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# Evaluating salinity sources of groundwater and implications for sustainable reverse osmosis desalination in coastal North Carolina, USA

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**Abstract** The natural and pumping-induced controls on groundwater salinization in the coastal aquifers of North Carolina, USA, and the implications for the performance of a reverse osmosis (RO) desalination plant have been investigated. Since installation of the well field in the Yorktown aquifer in Kill Devil Hills of Dare County during the late 1980s, the groundwater level has declined and salinity of groundwater has increased from ~1,000 to ~2,500 mg/L. Geochemical and boron isotope analyses suggest that the salinity increase is derived from an upflow of underlying saline groundwater and not from modern seawater intrusion. In the groundwater of four wells supplying the plant, elevated boron and arsenic concentrations were observed (1.3–1.4 mg/L and 8–53 µg/L, respectively). Major ions are effectively rejected by the RO membrane (96–99% removal), while boron and arsenic are not removed as effectively (16–42% and 54–75%, respectively). In coming decades, the expected rise of salinity will be associated with higher boron content in the groundwater and consequently also in the RO-produced water. In contrast, there is no expectation of an increase in the arsenic content of the salinized groundwater due to the lack of increase of arsenic with depth and salinity in Yorktown aquifer groundwater.

**Keywords** Coastal aquifers · Stable isotopes · Arsenic · Reverse osmosis desalination · USA

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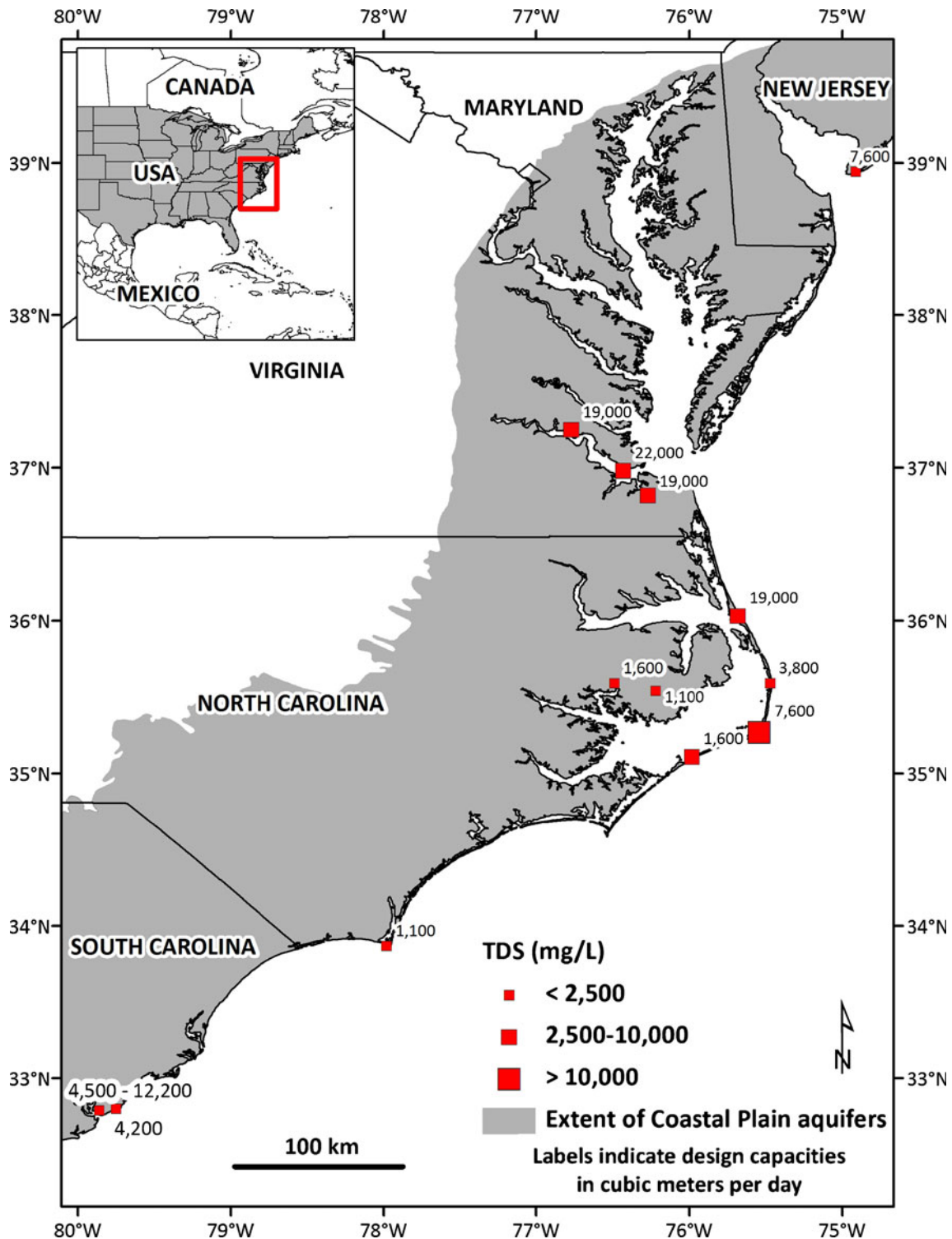
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## Introduction

Population growth in coastal areas has created significant pressure on, and depletion of, water resources in coastal aquifers (e.g., Jones et al. 1999; Barlow 2003; Ranjan et al. 2006), and climate change models predict increasing depletion of coastal freshwater resources during the coming decades (Ranjan et al. 2006). Desalination of seawater and saline groundwater is one alternative that could provide tap water to sustain the increasing demands in coastal areas (Salgot and Tapias 2004). While seawater desalination involves large capital investments and advanced technological solutions (e.g., the Ashqelon desalination plant in Israel, Gorenflo et al. 2007), using saline groundwater from coastal aquifers is a cheaper solution than seawater desalination, given the lower salinity of the groundwater resource. Yet, the ability to pump saline groundwater without major fluctuations in salinity is important for sustainable utilization of this water source for desalination.

This study is focused on saline groundwater and desalination from the southeastern Atlantic coast region of the USA. Coastal areas are the fastest growing regions in the USA, and are expected to continue to expand in the future (Barlow 2003). As with many other coastal areas, the southeastern Atlantic coast region is experiencing a large increase in population, resulting in increasing pressure on local groundwater resources. In Dare County, North Carolina, which includes the barrier island areas that are the setting for this study (Fig. 1), population grew from 23,000 to 34,000 from 1991 to 2009, a 48% increase (North Carolina, Office of State Budget and Management, State Demographics Branch 2010). In addition, Dare County has undergone a transition from high summer demand to year-round demand and a sharp increase in overall water demand (Dare County Water Department 2006). Similar to other inhabited coastal areas (Fig. 1), the approach in Dare County to meet increasing demand was the installation of several reverse osmosis (RO) desalination plants in which local saline groundwater is used as the water source (Oreskovich and Watson 2003; Dare County Water Department 2006). The hydrogeologic properties of the Atlantic coast (Meisler 1989; Barlow



**Fig. 1** Map showing locations and design capacities (m<sup>3</sup>/day) of RO desalination plants along the Atlantic coast. *Symbol size* is proportional to total dissolved solids (TDS) of feed groundwater to the RO plants. Data from the American Membrane Technology Association (AMTA 2011)

2003) enable water systems such as Dare County's to pump saline groundwater for the RO desalination plant instead of the more costly option of seawater desalination to replace limited supplies of surface water and fresh, shallow groundwater (Fig. 1). Currently, the Dare County Water Department operates three small desali-

nation plants with production rates of 230–7,570 m<sup>3</sup>/day (0.08–2.76 × 10<sup>6</sup> m<sup>3</sup>/year). The Dare County North RO Water Plant at Kill Devil Hills is the focus of this study, and generates 3,780 m<sup>3</sup>/day permeate (treated) water that is blended with raw well water to produce 4,055 m<sup>3</sup>/day (about 1.5 × 10<sup>6</sup> m<sup>3</sup>/year).

Desalination of brackish and/or saline groundwater presents other challenges such as the presence of naturally occurring contaminants in groundwater that are not removed effectively by RO desalination, including boron (US Environmental Protection Agency (EPA) 2008; Kloppmann et al. 2008) and uncharged forms of arsenic (Oreskovich and Watson 2003; Pawlak et al. 2006; George et al. 2006; Moore et al. 2008; Walker et al. 2008; Geucke et al. 2009). High boron concentrations are commonly observed in coastal aquifers due to boron desorption from marine sediments (e.g., D'Avino and Spandre 1995; Vengosh and Spivack 1999) and at near-neutral pH, boron occurs primarily as uncharged  $B(OH)_3^0$ , which is not efficiently adsorbed and can accumulate in groundwater. Although saline waters may contain high arsenic concentrations (Smedley and Kinniburgh 2002; Scanlon et al. 2009), high-As groundwater is commonly understood as a function of the solid-phase arsenic source and desorption processes that are sensitive to pH, redox conditions, and/or surface charge modification by cations (Smedley and Kinniburgh 2002; Haque et al. 2008; Scanlon et al. 2009). At near-neutral pH, oxidized As(V) occurs as anionic  $H_2AsO_4^-$  or  $HAso_4^{2-}$ , subject to pH-sensitive desorption from metal oxides; reduced As(III) exists primarily as uncharged  $H_3AsO_3^0$  that is less effectively adsorbed than anionic As(V). Redox processes subsequent to Fe and Mn oxide reduction such as sulfate reduction, may further affect As mobility in anoxic aquifers (e.g., Kirk et al. 2004).

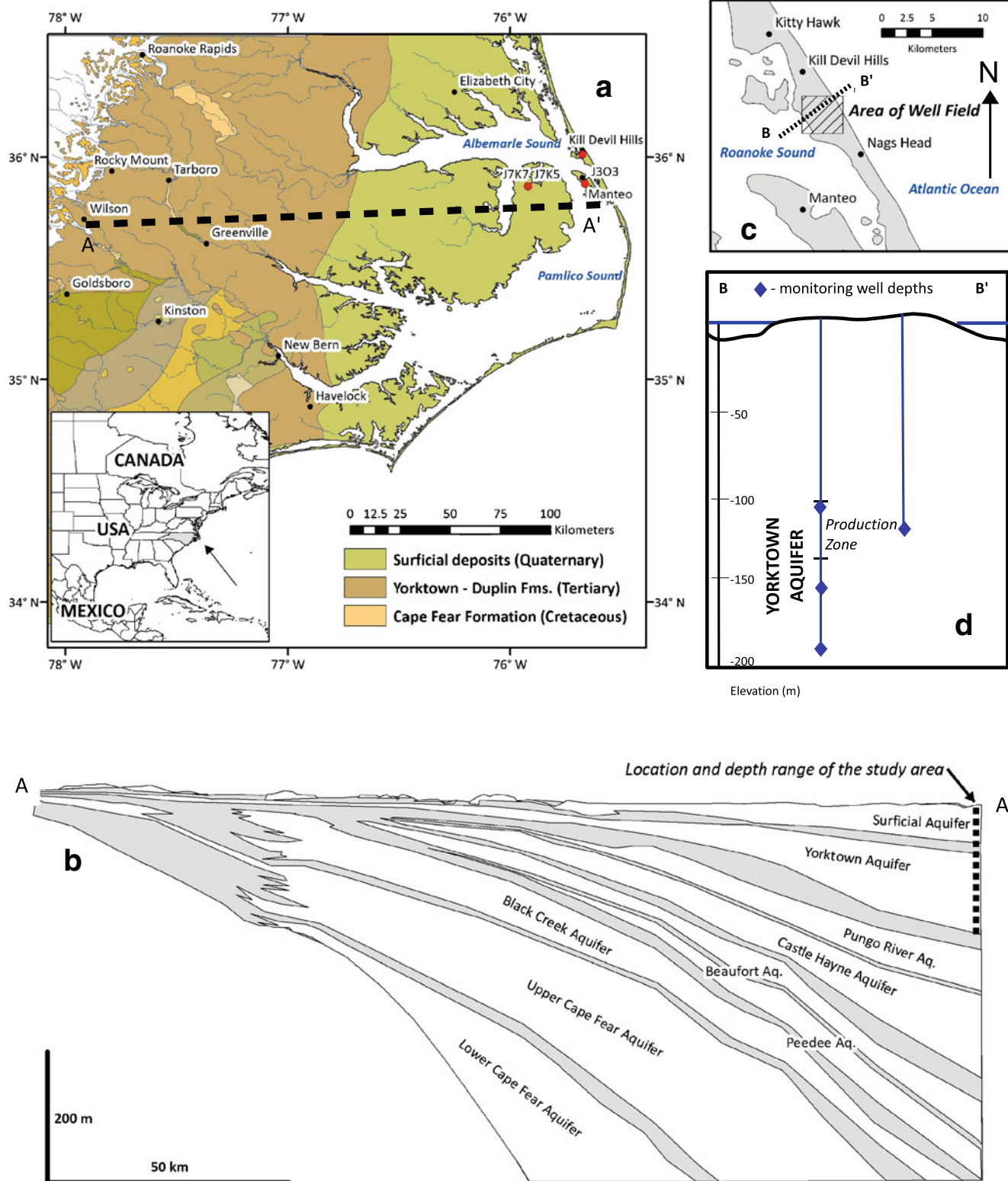
In addition to the potential water-quality problems introduced by natural contaminants, the stability of the quality of the saline-water source for the RO plant is in question, particularly for aquifers that are constantly being exploited beyond natural replenishment. This paper aims to investigate these two issues. First, water-quality changes that have occurred since the installation of the pumping wells for the RO desalination plant in Dare County during the late 1980s are investigated. Major elements coupled with stable oxygen, hydrogen, and boron isotopes are used as *indicators* for tracing the origin of the saline groundwater. Second, the relationship between the chemical composition of the saline groundwater and the rejection performance, particularly of boron and arsenic, by RO desalination in the Dare County North Reverse Osmosis Water Plant is assessed. In addition, predictions are made on how the long-term changes in the water quality of the saline groundwater source will affect the quality of the produced water generated by the RO plant. The case study of Dare County in North Carolina is representative of numerous areas along the Atlantic coast that are facing similar challenges for sustainable water supply under increasing water demands (Fig. 1).

## Hydrogeologic setting

The Atlantic Coastal Plain extends from Florida to New York and is comprised of thick clastic sediments and

marine limestones from Jurassic to Quaternary in age. In North Carolina, the area of this research, the Coastal Plain may be divided into nine distinct sand and limestone aquifers (Fig. 2a–b). Across a gently dipping outcrop belt about 200 km wide, these sediments reach a thickness of approximately 3,000 m (Winner and Coble 1996). In the aquifers of the Atlantic Coastal Plain, waters moving down-gradient undergo ion exchange reactions that remove Ca and Mg; thus, in the down-gradient, confined portions of the aquifers, Na-bicarbonate waters dominate (Chapelle and Knobel 1983; Knobel et al. 1998) before mixing with saline Na–Cl waters. Overall, physical and geochemical characteristics suggest that this saline source in the deep confined Coastal Plain aquifers is dilute fossil seawater and/or brine and that the salinity level of this water is derived from mixing caused by Quaternary sea level fluctuations (Manheim and Horn 1968; Meisler 1989; Barlow 2003). No confining unit separates the aquifer from the natural salinity source down-dip, whereas regional confining unit(s) separate the aquifer system from modern seawater. Therefore, intrusion of modern seawater is not suspected as a significant cause of the groundwater's salinity. Although the authors know of no isotopic measurements of the confined coastal aquifers of eastern North Carolina (e.g.,  $^{14}C$ ) that would directly address the antiquity of this saline-water source,  $^{14}C$  dating of inland waters in confined Cretaceous Coastal Plain aquifers at similar depths as this study indicates long groundwater residence time since recharge (3,200–26,000 years; Kennedy and Genereux 2007). Therefore, surface-derived inputs to these confined aquifers are not substantial. Redox conditions in the confined Coastal Plain aquifers are generally anoxic and sulfate-reducing (Chapelle and McMahon 1991; Knobel et al. 1998; Kennedy and Genereux 2007).

The Yorktown aquifer, in which the study wells are located, is an upper Miocene to Pliocene marine sand containing abundant silt, clay, and carbonate shell material and is the uppermost confined aquifer in the Atlantic Coastal Plain (Fig. 2d; Winner and Coble 1996). The western, relatively shallow section of the Yorktown aquifer receives sufficient recharge from the surface that only localized water level declines have been observed (dePaul et al. 2008). However, the eastern one third of the Yorktown aquifer in North Carolina, including the study area, exhibits higher hydraulic head than overlying aquifers as is generally true in the confined Coastal Plain aquifers (Winner and Coble 1996). Like other Coastal Plain aquifers, the Yorktown aquifer becomes thicker and more saline down-dip towards the Atlantic Ocean; the point at which  $Cl < 250$  mg/L at the base of the Yorktown aquifer lies approximately 60 km inland of the study area (Lautier 2009). In the vicinity of the study site, the Yorktown aquifer extends from a depth of ~50 m to at least 200 m below sea level and is overlain by a silt- and clay-rich confining unit up to 15 m thick and by the Quaternary surficial aquifer (Fig. 2c–d; Winner and Coble 1996).



**Fig. 2** Map and cross sections showing location of the study site and depths of wells sampled: **a** Geologic map based on North Carolina Geological Survey (1985) showing locations of wells J303, J7K5, and J7K7; **b** Schematic cross section of the North Carolina Coastal Plain modified from Winner and Coble (1996; plate 7); **c** Inset map showing location of Kill Devil Hills well field, where all other wells were sampled; and **d** Schematic diagram indicating approximate depths of wells sampled within the Yorktown aquifer (interval labeled Production Zone indicates the screen length of high-capacity production wells)

## Materials and methods

Water samples were collected from four production wells, screened at approximately 90–120 m depth; three nested monitoring wells adjacent to a production well (depth 95–190 m; Fig. 2d); two coastal monitoring wells seaward from the production well field (depth ~120 m); and seven points within the RO desalination plant at Kill Devil Hills, Dare County, North Carolina (Table 1). In addition to the wells in the Kill Devil Hills area, three monitoring wells (depth 24–67 m) on the mainland and near the town of Manteo on Roanoke Island (Fig. 2a) were sampled at sites maintained by the North Carolina Division of Water Resources. These three wells are shallower than the wells at Kill Devil Hills, chosen to represent shallow recharging waters away from possible marine sources, and thus may not represent the same stratigraphic level of the Yorktown aquifer. Monitoring wells were sampled after a period of continuous pumping to remove stagnant water. pH, electrical conductivity, dissolved oxygen, and temperature were measured in water samples on site (Table 1). The samples were returned to Duke University for the analysis of major and trace elements coupled with boron and stable oxygen and hydrogen isotopes. Concentrations of B, As, and Sr were determined by inductively coupled plasma-mass spectrometry calibrated using NIST 1643e trace element solution. Arsenic concentrations were corrected for chloride interference by the equivalent analyte concentration method (Taylor 2001). Ca, Mg, and Na concentrations were determined by direct current plasma spectrometry and potassium concentration was determined by flame atomic absorption spectrometry. Anion (chloride, sulfate, and bromide) concentrations were measured by ion chromatography. Effective detection limits and analytical precision vary by dilution factors (B 0.2–10 µg/L, As 0.01–0.6 µg/L). Bicarbonate concentrations were determined by titration to pH 4.5. Oxygen and hydrogen isotope ratios were determined in the Duke Environmental Isotope Laboratory by injection of 1 µL samples from a gas-tight syringe into a ThermoFinnigan thermochemical analyzer, using H<sub>2</sub> and CO gas peaks analyzed for isotope ratios with a ThermoFinnigan Delta+XL isotope ratio mass spectrometer and normalized against V-SMOW and V-SLAP. Precision is approximately 0.3‰ for δ<sup>2</sup>H and 0.1‰ for δ<sup>18</sup>O. Boron isotope ratios were determined by negative ion thermal ionization mass spectrometry using a Thermo Scientific TRITON thermal ionization mass spectrometer at Duke University. Filtered water samples were treated by H<sub>2</sub>O<sub>2</sub> oxidation, then ~2 ng of B was loaded onto outgassed rhenium filaments in a synthetic seawater solution containing Na, Mg, Ca, and K from high-purity single-element standard solutions in a laminar-flow hood with B-free filters (Dwyer and Vengosh 2008). Ratios are normalized to the NIST 951 standard and reported as δ<sup>11</sup>B. Repeated analysis of NIST 951 and seawater yielded average <sup>11</sup>B/<sup>10</sup>B of 4.0058 (1σ=0.0011 or 0.3‰, n=62) and 4.1630 (1σ=0.0025, n=17; δ<sup>11</sup>B = 39.2±0.6‰), respectively.

## Results and discussion

### Salinization of groundwater in the Yorktown aquifer

Groundwater from shallow monitoring wells exhibits relatively low salinity relative to the deep monitoring wells with chloride content of 8,200–9,900 mg/L (Fig. 3; Table 1). The Dare County RO desalination plant uses saline groundwater from several production wells at intermediate depth (Fig. 2d, Table 1). Since the installation of these production wells, a total volume of 70×10<sup>6</sup> m<sup>3</sup> has been extracted with a pumping rate in the range of 0.2 – 0.5×10<sup>6</sup> m<sup>3</sup>/year per well. Operation of the production wells since the late 1980s has coincided with a general decline in the water table as measured in the monitoring wells (Fig. 4a): from a depth of 10–12 m in the early 1990s to a depth range of 13–16 m during the late 2000s. This suggests that pumping rates have exceeded the natural replenishment of this aquifer. The salinity in these wells has also increased since the installation of the pumping. Historic data for the production wells show that the chloride content has increased from an initial concentration of 970 mg/L in August 1989 to approximately 2,500 mg/L by 2009 (Fig. 4). During the first five years of pumping, the salinity increase rate was high (~190 mg/L per year), followed by a lower salinization rate (~45 mg/L per year), indicated by the leveling of the chloride concentration trend (Fig. 4b).

### Tracing the source of the salinity by geochemical and isotope techniques

In order to evaluate the origin of salinization of the production wells, the geochemical composition of saline groundwater at different depths in the Yorktown aquifer was investigated (Table 1). First, ion ratios, δ<sup>2</sup>H, and δ<sup>18</sup>O are consistent with mixing between shallow freshwater and deep saline water. Mixing with upcoming saline water is supported by (1) variations of δ<sup>2</sup>H and δ<sup>18</sup>O (Fig. 5) that indicate a mixing relationship between seawater-like saline groundwater (δ<sup>2</sup>H and δ<sup>18</sup>O here approximated at 0‰ although analysis of North Carolina coastal surface water indicates median δ<sup>18</sup>O of +0.92‰; n=40; Schmidt et al. 1999) and low-salinity groundwater derived from local recharge (δ<sup>2</sup>H ≈ -20‰; δ<sup>18</sup>O ≈ -4.5‰; Table 2); and (2) a constant Br/Cl ratio near the seawater value of 1.5×10<sup>-3</sup> (Fig. 6). Water from the production zone wells is consistent with mixing between the deep and shallow groundwater, based on Br/Cl, Na/Cl, Mg/Cl, Ca/Cl, and Sr/Cl ratios, although these ion ratios are somewhat modified by cation exchange. For a hypothetical vertical mixture between wells 1–310 and 1–610, ion ratios consistently indicate that inputs of 20–25% deep saline water can explain the chemistry of produced water (Fig. 6).

Secondly, the nature of the deep saline water that contributes to the Kill Devil Hills well field was examined. Evaluating the source of the saline component (e.g., seawater, old modified seawater, brackish water, or

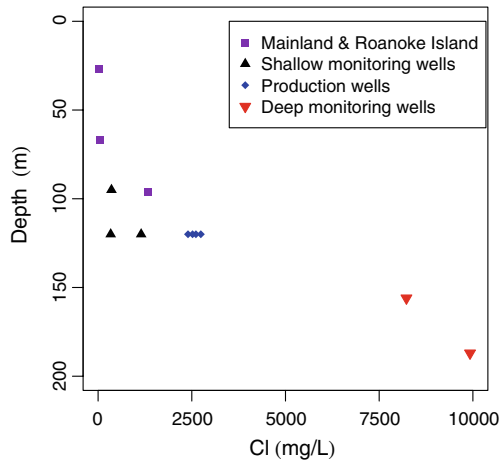
**Table 1** Field parameters, major and trace elements for groundwater and reverse osmosis plant waters. Steps in the reverse osmosis process are detailed in Figure 9

Sample name	Screen depth (m)	Date	pH	T (°C)	DO (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sr (mg/L)	Cl <sup>-</sup> (mg/L)	Br <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	HCO <sub>3</sub> <sup>-</sup> (mg/L)	B (mg/L)	As <sup>a</sup> (µg/L)
Mainland and Roanoke Island monitoring wells (NC Division of Water Resources)																
J7K7	24-27	11 Dec 2008	6.8	17.8		49.5	23.0	27.7	18	0.37	22	0.10	0.4	356	0.26	ND
J7K5	93-96	11 Dec 2008	7.9	18.5	0.3	17.9	29.0	1,080	42	0.70	1,340	4.9	64	586	1.19	125
J3O3	61-67	11 Dec 2008	7.2	17.5	0.3	54.0	4.2	67.0	4.9	0.27	50	0.21	0.2	265	0.11	ND
Kill Devil Hills coastal monitoring wells																
Ocean Bay	~120	21 Nov 2008	8.6	18.8	0.3	4.6	6.0	511	4.5	0.10	336	1.3	27.2	717	1.85	1.9
Albatross	~120	21 Nov 2008	8.0	18.8	0.3	20.6	42.7	950	3.7	0.90	1,150	4.1	21.5	515	1.42	18
Kill Devil Hills well field <sup>b</sup>																
1-310	95	21 Nov 2008	8.0	20.0	0.7	4.8	6.0	469	1.5	0.09	357	1.3	24.2	574	1.33	54
Production well 1	~90-120	28 Oct 2008	7.9	20.0	0.6	63.2	112	1,570	83	2.8	2,400	8.7	168	354	1.28	33
1-510	156	28 Apr 2009	7.2	21.4	0.2	232	479	4,990	168	13.8	8,180	29.6	764	333	2.19	ND
1-610	187	28 Apr 2009	7.2	21.4	0.1	270	527	5,820	207	18.0	9,890	36.4	719	458	2.60	ND
Production well 2	~90-120	29 Oct 2008	7.8	20.0	1.6	72.2	128	1,650	88	3.0	2,520	9.1	191	371	1.31	51
Production well 7	~90-120	21 Nov 2008	7.8	19.5	0.6	79.1	128	1,640	74	3.4	2,610	9.3	177	313	1.26	53
Production well 11	~90-120	21 Nov 2008	7.8	19.5	0.7	66.5	122	1,720	74	3.4	2,740	10.1	187	410	1.43	8
Reverse osmosis facility																
D1 (raw water blend)		29 Oct 2008	7.8	20.0	5.6	59	98	1,620	85	2.1	2,310	12.3	152	479	1.31	20
D3 (1st stage brine)		29 Oct 2008	7.9	20.7	3.2	107	201	3,120	250	4.7	4,860	18.7	217	1,020	1.82	35
D4 (2nd stage permeate)		29 Oct 2008	6.9	20.2	3.6	0.1	0.2	45.5	1.6	0.007	66	0.29	0.2	17	1.05	8.8
D5 (2nd stage brine)		29 Oct 2008	7.8	21.3	1.9	220	392	6150	736	9.6	9,530	37.0	434	1,390	2.51	55
D6 (combined permeate)		29 Oct 2008	7.9	20.9	3.3	0.2	0.2	51.8	1.9	0.007	78	0.13	0.3	14	1.10	9.3
D7 (drinking water)		29 Oct 2008	8.4	20.2	0.7	2.5	4.2	130	5.1	0.09	155	0.09	5.0	46	1.09	0.1
D8 (final brine)		29 Oct 2008	7.7	20.5	2.5	211	377	5,790	754	10.3	9,870	34.9	453	1,650	3.15	51
Seawater <sup>c</sup>			8.2			412	1,280	10,800	399	7.9	19,400	67	2,710	114	4.6	

<sup>a</sup> ND indicates not detected. Detection limit depends on dilution factor but in all cases ND indicates As < 1 µg/L. These are plotted as 0 µg/L

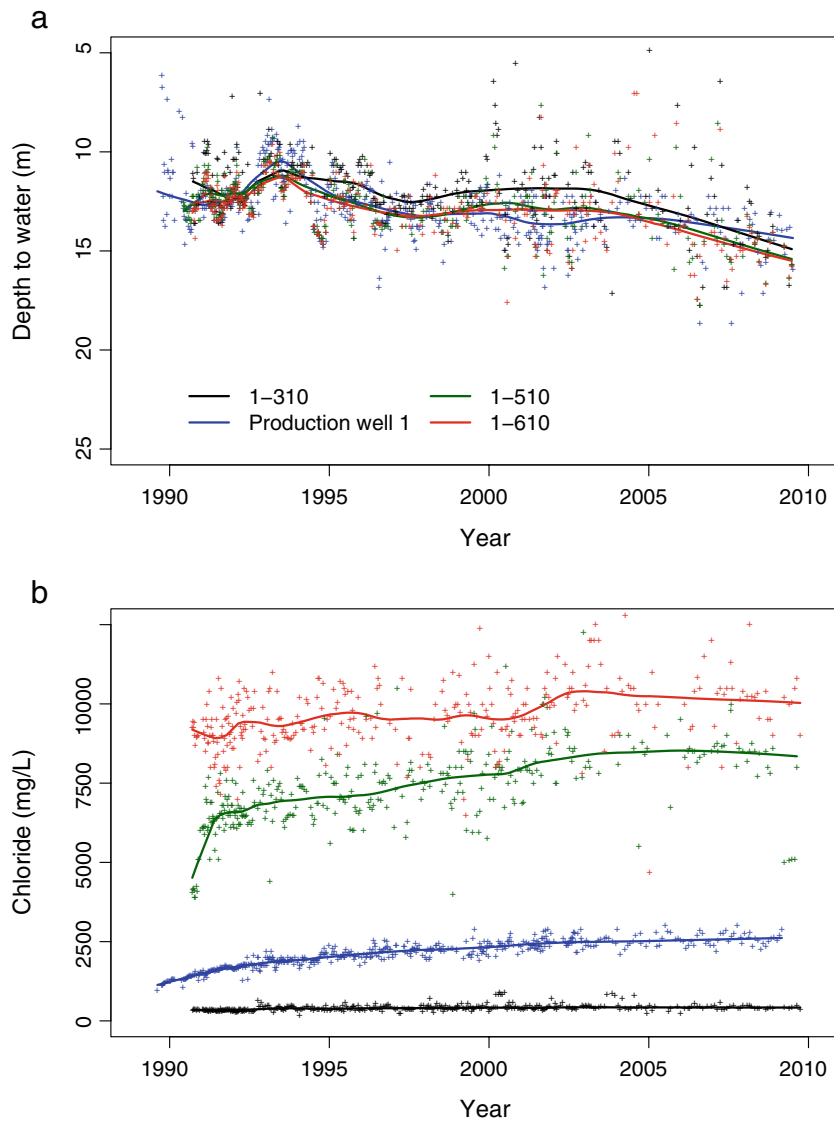
<sup>b</sup> Wells 1-310, production well 1, 1-510, and 1-610 are a nest at the same location

<sup>c</sup> Data from Millero and Sohn (1991), except B concentration from Vengosh and Spivaek (1999)

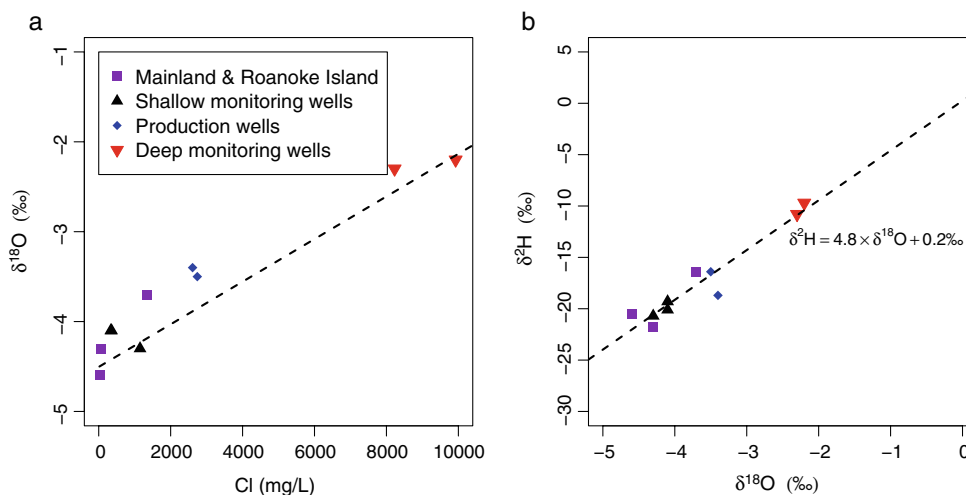


**Fig. 3** Relationship between chloride concentration and depth in studied groundwater arranged by location, depth, and type of wells

brine) affecting the Kill Devil Hills well field could have implications for predicting future salinity trends. The low-salinity groundwater in shallow wells at Kill Devil Hills (1-310, Albatross, and Ocean Bay; Table 2) exhibits high Na/Cl ( $>1$ ) and B/Cl ( $>2 \times 10^{-3}$ ), low Mg/Cl and Ca/Cl ratios, and low  $\delta^{11}\text{B}$  (23–29‰) relative to the composition of modern seawater ( $\delta^{11}\text{B}=39\text{‰}$ ;  $\text{B/Cl}=8 \times 10^{-4}$ ; Figs. 6 and 7). In contrast, the deep groundwater is saline and has some geochemical properties that resemble seawater (e.g., Na/Cl close to the seawater value of 0.86; Br/Cl close to the seawater value of  $1.5 \times 10^{-3}$ ; Table 2). This composition suggests reverse base-exchange reactions, in which Ca- and Mg-bearing recharge interacts with marine clays in which the exchange sites are occupied by Na due to prior contact with seawater. In a reverse base-exchange reaction,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are lost from the groundwater to the solids in exchange for  $\text{Na}^+$ , resulting in Na enrichment



**Fig. 4** Historical water data for production well 1 and adjacent monitoring wells (1-310, 1-510, 1-610) from 1989 through 2009: **a** water level measurements; **b** chloride concentrations. Data provided by Dare County Water Department. *Trend lines* calculated using LOWESS method in which smoothing is controlled by the nearest 20% of data points (R Development Core Team 2009)



**Fig. 5** **a** Oxygen and **b** hydrogen isotope ratios in groundwater plotted along possible mixing trends. In **a** the *dashed line* represents hypothetical mixing of fresh locally recharged groundwater (20 mg/L Cl,  $\delta^2\text{H} \approx -20\text{‰}$ ,  $\delta^{18}\text{O} \approx -4.5\text{‰}$ ) with a seawater-like saline groundwater (~19,000 mg/L Cl,  $\delta^2\text{H}$  and  $\delta^{18}\text{O} \approx 0\text{‰}$ ). In **b** the *dashed line* represents a linear regression of the  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  data. Note the *y*-intercept value of  $\delta^2\text{H} \approx 0\text{‰}$ , indicating a mixing relationship with seawater-like saline water rather than meteoric water that would exhibit deuterium excess

in the residual groundwater (Chapelle and Knobel 1983; Knobel et al. 1998). Reverse base-exchange reactions can also explain the relatively high B/Cl and low  $\delta^{11}\text{B}$  values (Fig. 7) that are consistent with the composition expected from boron desorption from clay minerals (Spivack et al. 1987). In contrast, in direct base-exchange reactions that characterize seawater intrusion zones, boron is retained by adsorption onto clay minerals, resulting in high  $\delta^{11}\text{B}$  and low B/Cl in the residual groundwater relative to seawater

values (Jones et al. 1999; Vengosh and Spivack 1999; Vengosh 2003). Although Ca/Cl and Sr/Cl ratios exceed seawater values in the deep saline groundwater, as is seen in seawater intrusion zones (Nadler et al. 1980; Vengosh et al. 2002; Andersen et al. 2005; Sivan et al. 2005), Mg/Cl is significantly depleted relative to the seawater ratio. Together, these ratios imply that mixing and divalent-for-monovalent exchange cations cannot completely explain the Ca and Mg concentrations in the groundwater system;

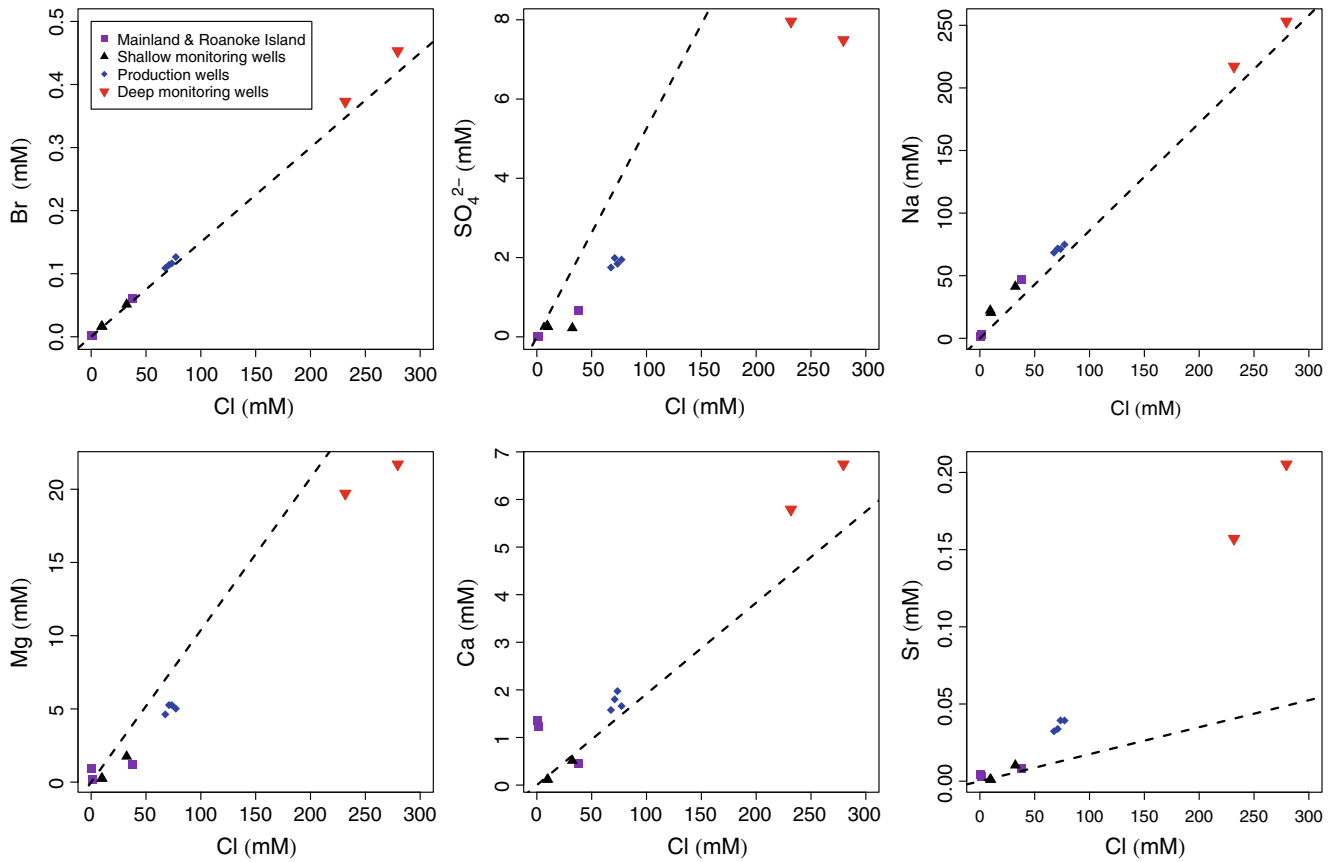
**Table 2** Ion (mol/mol) and isotopic ratios of groundwater and reverse osmosis plant water

Sample name	Na/Cl	Mg/Cl	Ca/Cl	Sr/Cl ( $\times 10^{-4}$ )	$\text{SO}_4^{2-}/\text{Cl}$	B/Cl ( $\times 10^{-3}$ )	$\delta^{11}\text{B}$ (‰)	$\delta^2\text{H}$ (‰)	$\delta^{18}\text{O}$ (‰)
Mainland and Roanoke Island monitoring wells									
J7K7	1.93	1.52	2.16	22	0.007	40	20.9	-20.5	-4.6
J7K5	1.24	0.032	0.012	2.1	0.018	2.9	33.4	-16.4	-3.7
J3O3	2.08	0.12	0.88	68	0.001	7.3		-21.8	-4.3
Kill Devil Hills coastal monitoring wells									
Ocean Bay	2.35	0.026	0.012	1.2	0.030	18	24.8	-20.1	-4.1
Albatross	1.28	0.054	0.016	3.2	0.007	4.1	29.8	-20.7	-4.3
Kill Devil Hills well field									
1-310	1.76	0.024	0.010	1.0	0.025	12	22.6		
Production well 1	1.01	0.071	0.023	4.7	0.026	1.8	25.8		
1-510	0.94	0.091	0.025	6.8	0.035	0.88	34.5	-10.8 <sup>a</sup>	-2.3 <sup>a</sup>
1-610	0.91	0.083	0.024	7.4	0.027	0.86	34.7	-9.7 <sup>a</sup>	-2.2 <sup>a</sup>
Production well 2	1.01	0.072	0.025	4.8	0.028	1.7	27.9		
Production well 7	0.97	0.081	0.027	5.3	0.025	1.6	27.3	-18.7	-3.4
Production well 11	0.97	0.071	0.021	5.0	0.025	1.7	28.8	-16.7	-3.5
Reverse osmosis facility									
D1	1.08	0.062	0.022	3.7	0.024	1.9	29.1		
D3	0.99	0.060	0.019	3.9	0.016	1.2	28.3		
D4	1.06	0.005	0.002	0.43	0.001	51.9	28.1		
D5	1.00	0.060	0.020	4.1	0.017	0.86	28.7		
D6	1.02	0.004	0.002	0.47	0.001	46	28.3		
D7	1.29	0.040	0.014	2.3	0.012	23	29.2		
D8	0.91	0.056	0.019	4.2	0.017	1.0	32.6		
Seawater	0.86	0.096	0.019	1.6	0.052	0.78	39 <sup>b</sup>		

<sup>a</sup>From samples collected 20–21 Nov 2008

<sup>b</sup>Vengosh and Spivack (1999)

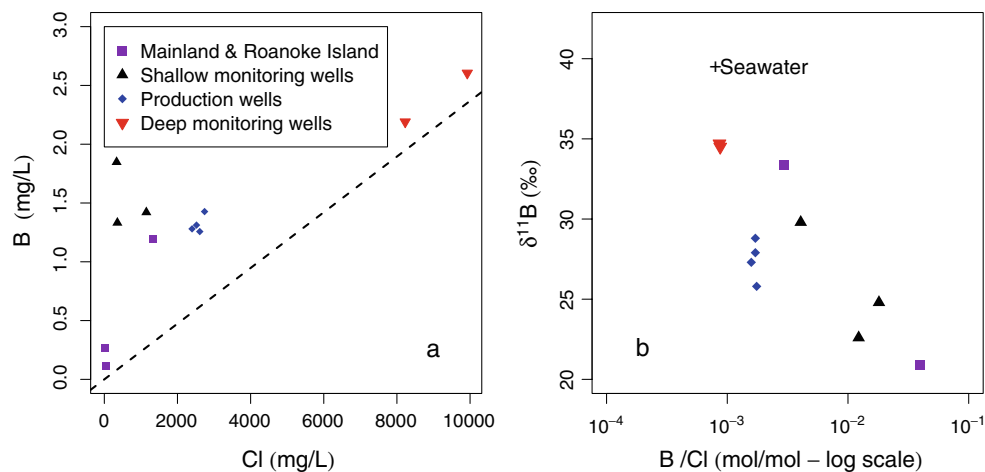




**Fig. 6** Relationships between chloride and major ion concentrations in the investigated groundwater. Dashed lines represent hypothetical dilution of seawater. Note that the compositions of the production wells show a mixing relationship between deep and shallow groundwater representing about 20–25% input of deep, saline water

some other phenomenon such as carbonate equilibrium may be necessary. The highest Ca/Cl and Mg/Cl ratios in the study area are seen in shallow wells inland from the Kill Devil Hills well field (J3O3 and J7K7; Table 2) that are less affected by reverse cation exchange due to the freshening impact of recharge. Overall, ion ratios and  $\delta^{11}\text{B}$  values suggest that the salinity of the pumping wells is derived from mixing

of modified and apparently old seawater with local recharge, and not modern seawater intrusion. This mixing relationship is also modified by reverse base-exchange reactions and boron desorption in the shallow, fresh portion of the aquifer. Mixing with old seawater at depth is consistent with previous studies of the Atlantic Coastal Plain (see section [Hydrogeologic setting](#)), and can also explain the relatively low rate of



**Fig. 7** Relationship between **a** boron and chloride contents and **b**  $\delta^{11}\text{B}$  and B/Cl ratios (log scale) in the investigated groundwater. Note that studied groundwater samples have higher B/Cl and lower  $\delta^{11}\text{B}$  values relative to seawater

salinization of the pumping wells (Fig. 4b), compared to rapid, exponential salinization rates that characterize seawater intrusion fronts in over-exploited coastal aquifers (Vengosh 2003).

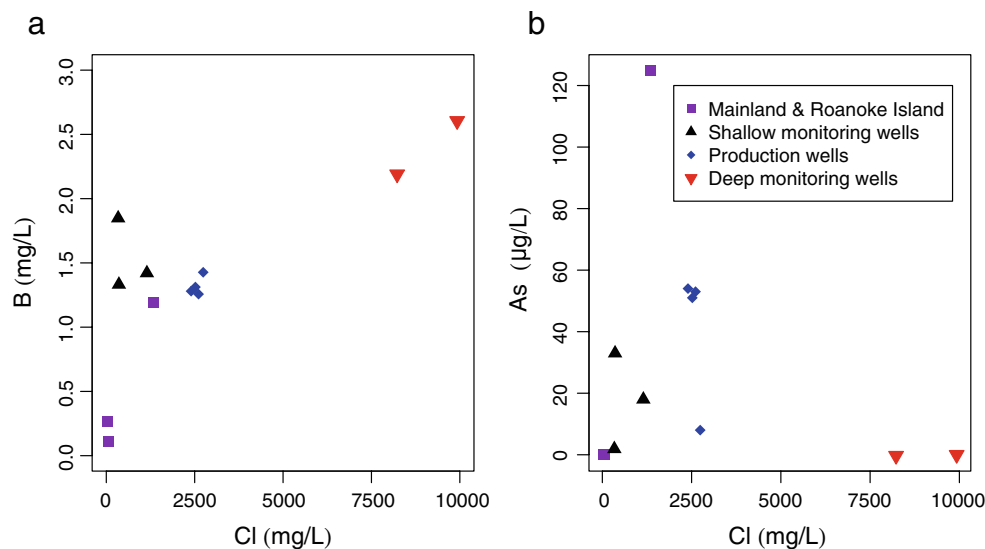
### **Arsenic, boron, and future salinity trends**

In addition to the overall salinity in the produced water, levels of naturally occurring contaminants affect the suitability of saline groundwater for reverse osmosis desalination. The wells in the production zone contain 8–53 µg/L arsenic and 1.3–1.4 mg/L boron (Table 1; Fig. 8). As addressed in the following discussion, the removal of these contaminants is relatively ineffective in reverse osmosis desalination, and they may remain at elevated concentrations in post-RO water. Thus, future increases of natural contaminants in groundwater as salinization proceeds could affect the quality of water produced by the RO system. Extrapolation of previous salinity trends suggests potential future levels of salinity and boron. The average rate of groundwater salinization in the production wells from 1994 to 2009 was ~45 mg/L chloride per year (Fig. 4b). Extrapolating a linear salinization rate for the next 20 years implies a ~35% increase in salinity. Thus, the current chloride content could increase to about 3,400 mg/L in 2030 and to about 4,300 mg/L in 2050. However, the recent leveling of the salinization trend (Fig. 4b) implies that a linear extrapolation of the salinization rate may be excessive, and that a near-equilibrium condition may be reached that is significantly less saline than seawater but represents a larger proportion of the deep brackish water as the shallow freshwater is depleted. Because boron concentration is associated to some degree with chloride concentration and depth (Fig. 8), the expected rise in salinity may be associated with an additional increase in

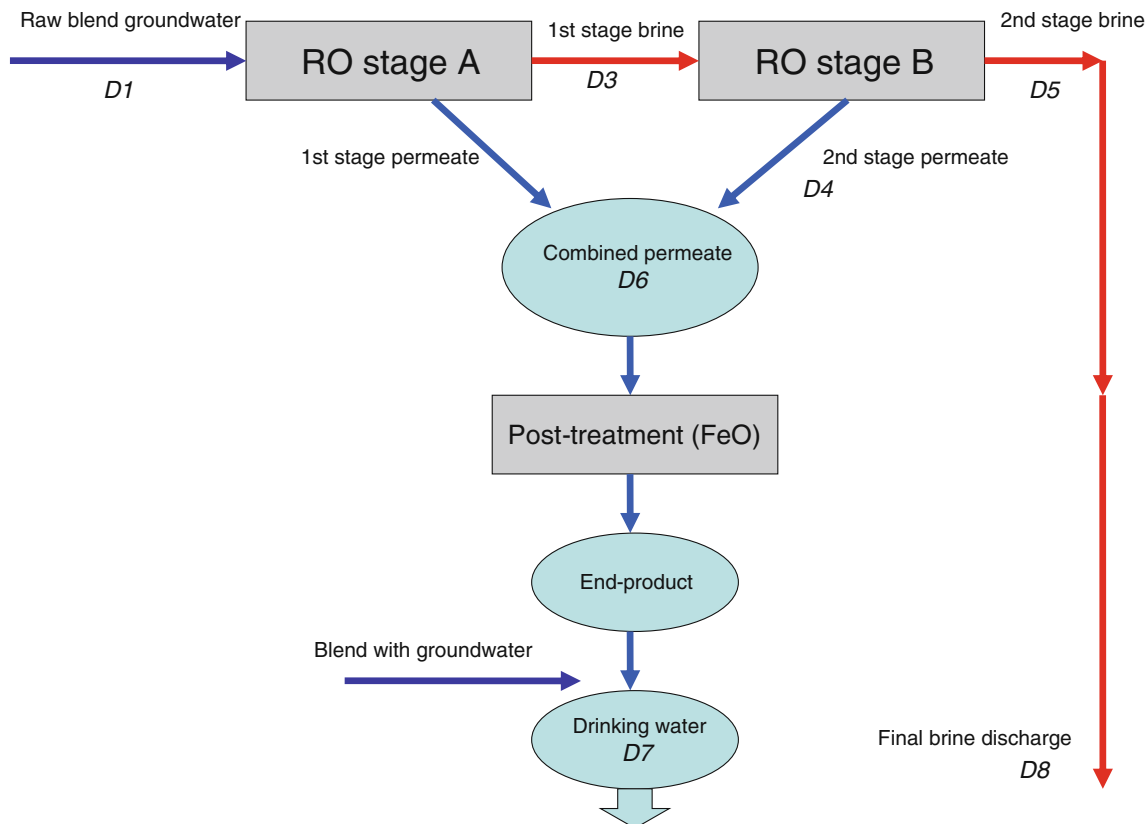
the boron content of the groundwater blend. The boron content in the produced groundwater could increase to approximately 2 mg/L in 2050. In contrast to boron, the results indicate that the deep and saline groundwater exhibits lower As concentration than the shallow and less saline groundwater. The high As occurrence is apparently limited to groundwater within certain depth intervals of the aquifer as a result of local water–rock interaction with a solid-phase arsenic source that varies spatially rather than being a systematic phenomenon associated with salinity (Fig. 8). The data suggest that increased mixing of the deep saline component should not cause net As transport into the production zone of the aquifer.

### **Selective rejection in RO desalination of saline groundwater**

The desalination plant in Kill Devil Hills, Dare County is composed of a cascade of two RO membrane systems and a post-treatment system specifically designed for arsenic removal (Fig. 9). A groundwater blend from the pumping wells is used as a water source. At the first stage, the groundwater is pressurized through RO stage A. The brine then flows through RO stage B, and permeates (treated water) from these two stages are mixed (sample D6; Table 1) before they are treated further for arsenic in the post-RO facility and are ultimately mixed with untreated groundwater (to increase hardness) for distribution. The residual brine is discharged to the ocean. Table 1 presents the chemical results for different constituents in permeate and concentrate (residual brine) solutions. The data show that in spite of the significant increase in salinity in the raw water during 20 years of operation, the RO system strongly rejects divalent and monovalent ions with removal efficiencies of 96–99% (Table 3). In contrast,



**Fig. 8** a Boron and b arsenic in relation to chloride concentrations in the investigated groundwater. Note that while boron is generally associated with chloride, arsenic is not, particularly for the deep and saline groundwater. This implies that further salinization may not induce an increase in As concentration



**Fig. 9** Schematic diagram of the Dare County North RO desalination water plant at Kill Devil Hills indicating samples collected at different water treatment steps

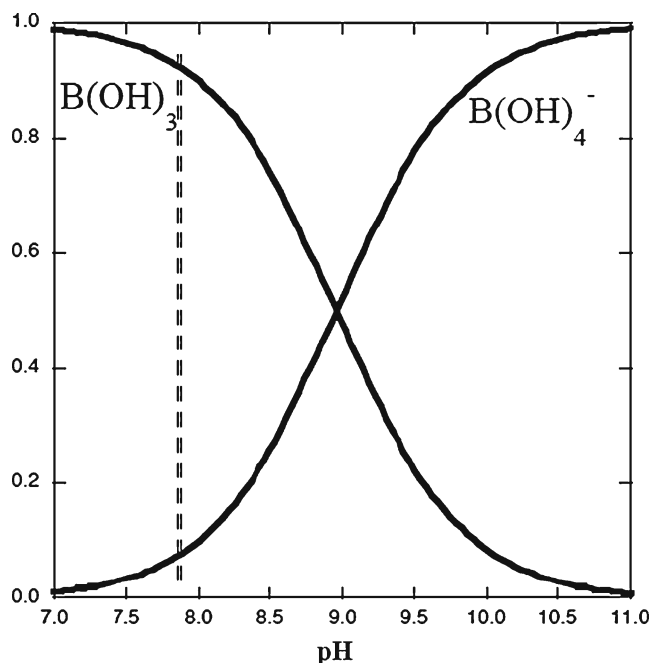
the removal of boron and arsenic by the RO membrane is significantly lower (16–42% and 54–75%, respectively). Consequently, the concentrations of boron (1.1 mg/L) and arsenic (9.3  $\mu\text{g/L}$ ) in the combined permeate water (sample D6; Table 1) are near or exceed the EPA maximum contaminant level for arsenic (10  $\mu\text{g/L}$ ) and World Health Organization (WHO) recommendations (0.5 mg/L B and 10  $\mu\text{g/L}$  As; WHO 2008). Other arsenic data from this system (Oreskovich and Watson 2003) are typically above 10  $\mu\text{g/L}$ . Boron concentrations are below the EPA Health Advisory, a US government recommendation (5 mg/L lifetime advisory; EPA 2008). In addition to these national and international advisories, six states in the USA, not including North Carolina, have adopted boron advisories between 0.6 and 1.0 mg/L (EPA 2008).

The relatively low rejection of boron from the RO membrane is related to the distribution of boron species and the mode of RO operation (Prats et al. 2000; Parks and Edwards 2005; Georghiou and Pashafidis 2007; Kloppmann et al. 2008; Cengeloglu et al. 2008; Ozturk et al. 2008; Mane et al. 2009). The data indicate that the second RO system removes almost 42% of boron (from

D3, the brine of the first stage, to D4, the second permeate; Fig. 9; Table 3), while overall removal performance is much lower (16%), implying that the removal capacity of the first RO system is very low. In Dare County, the pH of the inflow groundwater is about 7.8, which is not highly modified by the RO process (Table 1). Under conditions of salinity of  $\sim 5,000$  mg/L, temperature of 20°C (Table 1), and pressure of  $\sim 18$  bars (the average RO feed pressure at Dare County), the dissociation constant of boric acid ( $\text{p}K_{\text{B}}$ ) is 8.97 (calculated from empirical values made by Dickson 1990 and Millero 1995), and thus at  $\text{pH}=7.8$ , boron exists mostly in the form of uncharged boric acid (93%; Fig. 10). Several studies have shown differential permeation of boron species through the RO membranes and that the uncharged boric acid is not rejected effectively like the other charged ions (Sagiv and Samiat 2004; Hyung and Kim 2006; Kloppmann et al. 2008; Mane et al. 2009). Consequently, the boron rejection is low and the B/Cl molar ratios in the permeates (0.02–0.05) are significantly higher than that of the raw groundwater and brines (0.00086–0.0019; Table 2). In contrast, the original  $\delta^{11}\text{B}$

**Table 3** Removal percentages of major and trace elements from the RO desalination plant at Kill Devil Hills. Steps in the reverse osmosis process are indicated in Figure 8

Process	B	As	$\text{Sr}^{2+}$	$\text{Na}^+$	$\text{K}^+$	$\text{Cl}^-$	$\text{Br}^-$	$\text{SO}_4^{2-}$
%RO removal of second RO stage (D3–D4)	42.4	74.9	99.9	98.5	99.5	98.6	98.5	98.4
%RO removal of combined stages (D1–D6)	16.0	53.5	99.9	97.0	97.7	96.7	98.5	95.0



**Fig. 10** Prediction of boron species distribution as a function of pH. Calculations were based on modeling boric acid dissociation at salinity of 5,000 mg/L, temperature of 20°C, and pressure of 18 bars (combined  $pK_B=8.97$ ). Under conditions of RO desalination (pH=7.8, see dashed line), 93% of boron is in the form of uncharged boric acid

value of the source groundwater is not significantly modified (Table 3) due to the predominance of boric acid in the feed water (Fig. 10) and the lack of isotopic fractionation that could be induced by the separation of boron species (Kloppmann et al. 2008).

In addition to boron, arsenic rejection in the RO process is poor. The production wells contain As concentrations from 8 to 54  $\mu\text{g/L}$  and the rejection in the RO process is only ~54–75% (Table 3). Low rejection of As has been reported previously in RO systems (Oreskovich and Watson 2003; Pawlak et al. 2006; George et al. 2006; Moore et al. 2008; Walker et al. 2008; Geucke et al. 2009) and depends on the prevalence of charged As species. Arsenic speciation in water depends on oxidation state and pH. Under reducing conditions, arsenic occurs as arsenite (As(III)) in which the uncharged  $\text{H}_3\text{AsO}_3^0$  is the predominant species at pH below 9. Under oxic conditions, arsenate (As(V)) species are dominant, particularly the monovalent species  $\text{H}_2\text{AsO}_4^-$  (pH<6.5) and the divalent species  $\text{HAsO}_4^{2-}$  (pH>6.5). Consequently, RO rejection for the charged As(V) in oxygenated water is more effective (Oreskovich and Watson 2003; Pawlak et al. 2006; George et al. 2006; Moore et al. 2008; Walker et al. 2008; Geucke et al. 2009). In the production wells, dissolved oxygen concentration is typically below 1 mg/L (Table 1). Thus, essentially anoxic conditions support the presence of significant arsenic (III); previous research at the site has indicated that both arsenic (III) and arsenic (IV) species are present in untreated water from the Kill Devil Hills well field (As(III) <0.5–32  $\mu\text{g/L}$ ; As(V) <0.5–88  $\mu\text{g/L}$ ; Oreskovich and Watson 2003). This anoxic water is not aerated

throughout the RO process in order to avoid oxidation and scaling of the membrane system with iron and other oxides, and reported dissolved oxygen values of reverse osmosis process water (Table 1) are maximum values, subject to aeration during sampling. The presence of the uncharged  $\text{H}_3\text{AsO}_3^0$  results in the overall low As rejection. The resulting As concentrations, variable but typically exceeding 10  $\mu\text{g/L}$  in the post-RO permeate, are dominated by As(III) (Oreskovich and Watson 2003) and necessitated a post-treatment procedure (Fig. 9) composed of granulated ferric oxide with high adsorption capacity for As. The results indicate a significant (~99%) rejection of As in the post-treatment process, which reduces the As concentration (0.1  $\mu\text{g/L}$ ) to far below the EPA maximum contaminant level of 10  $\mu\text{g/L}$ . The brine that is produced from the Dare County RO plant contains total dissolved solids of 19,000 mg/L and is characterized by relatively high boron and arsenic concentrations of 3.2 mg/L and 51  $\mu\text{g/L}$ , respectively.

In light of the expected increase in boron concentrations as salinity increases in the future, the overall poor RO boron rejection is expected to continue. Given the potential health effects of elevated boron in drinking water (European Union 1998; Weinthal et al. 2005; EPA 2008; WHO 2008), the relatively high boron content in the RO produced water could be reduced by additional post-treatment procedures for boron removal (Parks and Edwards 2005; Jacob 2007) and/or changes in RO operation conditions (e.g., high pH; Sagiv and Samiat 2004; Hyung and Kim 2006; Kloppmann et al. 2008; Mane et al. 2009). However, future salinization is not expected to be associated with an increase in the As content of the blended groundwater, and the high rejection capacity of the post-treatment facility is expected to continue to be effective in removing As from the produced water.

### **The suitability of saline groundwater in coastal aquifers for RO desalination**

In general, three types of saline groundwater could possibly occupy coastal aquifers: (1) saline water originated from direct seawater inland encroachment; (2) saline groundwater that evolved from residue of entrapped fossil seawater originated from past intrusion of seawater during high sea levels; and/or (3) displacement of saline groundwater from underlying and adjacent aquifers (Custodio 1997; Jones et al. 1999). Formation of a cone of depression in a coastal aquifer due to pumping the saline groundwater for desalination would cause a displacement of the saltwater front and salinization of the pumping wells. Yet the different types of saline groundwater would cause different responses in salinization rate and water composition, which would have direct implications for their potential use for RO desalination. Numerous studies have shown (Jones et al. 1999; Vengosh 2003 and references therein) that rapid inland seawater encroachment involves a significant rise in salinity during relatively

short time frame of a few years, perhaps consistent with a sharp freshwater–saltwater interface as suggested by the Ghyben-Herzberg relationship (Freeze and Cherry 1979). In contrast, the long history of sea level fluctuation along the Atlantic Coastal Plain in eastern USA has resulted in large mixed areas of brackish groundwater (Manheim and Horn 1968; Meisler 1989), which suggests that pumping-induced salinity changes should be more gradual.

Consequently, two decades of pumping in the Outer Banks of Dare County in North Carolina has increased the relative contribution of the underlying fossil and diluted seawater in the upper section of the Yorktown aquifer. Salinity has increased by a factor of ~2.5, but this has not affected the performance of the RO membrane. A disadvantage of using this type of saline groundwater is the relatively high abundances of trace elements like boron and arsenic that are poorly rejected by the RO membrane as demonstrated in this study. Overall, saline groundwater in coastal aquifers can be an alternative to seawater desalination, but careful examination of the origin of the salinity and its water chemistry is essential for predicting the sustainable long-term utilization of the saline groundwater for RO desalination.

## Conclusions

This study examines the changes in salinity and chemical composition of saline groundwater from the southeastern Atlantic coast in the USA that is used for RO desalination. The salinity of water from the wells in the Yorktown aquifer in the coastal plain of North Carolina that produce feed water for RO desalination in Dare County North Reverse Osmosis Water Plant has increased from about 1,000 to about 2,500 mg/L since its installation in the late 1980s. Geochemical, oxygen, hydrogen, and boron isotope analysis suggests that the salinity increase is derived from upconing of higher-salinity underlying groundwater. Mass balance calculations indicate that the current level of salinity is associated with a contribution of about 20% of the underlying high-salinity groundwater. The geochemical data rule out contribution of modern seawater intrusion into the Yorktown aquifer. In spite of the salinity increase, the plant demonstrates high rejection performance for monovalent and divalent ions (96–99% removal). In contrast, the inferred uncharged nature of nearly all of the boron and much of the arsenic results in overall low removal of boron (16–43%) and arsenic (54–75%) by the RO membrane. This requires an additional treatment step in which arsenic is removed by reaction with an iron oxide media. Future salinization may increase the boron content of the raw water and consequently the produced water to as much as 2 mg/L, which would exceed international recommendations for drinking water. In contrast, further salinization should not significantly increase the arsenic content of water produced from the well field. In conclusion,

sustainable operation without resorting to higher-cost, higher-salinity seawater desalination is possible due to the large volume of fossil and diluted seawater that occupies the southeastern Atlantic coastal aquifers.

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