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

1. Introduction

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

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

3

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 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   1.7×10^{-3} m s^{-1}, with a geometric mean of 6×10^{-4} 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 m^3 s^-

151 ^{1} or 34 % of the freshwater input to the bay. The rest is derived from direct

152 precipitation (11 %; amounting to ~ 114 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 m^3 s^{-1} and a tidally driven circulation rate (Q_t) of 0.013 m^3 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 μM Pall capsule filter to

170   remove particulates. Measurements of sample pH, salinity, conductivity, density and

171   O_2 were taken in the field using a YSI 600XLM multi-probe in a flow through cell.

172   The samples were further analyzed for $NO_3^- + NO_2^-$ (referred here to as NO_3^- only,

173   which constitutes the major fraction), NH_4^+, PO_4, dissolved organic carbon (DOC)

174   and total dissolved Fe (TDFe), of which a major fraction is in the form of Fe^{2+}

175   (Charette et al., 2005). Concentrations of nutrients were measured colorimetrically,

176   using a Lachat nutrient auto-analyzer (Zellweger Analytics, QuickChem 8000 series).

177   Analysis of TDFe was carried out on acidified samples (pH 2) using inductively

178   coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma optical

179   emission spectroscopy (ICP-OES) was used to analyze the major ions (Ca^{2+}, Mg^{2+},

180   Na^+, K^+ and Cl^-). DOC was measured using a total organic carbon analyzer. Further

181   details on the methods of analysis employed during four field campaigns (2002-2005)

182   can found in Talbot et al. (2003), Charette et al. (2005) and Charette and Allen

183   (2006). The time required for the high-resolution sampling of each piezometer was 4-

184   8 hours, and the entire transect was sampled over seven days. Therefore, the

185   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

195   assumed to be negligible. Although this is a simplifying assumption, the effect of the

196   precipitation and infiltration in the near-shore area is not expected to alter the local

197   flow regime significantly. The length of the model domain is chosen so that the

198   steady-state saltwater wedge that develops does not interfere with the left freshwater

199   boundary. Pressure is imposed on both the freshwater and seawater sides, while the

200   effect of seasonal variation in freshwater discharge is not taken into account.

201   Moreover, as model results are compared to tidally-averaged field measurements,

202   tidal pumping is not included in the model. The values of porosity (ϕ) and

203   longitudinal dispersivity (α_L) used in the simulations (Fig. 2a) are constrained by the

204   modeling work of Michael et al. (2005) for the same bay, whereas the permeability

205   (κ) estimate of 7 $\times 10^{-11}$ m^2, equivalent to a hydraulic conductivity of 6.9 $\times 10^{-4}$ m s^{-1},

206   falls within the measured range of measured hydraulic conductivities (Michael et al.

207   2005). The value of transverse dispersivity (α_T) is set by trial and error to 0.005 m, to

208   match the measured and modeled salinity profiles and the relatively sharp freshwater-

209   saltwater interface. We assume a simplified, idealized, yet realistic representation of

210   the local homogeneous flow regime and focus on the complexities that determine the

211   biogeochemical dynamics in this subterranean estuary. An analysis of the effect of

212   small-scale variations in the flow dynamics on the biogeochemical behaviour is

213   beyond the scope of this study.

214

215   The chemical constituents considered include salt, NO_3^-, NH_4^+, PO_4, adsorbed

216   phosphate ($PO_{4(ads)}$), ferrous iron (Fe^{2+}), iron oxide ($Fe(OH)_3$), dissolved oxygen (O_2)

217   and two fractions of dissolved organic carbon (a terrestrial, more refractory

218   component, DOC_1, and a marine labile fraction, DOC_2). All chemical species, except

219   for $PO_{4(ads)}$ and $Fe(OH)_3$, are mobile species. The solid species are considered

220   immobile and hence are only affected by local biogeochemical transformations. The

221   concentration at the freshwater side is fixed for the solute species and set via trial and

222   error to approximate the measured profiles at the first piezometer of the transect (PZ-

223   10) (Figs. 1 and 2a). At the seawater side, seawater is allowed to enter the domain

224   through advection. The boundary concentrations at the freshwater and seawater sides

225   for each species are given in Table 1. The initial concentration of the solid species

226   ($Fe(OH)_3$ and P_{ads}) is assumed to be zero throughout the entire model domain. Tables

227   2 and 3 show the rate formulations of the six transformation processes, including oxic

228   DOC degradation, denitrification, $Fe(OH)_3$ reduction, nitrification, Fe^{2+} oxidation and

229   PO_4 adsorption onto $Fe(OH)_3$, and the list of reaction parameter values used in the

230   simulations, respectively. The analysis of the major ions suggests conservative mixing

231   of groundwater and seawater (Fig. 3). This implies that at this site, ion exchange

232   processes for the major ions due to changes in the position of the freshwater-seawater

233   interface are not significant and hence, they are not included in the current reaction

234   network. Similarly, the effect of potential pH variations on reaction rates is not

235   explicitly accounted for. The modeled results presented here are for a total simulation

236   time of 11 years and are at steady-state with respect to the solute species. All results

237   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 PO_4, DOC and Fe^{2+} in the freshwater are largely unknown, and several

273   hypotheses exist on the occurrence of a reducing NH_4^+ plume on top of a more

274   oxidizing NO_3^- 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 NO_3^-

277   and NH_4^+ 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   Fe^{2+}-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" Fe^{2+} 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 1.5×10^{-6} 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^{-}

298   ^{1} 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 9-43 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 2.7×10^{-5} 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 1.4×10^{-5} 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 2.4×10^{-7} 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 $PO_{4(ads)}$, which falls

369   within the range of 25-200 ppm P found in the same sediment cores. The thin PO_4

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 Fe^{2+} oxidation in PZ-3 and PZ-5 (5×10^{-7} and 4.8×10^{-8} mol m$^-$

376   ^{2} 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 Fe^{2+} (and NH_4^+) 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 (DOC_1) that reaches the coast is rather

386   refractory, with a degradation rate constant of 3.0×10^{-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 NH_4^+ porewater

389   concentrations in the saltwater wedge might be produced from the remineralization of

390   labile organic carbon in saline estuarine sediments (DOC_2) (Kroeger and Charette,

391   2008), followed by dilution due to the landward advecting seawater. If a degradation

392   rate constant of 3.0×10^{-7} s^{-1} (10 yr^{-1}) is used (Figs. 5c, d and f), the model is able to

393   reproduce the drop in DOC_2 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   (DIN=NO_3^- + NH_4^+) and inorganic PO_4 concentrations (DIN:PO_4 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   m^3 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 m^2), which is much larger than the seepage face

434   considered in this study (168 m^2; 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 µmol m^{-2} d^{-1}) than the one obtained in

437   this study (1.5×10^5 µmol m^{-2} 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 PO_4 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 DOC_1 ($kf_{ox1} = 0.1$

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 NO_3^- removal is predominantly limited by the

452   lack of spatial overlap between the DOC and NO_3^- plumes. Upon convergence of the

453   two plumes within the intertidal area, denitrification is still inhibited by the presence

454   of O_2 in the surface sediments. Conversely, nitrification of the NH_4^+ produced from

455   the degradation of the reactive DOC_1 fraction causes the NO_3^- 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, NO_3^- 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 PO_4 concentrations is tested by

462   comparing the SGD of PO_4 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 PO_4. 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   DOC_2. Yet, overall, the SGD of DIN and PO_4 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 NO_3^- 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 O_2 from the beachface sustains elevated nitrification and Fe^{2+}

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 PO_4

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 NH_4^+ and

513   PO_4 porewater concentrations. While NO_3^- concentrations in SGD reflect those of the

514   freshwater source, the concentrations of PO_4 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:PO_4 ratio of SGD is close to 50.

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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 (DOC_1 + 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-O_2 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) O_2 concentration profiles PZ-11, PZ-3 and PZ-5 and imposed O_2 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) NO_3^-, (c) NH_4^+ and (e) PO_4 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 NO_3^-, NH_4^+ and PO_4, respectively.

Figure 8   Breakthrough curves for PO_4 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) NO_3^-, (c) NH_4^+ and (e) PO_4 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 NO_3^-, NH_4^+ and PO_4, respectively.

Figure 10   Schematic representation of the nutrient distributions and biogeochemical

transformations in the subterranean estuary of Waquoit Bay.

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