based on a ²²⁶Ra 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.

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

189

190 **4. Results and Discussion**

191 *4.1 Resolution of tracer surveys*

192 The mapping system provides in-situ estimates of radon and methane
193 concentrations in real-time during mapping. This makes it possible to efficiently identify
194 and focus measurements at sites where SGD is occurring, thereby providing better
195 estimates of tracer distributions and the spatial extent of groundwater discharge. This
196 new system has the advantage of a better spatial resolution due to the high resolution
197 methane sampling (every 30 seconds) and an improved radon mapping system.

198 Ultimately the spatial resolution for each of the system's component technologies is a
199 function of sampling interval and survey velocity.

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

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

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

216

217 *4.2 SGD rates derived from tracers*

218 Unlike radon, methane is a non-conservative gas and its concentration may be
219 influenced by microbial and biochemical processes during which it can be produced or
220 consumed in the sediments and water column. It is therefore only useful in areas where a
221 significant concentration gradient exists between groundwater and surface water, in
222 principle, when there is enough anaerobic organic matter decomposition in the aquifer.
223 Correspondingly, groundwater redox pE measured in the subterranean estuary at the head
224 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 recirculated 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:

$$264 \quad Q_{SGD_{tot}} = \frac{A_{Rn_{cw}} * V}{\tau * A_{Rn_{gw}}}, \quad (1)$$

265 and

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

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

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

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

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

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

$$282 \text{ Excess } ^{222}\text{Rn} = \text{total } ^{222}\text{Rn} - ^{226}\text{Ra} \quad (3)$$

283 b. The amount of radon diffusing from the bottom sediments can be
284 estimated from an experimentally defined relationship between
285 ^{226}Ra content of sediments and the corresponding measured ^{222}Rn
286 flux by diffusion (Burnett et al., 2003). That empirical
287 relationship was derived from experimental data from several
288 different environments (both marine and fresh), where

$$289 \text{ Radon flux by diffusion (dpm m}^{-2} \text{ day}^{-1}) = 495 \times ^{226}\text{Ra activity} + \\ 290 18.2. \quad (4)$$

291 Bottom sediment ^{226}Ra activity in Waquoit Bay is $<0.5 \text{ dpm g}^{-1}$
292 (Gonneea et al., 2008) and the radon diffusion calculated from Eq.
293 4 is $125 \text{ dpm m}^{-2} \text{ tide}^{-1}$. Diffusion therefore supports less than 3%

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

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

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

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

$$310 \quad F_{\text{atm}} = k(C_w - \alpha C_{\text{atm}}) \quad (5)$$

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

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

317

318 2) For each measurement the volume of the coastal water box (V) is
319 calculated from the length of the coastal segment, average water
320 column or mixed layer depth, and the width of the seepage face. The
321 length of the coastal segment is the half distance between the previous
322 and following measurements of the survey and it is variable depending
323 on the boat speed, for the surveys in WB it ranged between 10-300 m
324 and in BH 100-300 m. Since radon is measured as an integrated value
325 over this distance, it truly represents this section of the coastline. The
326 width of the seepage face in Waquoit Bay was 30 m (Michael et al.,
327 2005) and in the absence of better estimates we assumed the same for
328 Boston Harbor. SGD can also be expressed as discharge per meter of
329 coastline ($\text{m}^3 \text{m}^{-1} \text{d}^{-1}$) in which case the volume of the coastal box in Eq.
330 (1) and (2) is divided by the coastline length (half distance from the
331 previous plus half distance from the following measurement).

332 3) The flushing rate (τ) of the coastal box is considered one tidal cycle
333 (12.25 hours). This is based on our observation from a time series radon
334 measurement in Boston Harbor (Fig. 5) that at high tide the radon
335 values follow a baseline open bay activities indicating that the coastal
336 box is flushed with every tidal cycle. We assume the same for Waquoit
337 Bay. In case the mixing regime is significantly faster than tidal (i.e. due

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

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

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

366 As mentioned earlier we surveyed for SGD tracers at low tide in order to have the least
367 diluted water column by offshore waters during flood tide. At two sites in Waquoit Bay
368 (Childs River and Quashnet River) we tested how the water radon inventory (radon
369 activity[dpm m⁻³] x depth[m]) changes over a tidal cycle. Theoretically, if there was no
370 SGD and there were no currents and losses by mixing flood tide should dilute the radon
371 but the water column inventory should stay the same. However, variable SGD, currents
372 and mixing cause fluctuations in radon activity and we found that the radon inventories
373 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
374 Quashnet and Childs Rivers respectively. The observed 50% change in inventories is
375 equivalent to 50% difference in the calculated SGD. These findings support that the most
376 sensitive survey can be done at low tide when waters are least diluted and least
377 influenced by mixing losses and we expect the highest SGD.

378 Radon provides an estimate of total SGD but it cannot be used to determine the
379 fraction of fresh vs. saline groundwater discharge. In systems with little or no surface
380 runoff it is possible to use salinity and Eq. (2) to calculate fresh SGD. This calculation
381 uses some of the same terms (τ , V) and is based on similar assumptions as the radon
382 approach described above. Additional assumptions in Eq(2) are that we neglect salinity
383 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 °C and Boston Harbor Jul08 average temperature was 17.3 °C) than
388 during the winter survey (Waquoit Bay Dec06 average water temperature was 3.8 °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

407 distributions. Using equations (1) and (2) and the corresponding coastline length for
408 each value we derived that maximum SGD rates occur in Childs River ($5.5 \text{ m}^3 \text{ m}^{-1} \text{ d}^{-1}$ of
409 total SGD in summer and some sections as high as $30 \text{ m}^3 \text{ m}^{-1} \text{ d}^{-1}$ in winter), followed by
410 the head of the bay (2 and $3 \text{ m}^3 \text{ m}^{-1} \text{ d}^{-1}$ in the summer and winter, respectively). We
411 expected elevated SGD in Quashnet River, but due to low water levels we were not able
412 to survey it in such detail as the other parts of the bay. Total SGD fluxes for the whole
413 bay based on radon groundwater activities of $120\text{-}310 \text{ dpm L}^{-1}$ are $5.5\text{-}11 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ in
414 the summer and $28\text{-}56 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ in winter. From that, fresh SGD rates are
415 approximately $5 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ in the summer and $8 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ in winter, again these
416 estimates are skewed by the presence of surface runoff. Our calculation of total SGD
417 may also carry an uncertainty related to the change of flushing rate of the near-shore
418 zones for the two different seasons (τ in Eq. (1) and (2)).

419 There have been several SGD studies in Waquoit Bay (Mulligan and Charette,
420 2006; Michael et al., 2003; Michael, 2004; Cambareri and Eichner, 1998) with which we
421 can compare our results (Table 1). Our estimates for fresh (920 (Aug 06) and 2050 (Dec
422 06) $\text{m}^3 \text{ d}^{-1}$) and total (2845 and $4292 \text{ m}^3 \text{ d}^{-1}$) SGD for the head of the bay agreed very
423 well with all previous studies (950 to $2419 \text{ m}^3 \text{ d}^{-1}$). In Childs River our fresh SGD (2680
424 and $6159 \text{ m}^3 \text{ d}^{-1}$) was very close to Cambareri and Eichner's (1998) estimate which is a
425 representative of a yearly average ($2740 \text{ m}^3 \text{ d}^{-1}$). Our results for fresh SGD for the whole
426 bay are lower than Cambareri and Eichner's (1998) and we believe that is because we
427 could not properly survey Quashnet River and hence our estimates are missing a
428 relatively large fresh SGD component.

429 Radon is used in the calculation of total SGD in Boston Harbor surveyed in Sep
430 08 (Fig. 7). In general, radon levels were elevated throughout the bay with several SGD
431 hot-spots indicated by high radon in the Inner Harbor and Quincy Bay (red circles on Fig.
432 7). In some parts of the harbor radon and salinity showed a strong negative correlation
433 suggesting the discharge of low salinity high radon groundwater (Inner Harbor), in the
434 southern part of our survey (Quincy Bay) the lack of negative correlation between
435 salinity and radon indicates the presence of mostly brackish/saline groundwater
436 discharge.

437 SGD rates varied from 1.5 to $10 \text{ m}^3 \text{ m}^{-1} \text{ d}^{-1}$. The highest fluxes occurred in the
438 northern sectors of the harbor. This survey covered approximately 50% of the coastline
439 in North Harbor and 10% in South Harbor. The corresponding SGD rates were 90×10^3
440 $\text{m}^3 \text{ d}^{-1}$ and $20 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ in the surveyed sections. If extrapolated to represent discharge
441 from the total length of coastline would be 11 and 39% of river discharge in the North
442 and South Harbors, respectively (<http://waterdata.usgs.gov/nwis/rt>). These fluxes include
443 the discharge of fresh and marine groundwater components. In comparison, total
444 groundwater discharge determined from an earlier study in Quincy Bay (Wollaston
445 Beach) ranged from 1.3 to $2.2 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ on a coast-perpendicular transect that was
446 scaled up to represent a 4.6 km length of coastline. This flux was calculated to be
447 equivalent to 7-12% of surface discharge (Poppe and Moffett, 1993). Our survey results
448 at the Wollaston Beach suggest rates from 1.4 to $2.2 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ but our study also
449 indicates that SGD is variable and the rate doubles in the southeast section of the beach.
450 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 $41 \times 10^3 \text{ m}^3 \text{ d}^{-1}$ and the North Harbor
455 is $43 \times 10^3 \text{ m}^3 \text{ d}^{-1}$, 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.

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

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

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

490 DIN concentration in Waquoit Bay was much higher in the winter than summer.
491 In the summer, nitrate (the only measured N species) concentrations correspond nicely to
492 variations in SGD throughout the bay (Fig. 8) and peak at 6 μM in the Childs River
493 where total SGD rates also peak at 5.5 $\text{m}^3 \text{m}^{-1} \text{d}^{-1}$. Moderate groundwater fluxes in
494 Quashnet River (2 $\text{m}^3 \text{m}^{-1} \text{d}^{-1}$) are not accompanied by significant nitrate concentrations.
495 Winter nitrate concentrations are more evenly distributed with no apparent correlation
496 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 recirculated 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 ($4-12 \text{ dpm L}^{-1}$)
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 $\sim 5 \text{ } \mu\text{M}$. 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 ($1-5 \text{ } \mu\text{M}$). 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-](http://www.mwra.state.ma.us/harbor/graphic/4-1.gif)
545 [1.gif](http://www.mwra.state.ma.us/harbor/graphic/4-1.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,

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

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

584

585 **5. Conclusions**

586 By combining radon/methane/nitrate into a survey system we are able to quickly
587 and efficiently create detailed maps of submarine groundwater discharge in coastal
588 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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623 **References**

- 624 Bugna, G. C., J. P. Chanton, J. E. Cable, W. C. Burnett, and P. H. Cable, 1996. The
625 importance of groundwater discharge to the methane budgets of nearshore and
626 continental shelf waters of the northeastern Gulf of Mexico. *Geochimica et*
627 *Cosmochimica Acta* 60 (23): 4735-4746.
- 628 Burnett, W.C., J. P. Chanton, J. Christoff, E. Kontar, M. Lambert, W. S. Moore, D.
629 O'Rourke, C. Smith, L. Smith, and M. Taniguchi, 2002. Assessing methodologies for
630 measuring groundwater discharge to the ocean. *EOS* 83: 117-123.
- 631 Burnett, W. C., and H. Dulaiova, 2003. Estimating the dynamics of groundwater input
632 into the coastal zone via continuous radon-222 measurements. *Journal of*
633 *Environmental Radioactivity* 69: 21-35.
- 634 Burnett, W.C., P.K. Aggarwal, A. Aureli, H. Bokuniewicz, J.E. Cable, M.A. Charette, E.
635 Kontar, S. Krupa, K.M. Kulkarni, A. Loveless, W.S. Moore, J.A. Oberdorfer, J.
636 Oliveira, N. Ozyurt, P. Povinec, A.M.G. Privitera, R. Rajar, R.T. Ramessur, J.
637 Scholten, T. Stieglitz, M. Taniguchi, J.V. Turner, 2006. Quantifying submarine
638 groundwater discharge in the coastal zone via multiple methods. *Science of the Total*
639 *Environment* 367: 498–543
- 640 Cable, J.E. G. C. Bugna, W. C. Burnett, and J. P. Chanton, 1996. Application of ^{222}Rn
641 and CH_4 for assessment of groundwater discharge to the coastal ocean. *Limnology &*
642 *Oceanography* 41: 1347-1353.
- 643 Cambareri, T. C., and E.M. Eichner. 1998. Watershed Delineation and Ground Water
644 Discharge to a Coastal Embayment. *Ground Water* 36: 626-634.

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

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

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

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

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

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

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

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

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

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

674 Kim, G. and D.-W. Hwang, 2002. Tidal pumping of groundwater into the coastal ocean
675 revealed from submarine ^{222}Rn and CH_4 monitoring. *Geophysical Research Letters* 29
676 (14): 23-27.

677 Lee, Y.-W. and G. Kim, 2007. Linking groundwater-borne nutrients and dinoflagellate
678 red-tide outbreaks in the southern sea of Korea using a Ra tracer. *Estuarine, Coastal*
679 *and Shelf Science*, 71(1-2), 309-317

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

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

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

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

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

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

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

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

701 Mulligan, A. E. and M. A. Charette, 2006. Intercomparison of submarine groundwater
702 discharge estimates from a sandy unconfined aquifer. *Journal of Hydrology*, 327: 411-
703 425.

704 MWRA, 2008, The state of Boston harbor. The harbor and river monitoring program:
705 <http://www.mwra.state.ma.us/harbor/html/bhmonitoring.htm>

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

709 Robinson, C., B. Gibbes, and L. Li, 2003. Driving mechanisms for groundwater flow and
710 salt transport in a subterranean estuary, *Geophysical research letters*, 33, L03402,
711 doi:10.1029/2005GL025247.

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

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

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

719 Sumner, D. M. and G. Belaine, 2005. Evaporation, precipitation and associated salinity
720 changes at a humid, subtropical estuary. *Estuaries*, 28(6), 844-855.

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

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

- 729 Valiela, I., J. Costa, K. Foreman, J. M. Teal, B. Howes, D. Aubrey, 1990. Transport of
730 groundwater-borne nutrients from watersheds and their effects on coastal waters.
731 *Biogeochemistry* 10: 177-197.
- 732 Valiela I., K. Foreman, M. LaMontagne, D. Hersh, J. Costa, P. Peckol, B. DeMeo-
733 Andreson, C. D'Avanzo, M. Babione, C.-H. Sham, J. Brawley, K. Lajtha, 1992.
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 ($\text{m}^3 \text{d}^{-1}$) 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.

SGD ($\text{m}^3 \text{d}^{-1}$)	Head of bay			Childs River			Whole bay		
	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

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

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

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

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

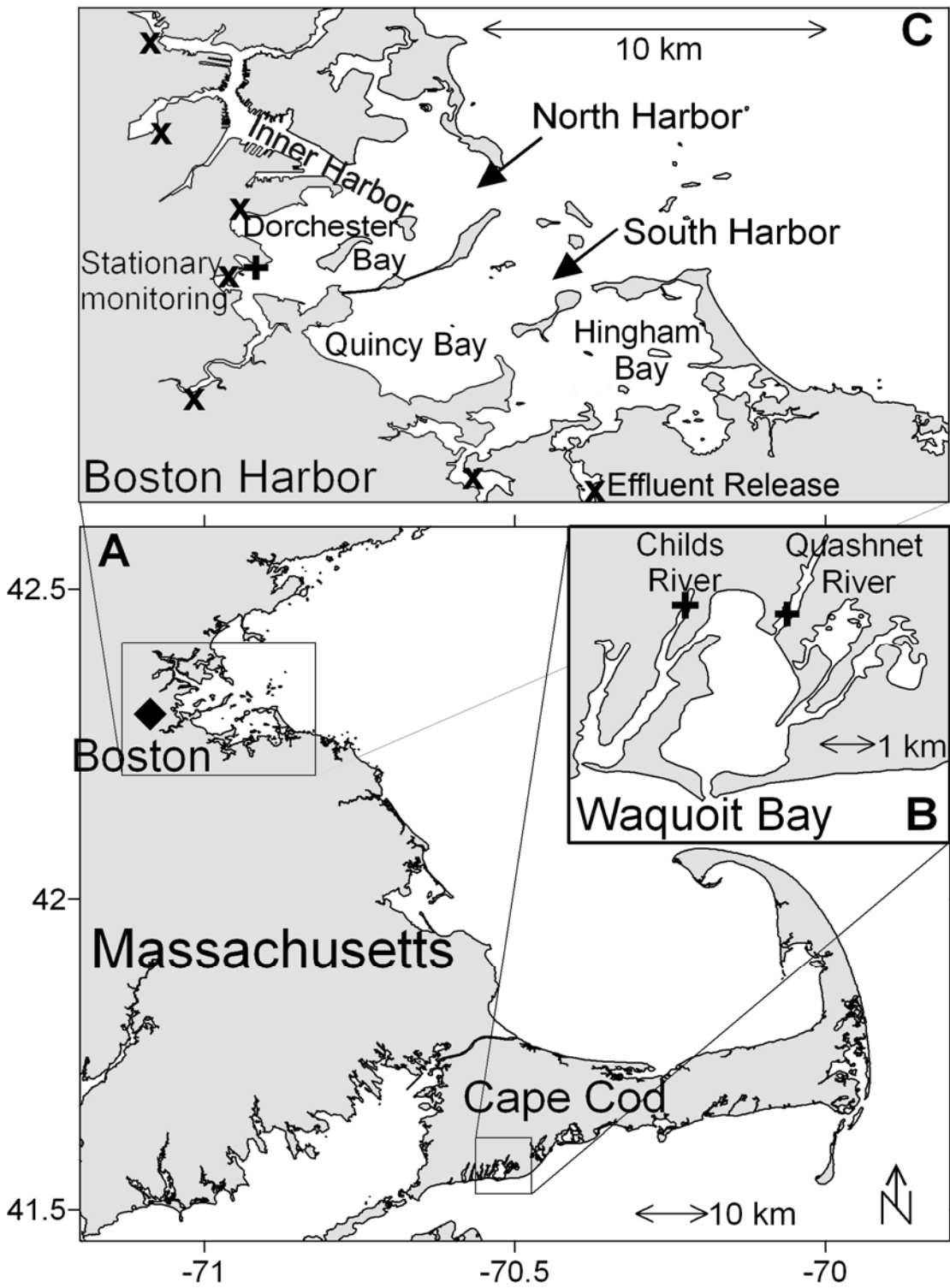
787 Fig. 9: Time series measurements of radon, salinity and nutrients for a period of a change
788 of low tide to high tide in A: Childs River and B: Quashnet River on Dec 5, 2007.
789 Water level, nitrate+nitrite, ammonium, phosphate, silicate, DIN, radon and salinity
790 parameters are indicated over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

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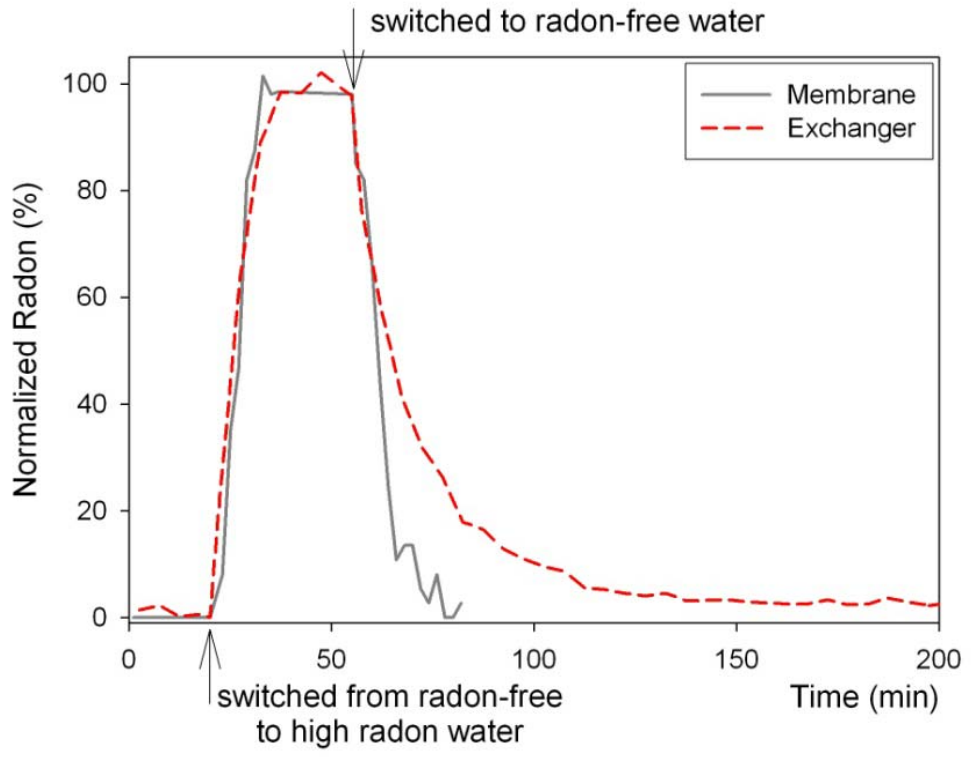
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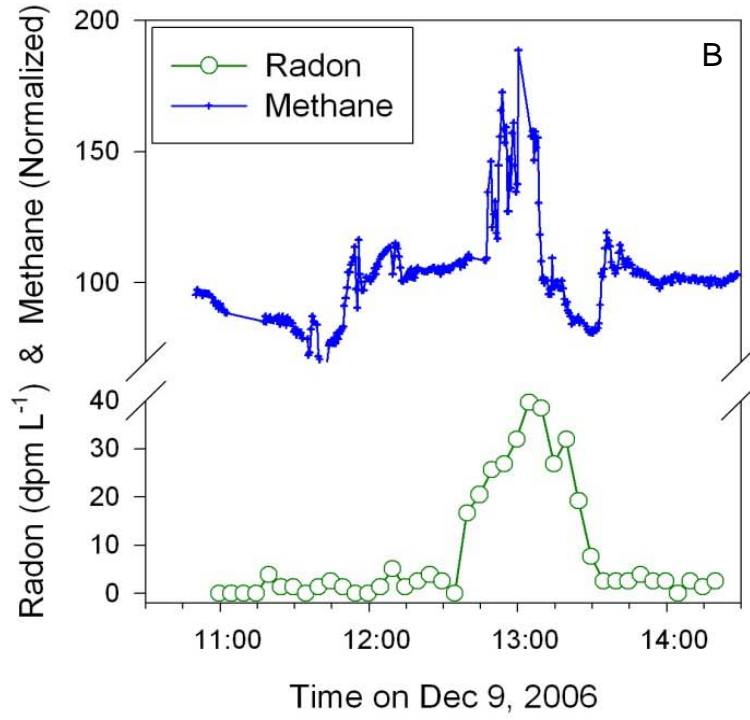
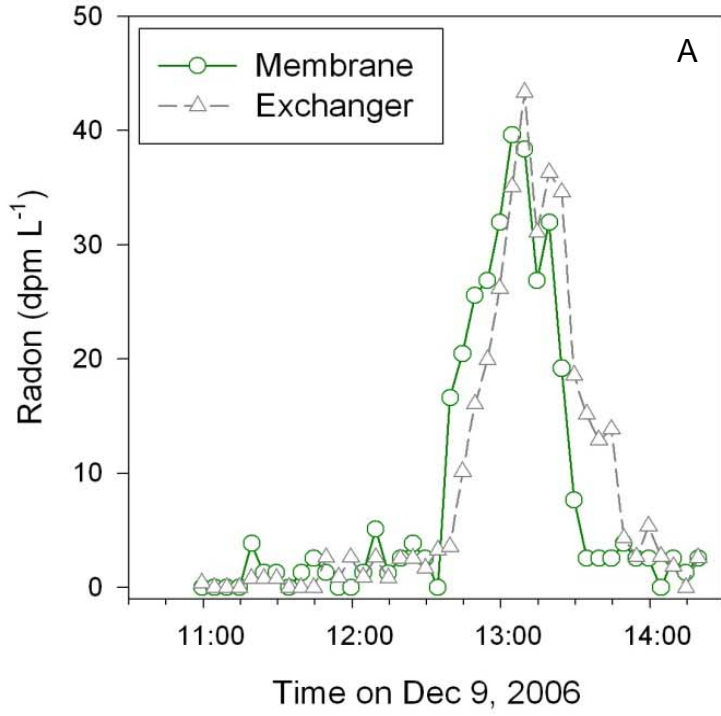
Fig. 1



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Fig. 2

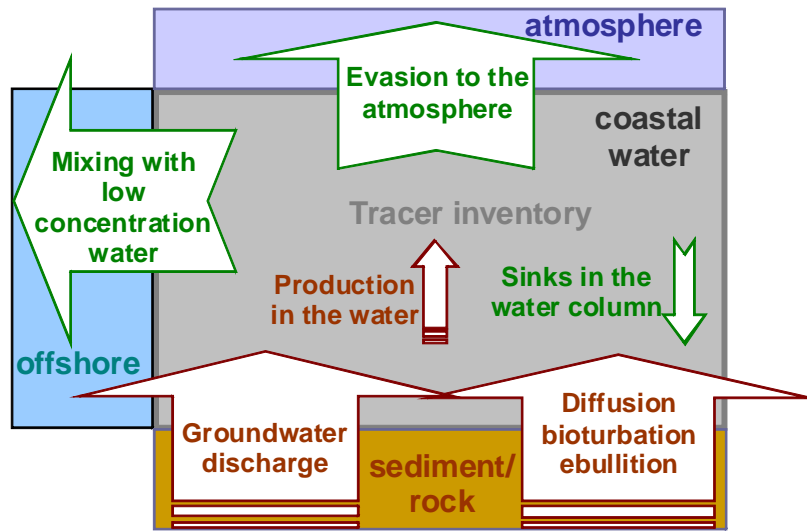
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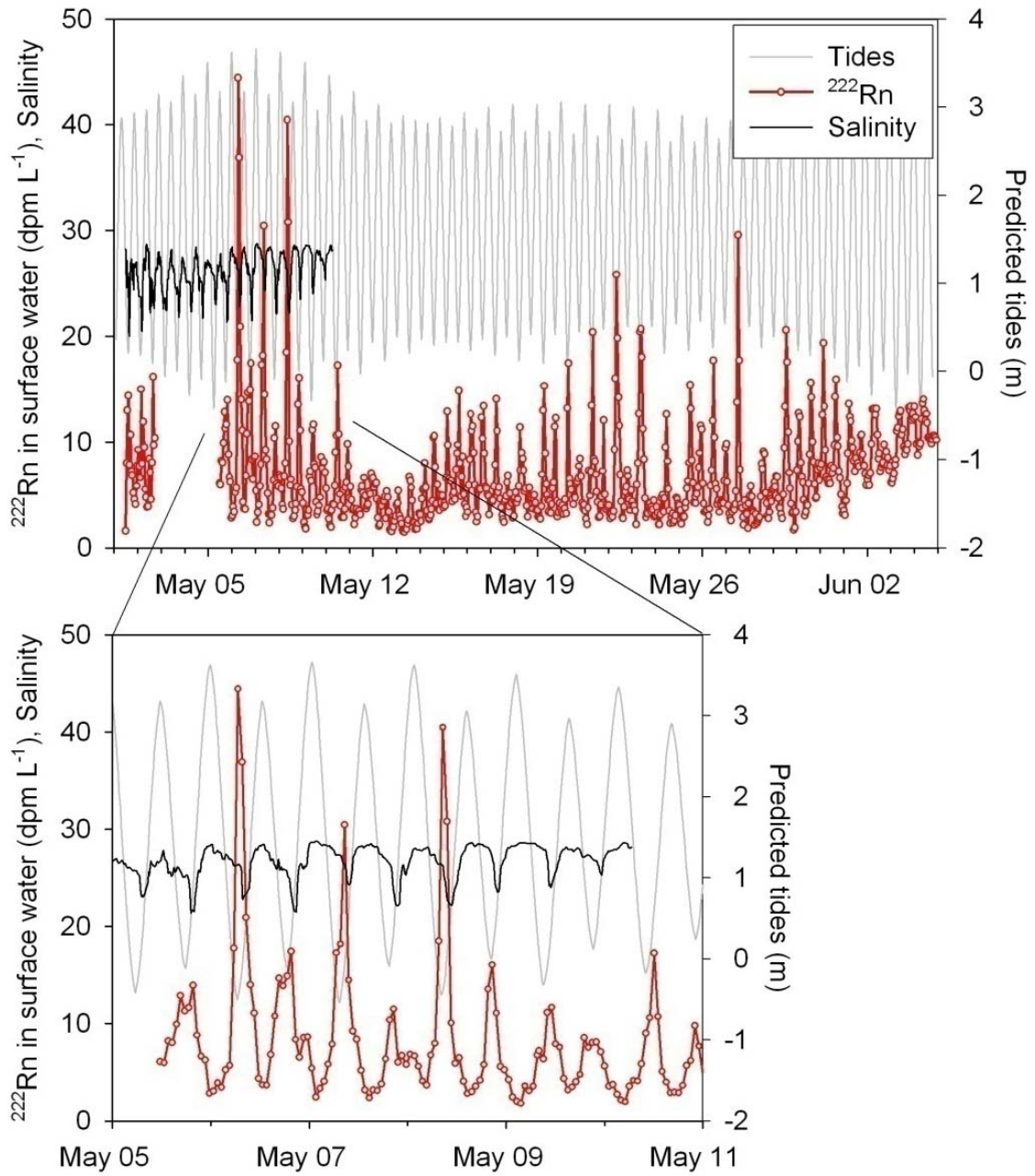
Fig. 3

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Fig. 4



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Fig. 5

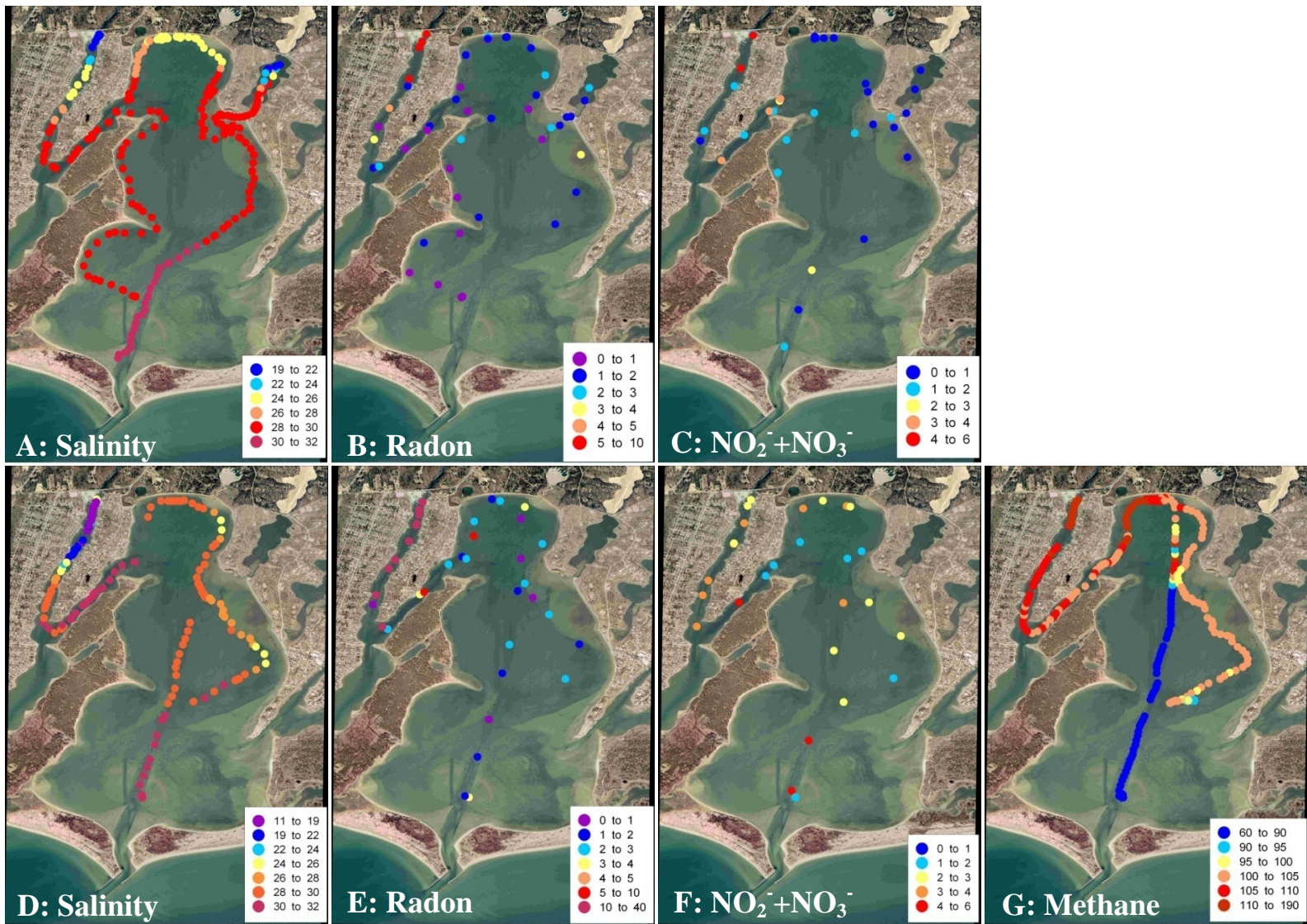


Fig. 6

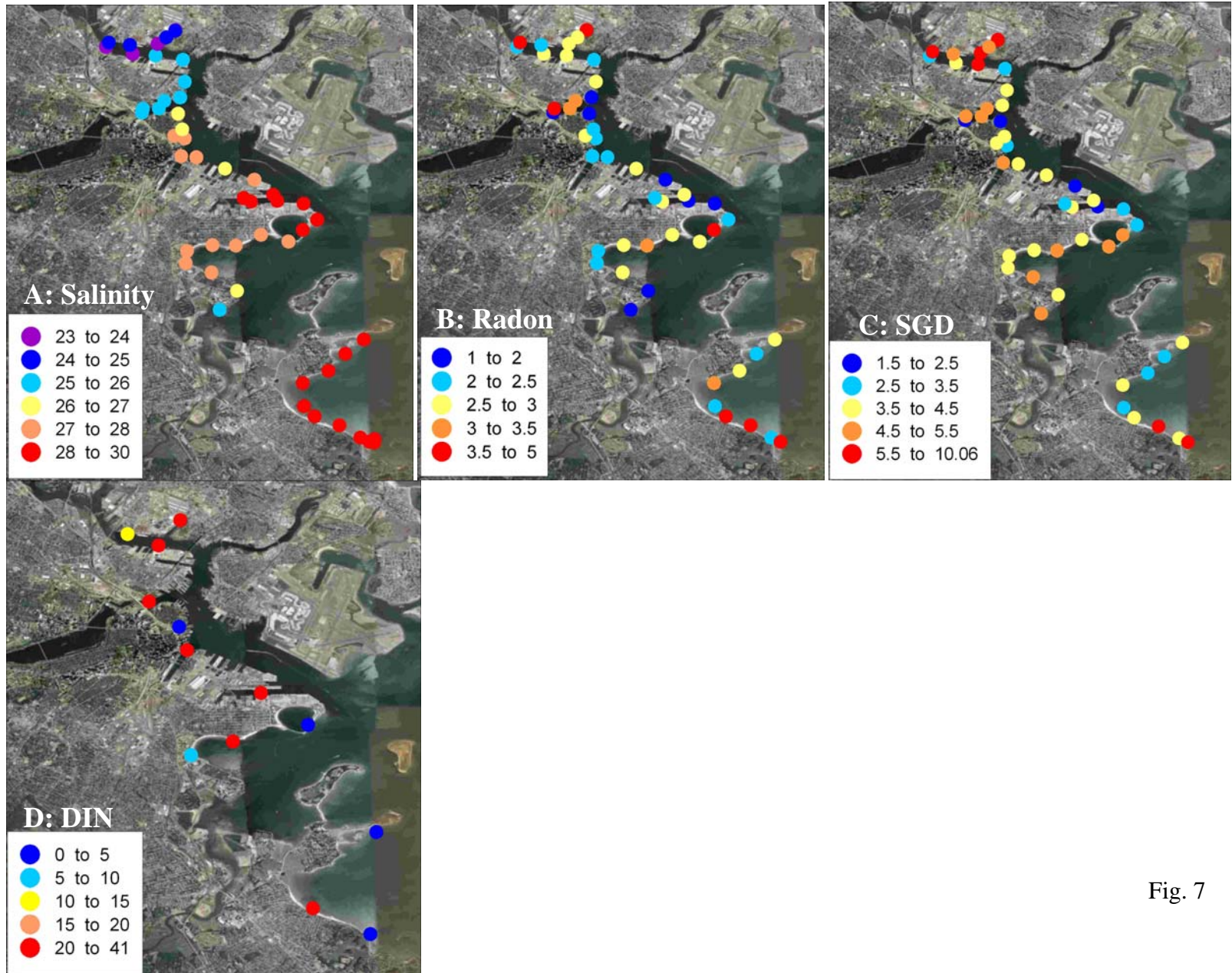


Fig. 7

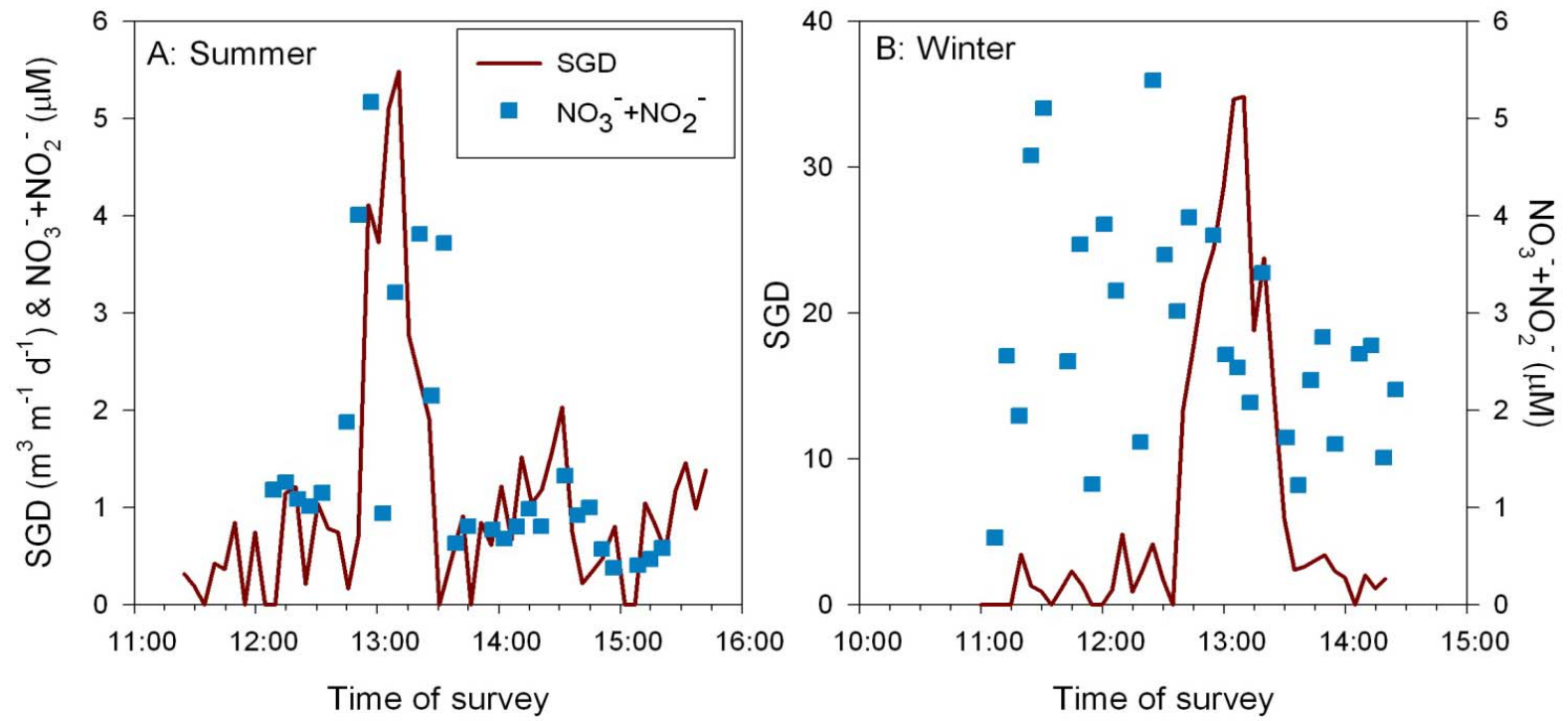


Fig. 8

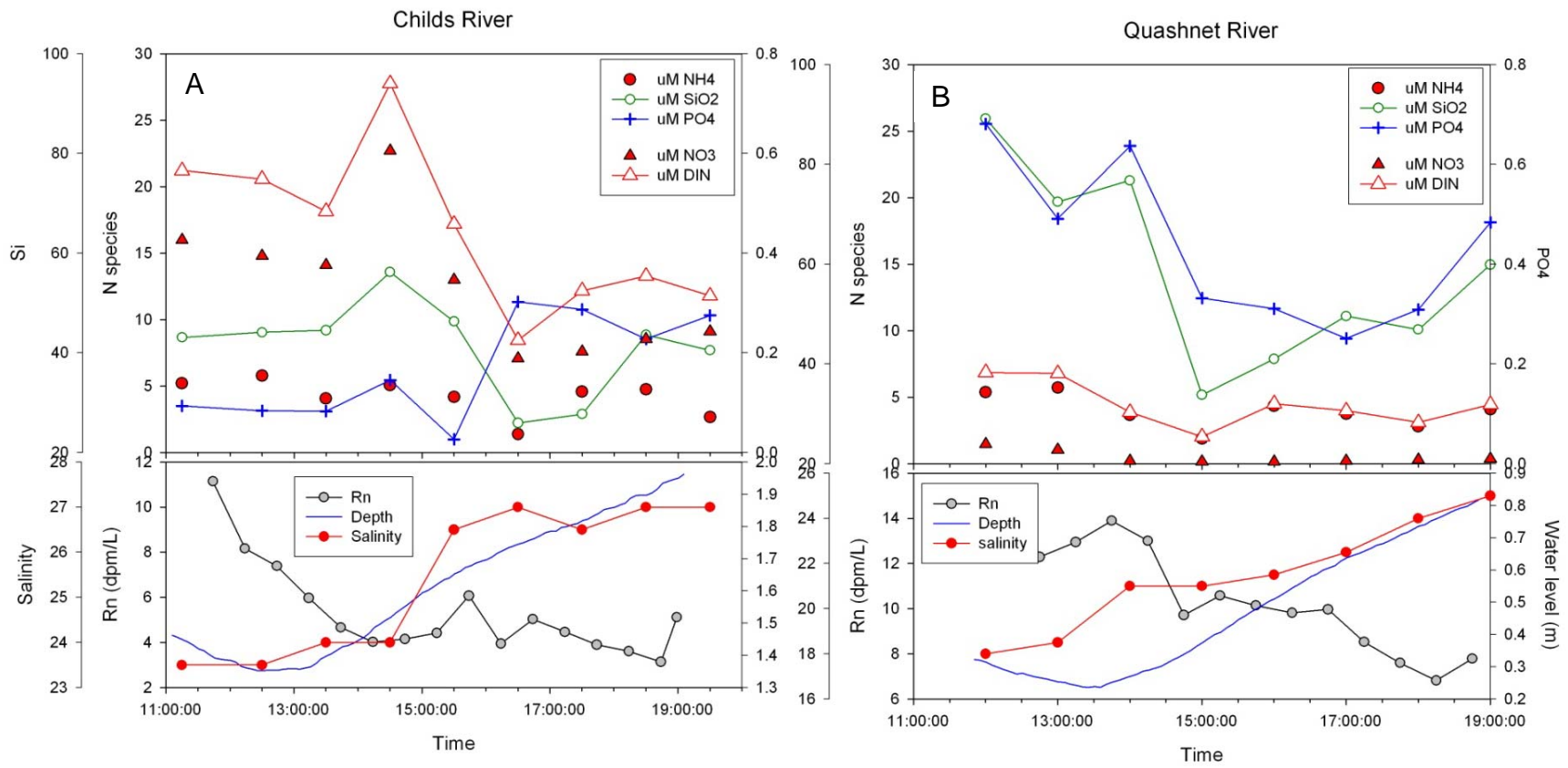


Fig. 9