

1 **Flow and nutrient dynamics in a subterranean estuary (Waquoit Bay, MA,**
2 **USA): field data and reactive transport modeling**

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26 ABSTRACT

27 A two-dimensional (2D) reactive transport model is used to investigate the controls on
28 nutrient (NO_3^- , NH_4^+ , PO_4) dynamics in a coastal aquifer. The model couples density-
29 dependent flow to a reaction network which includes oxic degradation of organic
30 matter, denitrification, iron oxide reduction, nitrification, Fe^{2+} oxidation and sorption
31 of PO_4 onto iron oxides. Porewater measurements from a well transect at Waquoit
32 Bay, MA, USA indicate the presence of a reducing plume with high Fe^{2+} , NH_4^+ , DOC
33 (dissolved organic carbon) and PO_4 concentrations overlying a more oxidizing NO_3^- -
34 rich plume. These two plumes travel nearly conservatively until they start to overlap
35 in the intertidal coastal sediments prior to discharge into the bay. In this zone, the
36 aeration of the surface beach sediments drives nitrification and allows the
37 precipitation of iron oxide, which leads to the removal of PO_4 through sorption. Model
38 simulations suggest that removal of NO_3^- through denitrification is inhibited by the
39 limited overlap between the two freshwater plumes, as well as by the refractory nature
40 of terrestrial DOC. Submarine groundwater discharge is a significant source of NO_3^-
41 to the bay.

42

43 Key words: coastal aquifer, reactive transport modeling, nutrients, submarine
44 groundwater discharge

45 1. Introduction

46

47 Coastal aquifers worldwide, in particular in areas strongly influenced by human
48 activities, are increasingly becoming contaminated with nutrients from fertilizer and
49 waste-water (Valiela et al., 1992). Discharge of this groundwater along beaches and
50 through the seafloor is now recognized as an important transport pathway of nutrients
51 to coastal waters (e.g. Burnett et al., 2006). The chemical composition of this
52 submarine groundwater discharge (SGD) not only depends on the landward
53 freshwater source(s) but also on the rates of groundwater flow and the biogeochemical
54 reactions that occur in the part of the coastal aquifer where freshwater and seawater
55 interact (“subterranean estuary”; Moore, 1999). Owing to the difficulties in sampling
56 coastal aquifers and the complex flow structure in subterranean estuaries (e.g. Burnett
57 et al., 2006), our quantitative understanding of nutrient dynamics in these systems is
58 still limited.

59

60 The biogeochemistry of nutrients (NO_3^- , NH_4^+ and dissolved inorganic phosphate,
61 PO_4^{3-}) in subterranean estuaries and the groundwater nutrient fluxes to coastal waters
62 are strongly affected by the redox conditions of the freshwater and seawater (e.g.,
63 Slomp and Van Cappellen, 2004; Spiteri et al., 2007). In groundwater systems, NO_3^-
64 supplied either by infiltrating water or produced through nitrification (Nowicki et al.,
65 1999) can be removed by denitrification under anoxic conditions. However, field
66 studies often report only limited NO_3^- removal prior to discharge to coastal waters.
67 This is primarily attributed to a lack of labile dissolved organic matter (e.g., Slater and
68 Capone, 1987; Desimone and Howes, 1996) or high groundwater velocities (Capone
69 and Slater 1990; Giblin and Gaines, 1990) which do not allow for significant

70 biogeochemical transformations in the subterranean estuary. Organic matter
71 degradation is often the major source of both groundwater NH_4^+ and PO_4 . Under oxic
72 conditions, NH_4^+ is effectively removed through nitrification while phosphorus (P) is
73 attenuated through sorption onto iron and aluminum oxides. The formation of iron
74 oxide at the freshwater-seawater interface is driven by the oxidation of Fe^{2+} as it is
75 transported through oxic surface beach sediments (Charette and Sholkovitz, 2002).
76 Other studies (Davison and Seed, 1983; Spiteri et al., 2006) suggest that the pH
77 increase from freshwater to seawater can also play an important role in the
78 precipitation of iron oxides in coastal sediments.

79

80 The contamination of many coastal aquifers by nitrogen (N) of anthropogenic origin,
81 the limited loss by denitrification, in combination with efficient P removal may lead
82 to SGD with an N:P ratio higher than the Redfield ratio of phytoplankton (N:P= 16:1).
83 This can potentially drive the N-limited coastal primary production to P-limitation
84 (Slomp and Van Cappellen, 2004), causing a shift in the ecological community
85 structure. In Waquoit Bay, increased nitrogen input to the watershed, primarily
86 through atmospheric deposition, fertilizers and waste-water, has lead to an increase in
87 the nutrient loading in its subestuaries (Valiela et al., 1992; 2002). The resulting
88 alterations in these aquatic systems include greater primary productivity by
89 phytoplankton, recurrent bottom anoxia and loss of eelgrass abundance (Valiela et al.,
90 1992).

91

92 Recent literature on SGD has mostly focused on the location of discharge hotspots
93 and the quantification of discharge rates using a suite of different methods (e.g.,
94 Giblin and Gaines, 1990; Corbett et al., 2000; Sholkovitz et al., 2003; Breier et al.,

95 2005; Michael et al., 2005; Stieglitz, 2005; Moore, 2006). Fewer studies (e.g., Krest et
96 al., 2000; Charette et al., 2001; Hwang et al., 2005; Shellenbarger et al., 2006) have
97 estimated the magnitude of nutrient fluxes through SGD, which is generally done
98 through simple multiplication of the measured SGD rates with the average nutrient
99 concentrations in groundwater. If not done at the point of seepage, this approach does
100 not account for any transformation/removal processes that might alter the
101 biogeochemical fate of nutrients as groundwater travels through the subterranean
102 estuary (e.g. Beck et al., 2007).

103

104 The aim of this study is to attain a better understanding of nutrient dynamics in
105 subterranean estuaries and the implications for SGD of nutrients. We first analyze the
106 porewater concentration profiles for various chemical species along a transect at the
107 head of Waquoit Bay, MA, USA. We then use a two-dimensional (2D) density-
108 dependent reactive transport model (RTM) to simulate a) the tidally-averaged flow
109 dynamics and b) the main biogeochemical reactions affecting nitrogen and
110 phosphorus. This allows us to identify and quantify the removal and transformation
111 processes affecting NO_3^- , NH_4^+ and PO_4^{3-} in the coastal aquifer and estimate the
112 resulting rates of SGD of these nutrients. Finally, the response of the system to
113 changes in a) the reactivity of the terrestrial organic matter b) the landward source
114 concentration of phosphorus and c) the flow dynamics as a result of sealevel rise is
115 investigated.

116

117 2. Study site

118 Waquoit Bay is a shallow estuary, approximately 1220 m wide and 3350 m long,
119 located on the southern shoreline of Cape Cod (Fig. 1). It is part of the Waquoit Bay

120 National Estuarine Research Reserve (WBNERR) and has been used as a field site in
121 various previous scientific investigations, including physical oceanographical,
122 hydrological, geological, biological and geochemical studies (e.g., Cambreri and
123 Eichner, 1998; Valiela et al., 1992; Charette and Sholkovitz, 2002; Testa et al., 2002;
124 Sholkovitz et al., 2003; Talbot et al., 2003). The sedimentary deposits on Cape Cod
125 generally consist of outwash gravel, sand, silt, and occasional lacustrine deposits of
126 silts and clays (Oldale 1976; 1981). The aquifer is 100-120 m thick and is underlain
127 by less permeable deposits of basal till and bedrock (LeBlanc et al., 1986). Further
128 details on the stratigraphy of the Cape Cod aquifer can be found in Cambreri and
129 Eichner (1998) and Mulligan and Charette (2006).

130

131 The bay has an average depth of 1 m and a tidal range of ~1.1 m (Mulligan and
132 Charette, 2006). The head of Bay is the smallest of the seven sub-watersheds that
133 border Waquoit Bay and has a human population density of 190 persons km^{-2} . It
134 covers an area of 0.76 km^2 extending approximately 2 km north with a maximum
135 width of about 1 km between Childs River and Quashnet River (Masterson and
136 Walter, 2000; Fig. 1). Three freshwater ponds, Bog, Bourne and Caleb Pond (Fig. 1),
137 also drain at the northern end of the bay. Hydrogeological cross sections along the
138 Waquoit Bay watershed reveal a thinning in the depth of the upper unconfined aquifer
139 at the head of Bay to ~11 m (Cambareri and Eichner, 1988), where it consists of
140 relatively homogeneous medium to fine sands, bounded by a less permeable layer of
141 fine sand, silt and clay (Masterson et al., 1997). In the upper aquifer, the range of
142 hydraulic conductivity values obtained from slug tests varies between 3.7×10^{-4} and
143 $1.7 \times 10^{-3} \text{ m s}^{-1}$, with a geometric mean of $6 \times 10^{-4} \text{ m s}^{-1}$ (Mulligan and Charette, 2006).
144 The landward topography at the head of the Bay is characterized by a low-lying valley

145 in the middle of two large bluffs (Mulligan and Charette, 2006), which give rise to
146 spatially-variable groundwater velocities.

147

148 Due to the highly permeable soils and coarse-grained sands on Cape Cod, surface
149 runoff is rather low, while groundwater discharge into streams, rivers and the bay is
150 relatively high. SGD in the seven watersheds of Waquoit Bay accounts for $0.028 \text{ m}^3 \text{ s}^{-1}$
151 or 34 % of the freshwater input to the bay. The rest is derived from direct
152 precipitation (11 %; amounting to $\sim 114 \text{ cm yr}^{-1}$ on the Upper Cape) and surface
153 runoff (55 %) (Cambareri and Eichner, 1988). Assuming a freshwater discharge rate
154 (Q_f) of $0.028 \text{ m}^3 \text{ s}^{-1}$ and a tidally driven circulation rate (Q_t) of $0.013 \text{ m}^3 \text{ s}^{-1}$ (Michael,
155 2004), the calculated flow ratio (Q_f/Q_t) is ~ 2.0 . Following the classification of
156 subterranean estuaries presented in Robinson et al. (2007), with a flow ratio > 1 , this
157 subterranean estuary is “stratified”. This implies that the upper saline plume that may
158 be present in addition to the classical salt-wedge, is of minor importance.

159

160 3. Field measurements

161 A 22-m transect, consisting of seven piezometers perpendicular to the shoreline was
162 installed in the low-lying region at the head of the bay (Fig. 1). Porewater samples
163 were taken using a stainless steel drive point piezometer system (Retract-A-Tip from
164 AMS (Idaho USA), INC.; Charette and Allen, 2006). These non-conventional
165 piezometers were used to sample groundwater at multiple depths with a sample
166 interval of 0.45 m down to a depth of 8 m. The sample depth resolution along the
167 freshwater-seawater interface was further increased to ~ 0.15 m. Groundwater
168 samples were brought to the surface through acid-cleaned Teflon or polypropylene
169 tubing using a peristaltic pump and filtered through a $0.45 \mu\text{M}$ Pall capsule filter to

remove particulates. Measurements of sample pH, salinity, conductivity, density and O₂ were taken in the field using a YSI 600XLM multi-probe in a flow through cell. The samples were further analyzed for NO₃⁻ + NO₂⁻ (referred here to as NO₃⁻ only, which constitutes the major fraction), NH₄⁺, PO₄, dissolved organic carbon (DOC) and total dissolved Fe (TDFe), of which a major fraction is in the form of Fe²⁺ (Charette et al., 2005). Concentrations of nutrients were measured colorimetrically, using a Lachat nutrient auto-analyzer (Zellweger Analytics, QuickChem 8000 series). Analysis of TDFe was carried out on acidified samples (pH 2) using inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to analyze the major ions (Ca²⁺, Mg²⁺, Na⁺, K⁺ and Cl⁻). DOC was measured using a total organic carbon analyzer. Further details on the methods of analysis employed during four field campaigns (2002-2005) can be found in Talbot et al. (2003), Charette et al. (2005) and Charette and Allen (2006). The time required for the high-resolution sampling of each piezometer was 4-8 hours, and the entire transect was sampled over seven days. Therefore, the porewater measurements are assumed representative of tidally-averaged conditions.

186

187 4. Reactive transport model

188 A 2D/3D finite element reactive transport model including density dependent flow
189 (Spiteri et al., 2007) is used to simulate the coupled flow and biogeochemistry in the
190 coastal aquifer of Waquoit Bay. A schematic diagram of the model domain and the
191 values of model parameters used in the simulations are given in Fig. 2a. In the model,
192 we impose an impermeable (no flux) boundary condition at the top and bottom
193 boundaries. The lower boundary represents the delimiting confining layer of the 11
194 m-deep upper aquifer while the effect of recharge through the top boundary is

assumed to be negligible. Although this is a simplifying assumption, the effect of the precipitation and infiltration in the near-shore area is not expected to alter the local flow regime significantly. The length of the model domain is chosen so that the steady-state saltwater wedge that develops does not interfere with the left freshwater boundary. Pressure is imposed on both the freshwater and seawater sides, while the effect of seasonal variation in freshwater discharge is not taken into account. Moreover, as model results are compared to tidally-averaged field measurements, tidal pumping is not included in the model. The values of porosity (ϕ) and longitudinal dispersivity (α_L) used in the simulations (Fig. 2a) are constrained by the modeling work of Michael et al. (2005) for the same bay, whereas the permeability (κ) estimate of $7 \times 10^{-11} \text{ m}^2$, equivalent to a hydraulic conductivity of $6.9 \times 10^{-4} \text{ m s}^{-1}$, falls within the measured range of measured hydraulic conductivities (Michael et al. 2005). The value of transverse dispersivity (α_T) is set by trial and error to 0.005 m, to match the measured and modeled salinity profiles and the relatively sharp freshwater-saltwater interface. We assume a simplified, idealized, yet realistic representation of the local homogeneous flow regime and focus on the complexities that determine the biogeochemical dynamics in this subterranean estuary. An analysis of the effect of small-scale variations in the flow dynamics on the biogeochemical behaviour is beyond the scope of this study.

The chemical constituents considered include salt, NO_3^- , NH_4^+ , PO_4^{2-} , adsorbed phosphate ($\text{PO}_{4(\text{ads})}$), ferrous iron (Fe^{2+}), iron oxide (Fe(OH)_3), dissolved oxygen (O_2) and two fractions of dissolved organic carbon (a terrestrial, more refractory component, DOC_1 , and a marine labile fraction, DOC_2). All chemical species, except for $\text{PO}_{4(\text{ads})}$ and Fe(OH)_3 , are mobile species. The solid species are considered

immobile and hence are only affected by local biogeochemical transformations. The concentration at the freshwater side is fixed for the solute species and set via trial and error to approximate the measured profiles at the first piezometer of the transect (PZ-10) (Figs. 1 and 2a). At the seawater side, seawater is allowed to enter the domain through advection. The boundary concentrations at the freshwater and seawater sides for each species are given in Table 1. The initial concentration of the solid species (Fe(OH)_3 and P_{ads}) is assumed to be zero throughout the entire model domain. Tables 2 and 3 show the rate formulations of the six transformation processes, including oxic DOC degradation, denitrification, Fe(OH)_3 reduction, nitrification, Fe^{2+} oxidation and PO_4 adsorption onto Fe(OH)_3 , and the list of reaction parameter values used in the simulations, respectively. The analysis of the major ions suggests conservative mixing of groundwater and seawater (Fig. 3). This implies that at this site, ion exchange processes for the major ions due to changes in the position of the freshwater-seawater interface are not significant and hence, they are not included in the current reaction network. Similarly, the effect of potential pH variations on reaction rates is not explicitly accounted for. The modeled results presented here are for a total simulation time of 11 years and are at steady-state with respect to the solute species. All results refer to the sampling transect enclosed in the top right corner in Fig. 2a.

238

239 5. Results and Discussion

240 5.1 Field results

241 Field data collected over the four consecutive sampling years (2002-2005) show
242 similar general trends in the positioning of the freshwater-seawater interface and the
243 occurrence of the major plumes, as illustrated by the salinity, NO_3^- , NH_4^+ and PO_4

244 profiles in PZ-6 (Fig. 4a-d). Here, we do not present the entire field dataset but focus
245 the model application on the June 2004 sampling campaign.

246

247 The 2D salinity distribution along the piezometer transect (Fig. 5a) shows a large
248 salinity gradient, in which the porewater salinity increases from 0 to 28 over a vertical
249 depth interval of ~1.5 m. This transition zone separates the upper freshwater lens that
250 tapers towards the shore from a distinct lower saltwater wedge. Analysis of the
251 porewater data for the other major chemical species, namely NO_3^- , NH_4^+ , PO_4 , Fe^{2+}
252 and DOC (Fig. 5b-f) shows that relatively high concentrations of NH_4^+ (Fig. 5c) and
253 PO_4 (Fig. 5d) co-occur in the salt-water wedge, with values falling within the range
254 commonly found in coastal marine sediments (Lohse et al., 1995; Slomp et al., 1998).
255 NO_3^- is completely absent in the saltwater wedge (Fig. 5b).

256

257 In the freshwater part, two distinct “streamlines” with different geochemical
258 composition are observed: An oxidizing, high- NO_3^- plume present at a depth of ~ 4 m
259 at PZ-10, which bends upwards over the saltwater wedge (Fig. 5b) and an upper
260 freshwater “geochemical streamline”, characterized by more reducing conditions
261 containing high NH_4^+ (Fig. 5c), PO_4 (Fig. 5d), Fe^{2+} (Fig. 5e) and DOC (Fig. 5f). The
262 reduced freshwater plume reaches down to a depth of 3 m at PZ-10, becoming
263 progressively narrower as the groundwater travels seaward. The NH_4^+ peak
264 concentration increases from ~ 0.05 mM at PZ-10 to ~ 0.15 mM in PZ-6 and PZ-11,
265 decreasing to ~0 mM between PZ-3 and PZ-5 (Fig. 5c). A gradual decrease in the
266 peak PO_4 (Fig. 5d) and DOC (Fig. 5f) concentration is observed from the most
267 landward piezometer PZ-10 to the intertidal piezometer PZ-5. The fourfold increase in
268 the peak Fe^{2+} concentration from ~0.1 mM at PZ-10 to ~0.4 mM at PZ-7 is followed

269 by its near-complete disappearance in PZ-3 and PZ-5, as the leading edge of the
270 plume moves towards the shore.

271

272 The sources of PO₄, DOC and Fe²⁺ in the freshwater are largely unknown, and several
273 hypotheses exist on the occurrence of a reducing NH₄⁺ plume on top of a more
274 oxidizing NO₃⁻ plume. Spiteri et al. (2007) showed that such plumes can result from
275 simultaneous nitrification and denitrification further inland within the aquifer.
276 Kroeger and Charette (2008) speculate on the possible sources of the freshwater NO₃⁻
277 and NH₄⁺ plumes, and suggest either i) recharge from the inland Bog and Bourne
278 ponds, or ii) displacement of adsorbed nitrogen with seasalt in the freshwater part of
279 the aquifer or iii) a common nitrogen source for both plumes, developing into a
280 reduced inner core and oxidized edge of the same plume.

281

282 As the freshwater lens gets thinner towards the beachface, the two freshwater
283 “streamlines” converge, overlap and mix before discharging in the intertidal area
284 between PZ-3 and PZ-5, a zone which is highly subject to high dispersive mixing due
285 to the effect of waves and tides. This intertidal area at the head of the Bay is
286 characterized by a zone of iron oxide accumulation, referred to as the “iron curtain”.
287 Sediments in this zone (around PZ-3 and PZ-5) have a dark red, yellow and orange
288 color down to a depth of at least 2 m and an iron content that is 10 to 15 times higher
289 than elsewhere in the aquifer (Charette and Sholkovitz, 2002). Upward transport of
290 Fe²⁺-rich saline pore water (Fig. 5e) could serve as a source of some of the
291 precipitated Fe (Charette et al., 2005), although the freshwater plume is the ultimate
292 source of “new” Fe²⁺ to the coastal sediments.

293

294 5.2. Modeling results

295 5.2.1 Flow dynamics

296 The modeled groundwater velocity at the landward freshwater side is $1.5 \times 10^{-6} \text{ m s}^{-1}$
297 (13 cm d^{-1}), when a freshwater head of 0.24 m and a hydraulic gradient of 0.004 m m^{-1}
298 is assumed (Fig. 2b). The latter corresponds to the upper limit of the range of
299 hydraulic gradients measured in the valley area between high tide (0.002 m m^{-1}) and
300 low tide (0.004 m m^{-1}) (Mulligan and Charette, 2006). The modeled landward
301 velocity falls within the range of $9\text{-}43 \text{ cm d}^{-1}$ given in Mulligan and Charette (2006)
302 for the low-lying region of the bay. It is also in good agreement with their average
303 value of 15 cm d^{-1} , calculated using Darcy's law, hydraulic gradient data and the
304 geometric mean of the measured hydraulic conductivities. On approaching the coast,
305 the groundwater flow rates increase up to $2.7 \times 10^{-5} \text{ m s}^{-1}$ (235 cm d^{-1}) in the discharge
306 zone due to the constriction of the freshwater in a smaller area (Fig. 2b). The model
307 predicts the localized occurrence of SGD along the last 0.8 m of the top boundary,
308 representing the seepage face on the beach parallel to the shoreline. SGD flows with
309 an average rate of $1.4 \times 10^{-5} \text{ m s}^{-1}$ (156 cm d^{-1}) and an average salinity of 5 ‰ (ranging
310 from 0.6 to 14 ‰). As suggested by Kroeger and Charette (2008), much of the fresh
311 groundwater ultimately discharges as brackish water due to significant mixing with
312 saline porewater in the shallow beach sediments prior to discharge. Unlike other SGD
313 studies of Waquoit Bay using seepage meters (Michael et al., 2003; Sholkovitz et al.,
314 2003), the predicted seepage face does not include offshore seepage areas but is
315 restricted to the beachface, delimited by the position of the seaward piezometer PZ-
316 12. In the saltwater wedge, the modeled flow velocity of the intruding seawater is as
317 low as $2.4 \times 10^{-7} \text{ m s}^{-1}$ (2 cm d^{-1}).

318

319 5.2.2 Nitrogen dynamics

320 The measured and modeled results for NO_3^- and NH_4^+ are shown in Fig. 5b and c. In
321 the landward section (from PZ-10 to PZ-11), the freshwater NO_3^- plume travels nearly
322 conservatively (Fig. 5b), indicating that the conditions for effective denitrification are
323 not met. In their analysis of the nutrient data collected in spring 2003 from the same
324 sampling transect, Kroeger and Charette (2008) propose the occurrence of
325 denitrification of the NO_3^- in the freshwater plume prior to its discharge, based on the
326 substantial observed loss of NO_3^- around PZ-5. In our case, however, the peak NO_3^-
327 concentration increases from PZ-11 to PZ-3, and stays rather elevated in intertidal
328 piezometer PZ-5 where it is partially discharged. The model overestimates the NH_4^+
329 concentrations and concurrently underestimates the NO_3^- concentrations at PZ-3 and
330 PZ-5 (solid lines in Fig. 5b and c), as modeled nitrification rates are limited by the
331 landward O_2 supply. This points towards the need for an additional O_2 source in the
332 surface intertidal beach sediments. As reported by Ullman et al. (2003), tidal pumping
333 and wave action may provide a constant source of O_2 to sustain nitrification, as well
334 as oxic degradation of the locally produced, labile organic matter higher on the
335 beachface. In line with these observations, the O_2 measurements in the surface
336 intertidal sediments (PZ-3 and PZ-5) indicate higher concentrations, which do not
337 originate from landward transport but are more likely supplied through aeration of the
338 surface beachface sediments at low tide (Fig. 6). When an intertidal high O_2 -zone is
339 considered in the simulations (between $x = 52.5$ and $x = 58.5$ m) overlying the
340 freshwater-seawater interface; Fig. 6), the model fits for NO_3^- and in particular NH_4^+
341 are significantly improved (dashed lines in Fig. 5b and c) due to enhanced
342 nitrification.

343

344 The relative increase in the depth-integrated intertidal NO_3^- content due to nitrification
345 is found to be 63% in PZ-3 and 73% in PZ-5 when an the additional O_2 supply is
346 considered. The corresponding model-derived, depth-integrated nitrification rates in
347 PZ-3 and PZ-5 are 4×10^{-7} and 1×10^{-7} mol m^{-2} s^{-1} , respectively. Our results indicate
348 that a sharp redox front develops over a short distance in the intertidal area due to the
349 efficient removal of the reactant (NH_4^+) as soon as it comes in contact with O_2 . The
350 computed rates are higher than those reported for freshwater lake sediments (7×10^{-9}
351 mol N m^{-2} s^{-1} ; Canavan et al., 2006) and shallow coastal marine sediments (3.6×10^{-9}
352 mol N m^{-2} s^{-1} ; Wang and Van Cappellen, 1996).

353

354 5.2.3 Phosphorus and iron dynamics

355 Analogous to the oxidation of NH_4^+ to NO_3^- through nitrification, the oxidation of
356 Fe^{2+} and disappearance of the Fe^{2+} plume in the intertidal area (Fig. 5e) is obtained
357 when accounting for O_2 infiltration (Fig., 5a; dashed lines). Model results for the O_2
358 infiltration scenario closely match the observed simultaneous precipitation of Fe(OH)_3
359 as an “iron curtain” (not shown) and the subsequent removal of freshwater PO_4
360 through adsorption (Fig. 5d) in the intertidal area. The mitigation of the Fe^{2+} plume is
361 more likely attributed to Fe^{2+} oxidation with O_2 rather than to autotrophic
362 denitrification with Fe^{2+} , since NO_3^- concentrations increase between PZ-3 and PZ-5
363 (Fig. 5b). Changes in pH along the freshwater-seawater continuum may also play a
364 role in enhancing Fe^{2+} oxidation (Spiteri et al., 2006). The simulation time required to
365 precipitate 103 mmol dm^{-3} Fe(OH)_3 in the intertidal area, corresponding to the ~ 3000
366 ppm Fe measured in the intertidal sediment cores taken from the head of Waquoit Bay
367 (Charette et al., 2005), is 11 years. During the same time period, the model predicts
368 the formation of a maximum of 3.9×10^{-3} mol dm^{-3} or 60 ppm $\text{PO}_{4(\text{ads})}$, which falls

369 within the range of 25-200 ppm P found in the same sediment cores. The thin PO₄
370 plume observed along the freshwater-seawater interface may be associated either with
371 the mobilization of iron oxides (Charette et al., 2005), or with changes in porewater
372 pH with salinity along the interface, which are not resolved with the current model
373 formulation.

374

375 Depth-integrated rates of Fe²⁺ oxidation in PZ-3 and PZ-5 (5×10^{-7} and 4.8×10^{-8} mol m⁻
376 s^{-1} , respectively) are higher than those reported by Canavan et al. (2006) for
377 freshwater lake sediments (3.5×10^{-9} mol Fe m⁻² s⁻¹) and Wang and Van Cappellen
378 (1996) for shallow coastal marine sediments (3.5×10^{-9} mol Fe m⁻² s⁻¹). The higher
379 process rates in the coastal sediments of Waquoit Bay, despite the relatively lower
380 values for rate constants used here (see Table 3), could be the result of the
381 predominantly advective transport, which supplies a higher input Fe²⁺ (and NH₄⁺) than
382 normally observed in typical freshwater or marine sediments.

383

384 5.2.3 DOC dynamics

385 Model results suggest that the terrestrial DOC (DOC₁) that reaches the coast is rather
386 refractory, with a degradation rate constant of $3.0 \times 10^{-10} s^{-1}$ (0.01 yr^{-1}) (Fig. 5f). The
387 model, however, overestimates the concentrations of the terrestrial refractory DOC in
388 the intertidal area. The simulation also reveals that the relatively high NH₄⁺ porewater
389 concentrations in the saltwater wedge might be produced from the remineralization of
390 labile organic carbon in saline estuarine sediments (DOC₂) (Kroeger and Charette,
391 2008), followed by dilution due to the landward advecting seawater. If a degradation
392 rate constant of $3.0 \times 10^{-7} s^{-1}$ (10 yr^{-1}) is used (Figs. 5c, d and f), the model is able to
393 reproduce the drop in DOC₂ from ~0.7 mM at PZ-12 to 0.1 mM at PZ-5. At the same

394 time, a satisfactory model fit is obtained for both NH_4^+ and PO_4 saltwater profiles,
395 pointing towards a common origin. This seaward source of reactive DOC possibly
396 originates from the leaching of organic matter deposits, derived from the brown and
397 green algal blooms that cover the bay, beach and intertidal area in late spring and
398 summer (Charette et al., 2005).

399

400 5.3 SGD of nutrients

401 A budget of NO_3^- , NH_4^+ and PO_4 for the entire coastal aquifer of Waquoit Bay is
402 shown in Fig. 7. A comparison of the computed fluxes of nutrients through SGD (Fig.
403 7a, c and e) clearly shows that NO_3^- is the major nutrient source to the bay, with
404 fluxes being 16 and 80 times higher than those of NH_4^+ and PO_4 , respectively. The
405 ratio of the influx of NO_3^- through freshwater and seawater (Fig. 7a) indicates that the
406 source of NO_3^- in SGD is predominantly freshwater. Most of the freshwater NH_4^+
407 input is removed by nitrification prior to discharge, which is by far the most
408 prominent nutrient transformation process (Fig. 7d). In fact, the contribution of
409 nitrification to SGD of NO_3^- exceeds the groundwater input of NO_3^- from terrestrial
410 sources (Fig. 7a, b). Therefore, the NH_4^+ present in SGD is presumably the result of
411 DOC degradation in the saltwater wedge, which is recycled out back to the coastal
412 waters through recirculated seawater. This remineralized NH_4^+ flux becomes even
413 more significant when off-shore seepage areas are considered (Kroeger and Charette,
414 2008). Seawater contributes to approximately one third of the PO_4 influx into the
415 subterranean estuary, since a major fraction of the freshwater PO_4 is sorbed as the
416 groundwater flows through the “iron curtain” (Fig. 7f). As a result of the limited
417 removal of NO_3^- through denitrification (Fig. 7b), in combination with the efficient
418 removal of PO_4 (Fig. 7f), the ratio of the average dissolved inorganic nitrogen

419 ($\text{DIN} = \text{NO}_3^- + \text{NH}_4^+$) and inorganic PO_4 concentrations (DIN:PO₄ ratio) in the SGD is
420 found to be 50. Note that DOP and DON can also be quantitatively important in
421 groundwater and can affect ratios of total N: total P in SGD (Burnett et al., 2007).

422

423 Table 4 shows the nutrient discharge rates extrapolated over the entire length of the
424 shoreline along the valley (210 m; Mulligan and Charette, 2006), as well as the
425 normalized fluxes per unit seepage area, assuming a beachface seepage width of 0.8
426 m. Up to 95 % of the total DIN flux (2.9×10^{-4} mol s⁻¹) is in the form of NO_3^- . There is
427 a significant discrepancy between the estimate of DIN flux derived from this study
428 and that given in Charette et al. (2001) (2.4×10^{-2} mol s⁻¹) for the same bay. In Charette
429 et al. (2001), the calculation of the flux is based on a DIN concentration in the
430 groundwater along the shoreline of 0.058 mM, which is very close to our average DIN
431 concentration in SGD (0.057 mM), and a radium-derived volumetric SGD rate of 0.43
432 m³ s⁻¹ (most of which is saline). However, the SGD rate was calculated over the total
433 surface area of the bay (39×10^5 m²), which is much larger than the seepage face
434 considered in this study (168 m²; 0.8 m x 210 m). Therefore, when the DIN loading is
435 expressed in moles per unit time per unit area, the estimate of Charette et al. (2001)
436 for the whole bay is in fact much lower (~500 $\mu\text{mol m}^{-2} \text{ d}^{-1}$) than the one obtained in
437 this study ($1.5 \times 10^5 \mu\text{mol m}^{-2} \text{ d}^{-1}$; Table 4).

438

439 5.4 Scenarios

440 In this section, we assess the effect of specific parameters that might alter the present-
441 day biogeochemical dynamics in the subterranean estuary of Waquoit Bay. In
442 particular, the response of the model to a change in the reactivity of terrestrial DOC,

443 an increase in landward PO₄ source concentration and a change in the flow regime is
444 investigated.

445

446 5.4.1 Increased reactivity of terrestrial DOC

447 We assess the effect of a hypothetical discharge of a highly reactive DOC₁ ($k_{f_{ox1}} = 0.1$
448 yr⁻¹), which could originate from the natural seepage of the eutrophied ponds located
449 upstream in the head of Bay. Model simulations show that despite the increase in
450 organic carbon reactivity compared to the baseline simulation, denitrification remains
451 marginal (not shown). This is because NO₃⁻ removal is predominantly limited by the
452 lack of spatial overlap between the DOC and NO₃⁻ plumes. Upon convergence of the
453 two plumes within the intertidal area, denitrification is still inhibited by the presence
454 of O₂ in the surface sediments. Conversely, nitrification of the NH₄⁺ produced from
455 the degradation of the reactive DOC₁ fraction causes the NO₃⁻ concentration in PZ-3
456 and PZ-5 to increase by up to 20 % (not shown). Therefore, given the present flow
457 conditions in Waquoit Bay, NO₃⁻ removal does not appear to be limited by organic
458 carbon reactivity.

459

460 5.4.2 Efficiency of the “iron curtain”

461 The capacity of the “iron curtain” to attenuate PO₄ concentrations is tested by
462 comparing the SGD of PO₄ with (Section 5.2.2) and without the presence of the “iron
463 curtain” in the intertidal area. The flow field is identical in both cases and is used to
464 simulate the propagation of a freshwater source contaminated with PO₄. The selected
465 concentration (0.18 mM) falls within the range observed in groundwater systems
466 affected by wastewater discharge (e.g., Robertson, 1995; Wilhelm et al., 1994). The
467 breakthrough curve obtained for the scenario without “iron curtain” shows a sharp

468 increase in SGD of PO_4 roughly 100 days after the start of infiltration (Fig. 8). In the
469 presence of an “iron curtain” in the intertidal zone, the increase in PO_4 concentration
470 in the SGD is significantly slower and more gradual. In this case, the predicted PO_4
471 concentration after 1000 days is still as low as 0.005 mM, with a retardation factor of
472 10^4 . Therefore, considering that PO_4 concentrations on the order of 0.001 mM (~0.03
473 mg/L) are sufficient to stimulate algal growth in aquatic environments (Dillon and
474 Rigler, 1974; Schindler, 1977), Fe oxide accumulations in coastal aquifers can act as
475 important geochemical barriers and could help prevent coastal eutrophication.

476

477 5.4.3 Effect of sealevel rise

478 A global-scale sealevel rise of 40 to 65 cm is predicted by the year 2100 (Gornitz,
479 1995). Here, we simulate the effect of a 50 cm-increase in sealevel on the
480 biogeochemistry of the subterranean estuary in Waquoit Bay. In this case, taking into
481 account the average slope of the land surface, the seawater infiltration along the
482 beachface could be extended significantly and occur over a distance of at least 4m
483 (between $x = 56$ and $x = 60$ m). The simulation reveals an upward shift in the
484 freshwater-seawater interface by roughly 1 m as a result of the sealevel rise. This
485 leads to a constriction of the freshwater part of the aquifer and a landward movement
486 of the zone of seepage. Yet, the model predicts only a marginal increase in the overlap
487 of the redox plumes. Assuming that the O_2 penetration is limited by the freshwater-
488 seawater interface (Fig. 6), the upward shift in the saline front results in a decrease in
489 the nitrification rate (Fig. 9b, d), which is no longer the main contributor of NO_3^- to
490 SGD (Fig. 9a). Production of NH_4^+ and PO_4 from DOC_2 degradation (Fig. 9d, f)
491 becomes also slightly more important, due to the increased influx of labile marine

492 DOC₂. Yet, overall, the SGD of DIN and PO₄ at this site is relatively insensitive to
493 variations in the sealevel.

494

495 6. Conclusions

496 A reactive transport model is used to characterize the biogeochemical dynamics in the
497 subterranean estuary of Waquoit Bay (Fig. 10). Results reveal the presence of three
498 distinct zones within the coastal aquifer. In the landward part (PZ-10 to PZ-11), redox
499 transformations are limited by the lack of spatial overlap between the two freshwater
500 “geochemical streamlines” and result in nearly conservative transport of the solute
501 species. In particular, the model predicts marginal NO₃⁻ removal through
502 denitrification, even if the reactivity of the terrestrial DOC is increased by one order
503 of magnitude. As the groundwater travels seaward, the redox plumes start converging
504 until they overlap completely and mix dispersively in the highly reactive intertidal
505 area. Despite the high advective groundwater flow rates prior to seepage, the
506 continuous supply of O₂ from the beachface sustains elevated nitrification and Fe²⁺
507 oxidation rates, which are found to be at least one order of magnitude higher than the
508 corresponding oxidation rates in fresh water lakes and shallow coastal marine
509 sediments. Iron oxidation leads to the formation of an “iron curtain” onto which PO₄
510 effectively sorbs. This narrow and dynamic mixing zone is currently poorly resolved
511 and warrants further experimental studies. In the saltwater wedge, the degradation of
512 the labile marine-derived DOC is a dominant process and results in elevated NH₄⁺ and
513 PO₄ porewater concentrations. While NO₃⁻ concentrations in SGD reflect those of the
514 freshwater source, the concentrations of PO₄ in SGD are significantly reduced due to
515 the adsorption on the iron oxide-rich barrier near the beachface. As a result, the
516 DIN:PO₄ ratio of SGD is close to 50.

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518

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676

677 Figure Captions

Figure 1 Map of Waquoit Bay, showing the position of piezometer transect (A'-A) perpendicular to the shoreline at the head of the bay, the three ponds and two rivers that flow into the bay. Note that the distance between PZ-10 and PZ-7 is 2 m whereas that between PZ-7 and PZ-6 is 7.25 m. The rest of the piezometers are equidistant, at 3 m apart.

Figure 2 Schematic diagram of model domain (a), including the set of model parameters and boundary conditions used in the simulations. The dotted box on the top right hand side corner encloses the transect of geochemical field measurements (Δx = space discretization in x-direction; Δz = space discretization in z-direction; Δt = time step; ϕ = porosity; α_L = longitudinal dispersivity; α_T = transverse dispersivity; κ = permeability). Resultant velocity vector field (b) representing density-dependent flow in the coastal aquifer.

Figure 3 Distribution of the major cation concentrations (Na^+ , Mg^{2+} and Ca^{2+}) versus salinity in all seven piezometers along the sampling transect. The solid lines indicate the conservative mixing lines between the freshwater and seawater endmembers for each cation.

Figure 4 Porewater measurements of (a) salinity, (b) NO_3^- , (c) NH_4^+ and (d) PO_4 for PZ-6 collected over four consecutive sampling campaigns (2002-2005).

Figure 5 Measured (dotted line with open circles) and modeled (solid line) depth profiles for (a) salinity, (b) NO_3^- , (c) NH_4^+ , (d) PO_4 , (e) Fe^{2+} and (f) DOC ($\text{DOC}_1 + \text{DOC}_2$) in the X-Z plane along the beach transect. The dashed

profiles in panels (b)-(e), PZ-3 and PZ-5, show the model fit obtained when the high-O₂ zone in the surface intertidal sediments is not taken into account. All porewater measurements, except for DOC, were collected in June 2004. Porewater DOC values collected in June 2005 are used due to the higher quality and completeness of the data set. The diagonal dotted line indicates the freshwater-seawater interface based on the salinity measurements.

- Figure 6 Measured (dotted line with open circles) O₂ concentration profiles PZ-11, PZ-3 and PZ-5 and imposed O₂ concentrations (solid line) in the intertidal area. The diagonal line indicates the freshwater-seawater interface.
- Figure 7 Calculated influx rates (fw = freshwater; sw = seawater), net transformation rates due to reaction and efflux rates through SGD for (a) NO₃⁻, (c) NH₄⁺ and (e) PO₄ in mol s⁻¹ m⁻¹ shoreline. Panels (b), (d) and (f) show the rates of the biogeochemical reactions which add up to the net transformation rates for NO₃⁻, NH₄⁺ and PO₄, respectively.
- Figure 8 Breakthrough curves for PO₄ concentration in SGD in the (i) absence and (ii) presence of an “iron curtain”. Note that the latter scenario assumes no feedback of the formation of the “iron curtain” on the flow pattern.
- Figure 9 Calculated influx rates (fw = freshwater; sw = seawater), net transformation rates due to reaction and efflux rates through SGD for (a) NO₃⁻, (c) NH₄⁺ and (e) PO₄ in mol s⁻¹ obtained when a hypothetical 50 cm sealevel rise is assumed. Panels (b), (d) and (f) show the rates of the biogeochemical reactions which add up to the net transformation rates for NO₃⁻, NH₄⁺ and PO₄, respectively.
- Figure 10 Schematic representation of the nutrient distributions and biogeochemical

transformations in the subterranean estuary of Waquoit Bay.

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