Geochemistry of shallow ground water in coastal plain environments in the southeastern United States: implications for aquifer susceptibility

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Abstract

Ground-water chemistry data from coastal plain environments have been examined to determine the geochemical conditions and processes that occur in these areas and assess their implications for aquifer susceptibility. Two distinct geochemical environments were studied to represent a range of conditions: an inner coastal plain setting having more well-drained soils and lower organic carbon (C) content and an outer coastal plain environment that has more poorly drained soils and high organic C content. Higher concentrations of most major ions and dissolved inorganic and organic C in the outer coastal plain setting indicate a greater degree of mineral dissolution and organic matter oxidation. Accordingly, outer coastal plain waters are more reducing than inner coastal plain waters. Low dissolved oxygen (O_2) and nitrate (NO_3^-) concentrations and high iron (Fe) concentrations indicate that ferric iron (Fe (III)) is an important electron acceptor in this setting, while dissolved O_2 is the most common terminal electron acceptor in the inner coastal plain setting.

The presence of a wide range of redox conditions in the shallow aquifer system examined here underscores the importance of providing a detailed geochemical characterization of ground water when assessing the intrinsic susceptibility of coastal plain settings. The greater prevalence of aerobic conditions in the inner coastal plain setting makes this region more susceptible to contamination by constituents that are more stable under these conditions and is consistent with the significantly ($p < 0.05$) higher concentrations of NO_3^- found in this setting. Herbicides and their transformation products were frequently detected (36% of wells sampled), however concentrations were typically low (<0.1 μg/L). Shallow water table depths often found in coastal plain settings may result in an increased risk of the detection of pesticides (e.g., alachlor) that degrade rapidly in the unsaturated zone.
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1. Introduction

Intense agricultural and urban development has placed a high demand on ground-water resources in coastal areas worldwide and has also placed these resources at greater risk to contamination (Kremer and Crossland, 2002). The risk of ground-water contamination is influenced by two factors: (1) the intrinsic properties of the hydrogeologic setting, primarily factors that influence the transport and stability of contaminants derived from the land surface and (2) contaminant loading, primarily from anthropogenic sources. In many instances, coastal areas have both the intrinsic properties and contaminant loading that result

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in a high risk of ground-water contamination. The depth to ground water is typically shallow in these areas, resulting in relatively short travel times (weeks to months) to the water table. Short travel times contribute to an increase in the intrinsic susceptibility of aquifers in coastal environments (United Nations Environmental Program, 2003). High contaminant loads from agricultural and urban development coupled with the intrinsic susceptibility of this setting often place these resources at risk to contamination. For example, in a national assessment of the vulnerability of aquifers to pesticide contamination, the Coastal Plain of the southeastern United States was considered to have the highest priority for further study (Kellogg et al., 1994). While anthropogenic sources of contamination are the more widespread cause of ground-water contamination in coastal areas, natural contaminants have caused significant risks to public health (e.g., arsenic (As) contamination in Bangladesh; Yokota et al., 2002).

A prerequisite to assessing the intrinsic susceptibility of a specific hydrogeologic setting (e.g., coastal plain environments) is a basic understanding of the environmental processes that affect the geochemistry of the aquifer systems of interest. Geochemical processes have been shown to have an influence on the prevalence of anthropogenic and natural contaminants in coastal environments worldwide (e.g., Kookana and Aylmore, 1994; Toda et al., 2002). While studies have been conducted on the chemical characteristics and evolution of ground water overlain by permeable deposits in the Coastal Plain of the eastern Untied States (e.g., Böhlke and Denver, 1995), few studies have examined the chemical evolution of water in the less well-drained, more organic-rich areas like those found in the Coastal Plain of the southeastern United States. Furthermore, this study includes an assessment of agrichemical occurrence in coastal plain environments with differing redox conditions.

The presence of electron donors (e.g., organic carbon (C), iron (Fe) sulfides) in soil and water is indicative of reducing conditions and appears to be a major factor affecting regional environmental differences in ground-water quality, particularly with respect to nitrate (NO_3^-) (e.g., Tesoriero et al., 2000) and volatile organic compounds (e.g., Tesoriero et al., 2001). A statistical analysis of ground-water-quality data indicated that bacterially mediated reduction of NO_3^- in the presence of organic matter is an important reaction in the Coastal Plain of the southeastern United States (Nolan, 1999). The presence of large and varied amounts of organic matter in the Coastal Plain of the Albemarle-Pamlico (ALBE) drainage basin makes this an ideal study area in which to examine the effects of organic matter on the evolution of ground-water chemistry in shallow aquifer systems.

The objectives of this paper are to: (1) characterize the chemistry of shallow ground water in coastal plain environments with different redox conditions, (2) establish the major differences in water chemistry between these two environments, and (3) predict the reactions responsible for the observed differences in water chemistry. Results from this investigation fill an important need in assessing the geochemical characteristics of shallow ground water in organic-rich coastal plain environments and linking these characteristics to its effect on contaminant occurrence. Findings from this investigation improve the knowledge of the geochemistry of shallow ground water in coastal plain environments and improve assessments of the risk of contamination of ground water in this critical setting.

2. Methods

The data presented in this report were collected in ground-water investigations conducted as part of the US Geological Survey's National Water-Quality Assessment (NAWQA) Program (Gilliom et al., 1995). Data were collected in two phases: an agricultural land-use study of corn and soybean fields and a regional shallow-aquifer study that did not target a particular land-use type. For the agricultural land-use study, 23 wells were randomly selected in counties with more than 20% agricultural land in corn and soybean. For the regional shallow-aquifer study, 27 wells were selected randomly throughout the ALBE Coastal Plain from databases maintained by the US Geological Survey (USGS), the Virginia Department of Environmental Quality, or the North Carolina Department of Environment and Natural Resources. While the regional shallow-aquifer study did not target a particular land use, the land use surrounding these wells was similar to that in the agricultural land-use study. (In the regional shallow-aquifer study, 62% and 21% of the wells were surrounded by crop and forest, respectively; in the agricultural land-use study, 62% and 23% of the wells were surrounded by crop and forest.)

A Mann–Whitney test was performed on the concentration values of major water-quality constituents linked to agricultural practices to determine if concentration values were significantly ($p < 0.05$) different between the agricultural land-use and the regional shallow-aquifer studies. No significant differences were identified between ranks of the concentration values of major cations and anions in samples from the two studies, indicating that differences in land-use effects on water quality were too small to be detected. As a result, data from the agricultural land-use and regional shallow-aquifer well networks were combined to form a larger data set for use in examining differences between inner and outer coastal plain ground-water chemistry.

All wells were sampled according to NAWQA protocols (Koterba et al., 1995; Lapham et al., 1995). Wells were sampled during the spring and summer of 1994 and analyzed for major ions, nutrients, pesticides, temperature, pH, dissolved oxygen (O_2), alkalinity, and specific conductance. Dissolved O_2 and pH were measured by using electrodes placed in a flow cell to minimize atmospheric interactions. Alkalinity was determined in the field by titration. Water samples for major ions and nutrients were filtered by using a 0.45 μm capsule filter. Sulfate was analyzed by ion chromatography. Magnesium, silica (SiO_2), Fe, and manganese (Mn) were analyzed by using inductively coupled plasma mass spectrometry. Nitrate plus nitrite (NO_2^-), NO_2^-, ammonium (NH_4^+) and bromide (Br^-) were analyzed by using colorimetric methods. Nitrate plus NO_2^- is hereafter referred to as NO_3^-, because concentrations of NO_2^- were negligible compared to NO_3^-. Detailed descriptions of the analytical methods for the above-mentioned major ions and nutrients are provided in Fishman and Friedman (1989). Dissolved organic C was analyzed by ultra-violet-promoted persulfate oxidation and infrared spectrometry (Brenton and Arnett, 1993). Samples were analyzed for 80 pesticides and transformation products by gas chromatography/mass spectrometry and by high-performance liquid chromatography (Werner et al., 1996; Zuagg et al., 1995). A complete list of the pesticide analytes is provided in Spruill et al. (1998). Concentration values are reported at a method-detection level that is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99% confidence that the concentration is greater than zero.

Saturation indices (SI) are calculated using ion activities as follows, using calcite as an example:

$$SI_{calcite} = \log \frac{\{Ca^{2+}\}\{CO_3^{2-}\}}{K_{sp,calcite}}, \qquad (1)$$

where $\{Ca^{2+}\}$ and $\{CO_3^{2-}\}$ are their activities in aqueous solution and $K_{sp,calcite}$ is the solubility product for calcite. Saturation indices greater than zero indicate supersaturation; less than zero indicate undersaturation. Speciation and saturation-index calculations were made using the PHREEQC program (Parkhurst, 1995). Given the low solubility of Fe (III) oxyhydroxides, siderite saturation index calculations were made assuming that Fe (II) is the dominant form of Fe.

Statistical tests were performed by using a Wilcoxon test or a two-way contingency table analysis. The Wilcoxon test is a non-parametric procedure (Helsel and Hirsch, 1992) that was used to determine whether major ion concentrations in shallow ground water from the inner and outer coastal plain differ. A two-way contingency table analysis employing the Fisher's exact test (Sokal and Rohlf, 1995) was used to test the null hypothesis that the frequency of pesticide detection was independent of the hydrogeologic setting (i.e., inner or outer coastal plain).

3. Study area

The ALBE drainage basin is a 72,500 km^2 area in central and eastern North Carolina and southern Virginia (Fig. 1). The Suffolk Scarp has been used to delineate the inner from the outer coastal plain setting (Harned et al., 1995). This scarp is the western border of a relatively flat or gently seaward-sloping terrace (Soller and Mills, 1991). Elevation and topographic relief generally increase inland from the scarp. Near the western boundary of the inner coastal plain setting, elevations may be 120 m above mean sea level with hills 60 m high. This contrasts with typical elevations in the outer coastal plain setting of 1.5–12 m above sea level.

Ground water is an important source of drinking water throughout much of the Coastal Plain of the Eastern United States. In North Carolina (Fig. 1), most coastal plain counties rely on ground water to meet more than 70% of their water-supply needs (Walters, 1997). Ground water also provides more than 50% of the annual stream flow in coastal plain streams in the ALBE drainage basin (McMahon and Lloyd, 1995), mostly from shallow aquifers. The shallow water table and intensive agricultural land use over much of the Coastal Plain in the ALBE drainage basin make drinking-water supplies and surface-water quality in this area potentially vulnerable to surface-derived contaminants (e.g., nutrients, pesticides).

Wells sampled in this study typically were screened in the uppermost aquifer, which in most instances corresponds to the surficial aquifer. Sediments of the surficial aquifer generally were deposited in marine transgressive–regressive cycles caused by sea-level fluctuations (Winner and Coble, 1996). In the inner coastal plain setting, the surficial aquifer generally corresponds to middle Pleistocene deposits (e.g., Windsor Formation), consisting of quartz, mica, feldspar and clay (Oaks et al., 1974). X-ray diffraction analyses of sediments from 5 core holes in the inner coastal plain setting indicate that quartz, potassium (K) feldspar, and plagioclase feldspar are the dominant minerals with lesser amounts of aragonite, calcite, dolomite, and mica. In the outer coastal plain setting, the surficial aquifer corresponds to late Pleistocene and/or Holocene deposits having a similar mineralogy as the inner coastal plain portion of the aquifer. Holocene deposits may have thick layers of peat (e.g., 2 m, Oaks et al., 1974).

The inner and outer coastal plain settings are quite different in terms of soils and land cover (e.g., wetlands). Approximately 45% of inner coastal plain soils are well drained to moderately well drained, while less
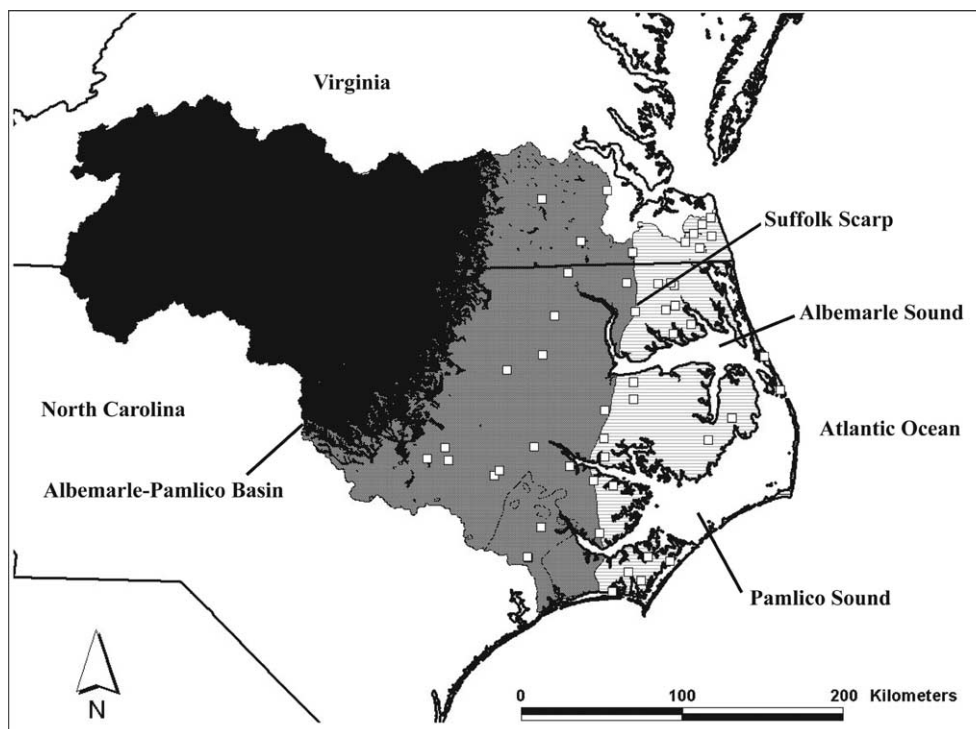
Fig. 1. Locations of the ALBE drainage basin and wells sampled in the inner (area shaded gray) and outer (lined area) Coastal Plain of North Carolina and Virginia.

than 17% of outer coastal plain soils are well drained or moderately well drained (Spruill et al., 1997). Another important difference between the two physiographic regions is the organic-matter content of the soils. Outer coastal plain soils typically have high concentrations of organic matter; upper soil horizons commonly have up to 15% organic matter and, in some cases, more than 50% organic matter (e.g., Tant, 1982). Inner coastal plain soils also have high amounts of organic matter (up to 5% organic matter is common in upper soil horizons) but generally in much lower amounts than in the outer coastal plain soils. Because organic C is an important electron donor in bacterial metabolic processes involving Fe, sulfur (S), and nitrogen (N) chemistry, its abundance is likely to have an important effect on biogeochemistry. With regard to land-use differences, the inner coastal plain setting is dominated by forested land (47%), agricultural land (35%), and wetlands (12%). The outer coastal plain setting is dominated by wetlands (37%), forested land (28%), and agricultural land (26%). Less than 5% of the inner and outer coastal plain settings consists of developed land. Crop types in the two environments are similar and are dominated by soybeans, corn, and wheat (McMahon and Lloyd, 1995).

4. Results and discussion

4.1. Concentrations and sources of major ions in the coastal plain

Given the similar mineralogy (quartz, feldspar, shell fragments) of the surficial aquifer in the inner and outer coastal plain settings, it is not surprising that no discernable difference in water type between these settings is observed (Fig. 2). The most prevalent water type is Ca^{2+}–HCO_3^- followed by water types Ca^{2+}–SO_4^{2-} and Na^+–Cl^-. While water types in both settings are similar, significant differences in ion chemistry between the two settings are observed. Ground water in the outer coastal plain setting has significantly higher concentrations of most major ions and dissolved organic C (Table 1). This likely is a result of the longer contact time between water and sediments and the higher concentrations of organic matter in the outer coastal plain setting. Ground water tends to have longer contact times with sediments in the outer coastal plain setting because recharge occurs through more poorly drained sediments. While age-dating information on these samples is not available, SiO_2 concentrations may provide a clue as to the relative residence times of ground water in these 2 settings. A
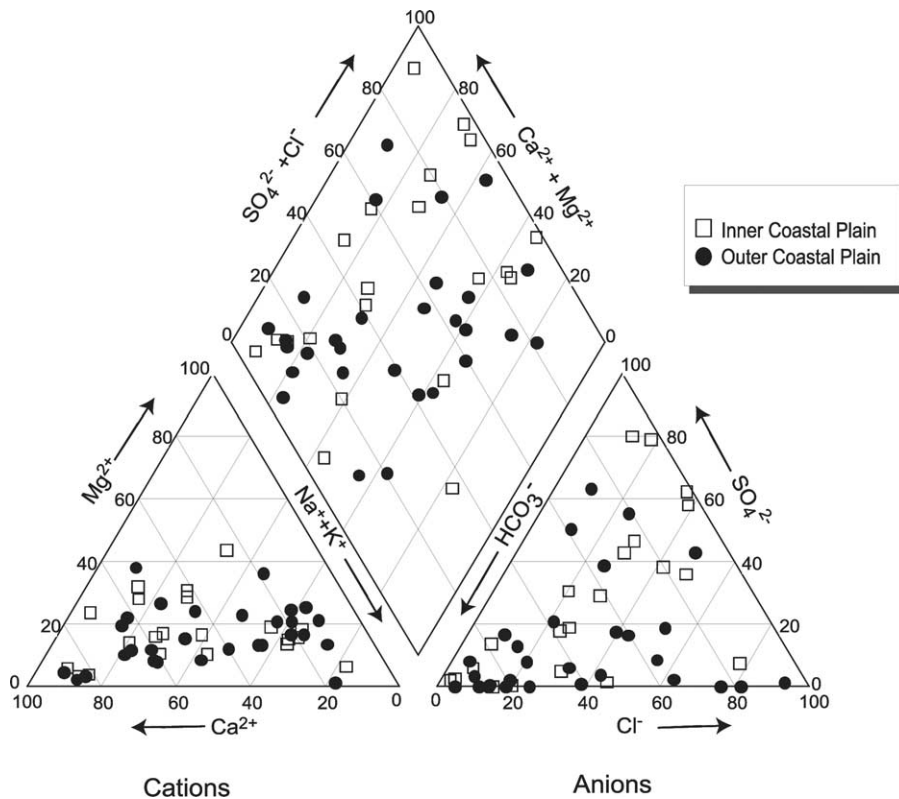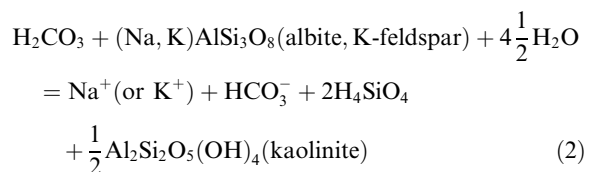
Fig. 2. Trilinear diagram of major ion chemistry of shallow ground-water samples collected from the inner and outer coastal plain settings of the ALBE basin.

strong positive correlation between SiO_2 concentrations and ground-water residence time was observed ($r^2 = 0.95$) in a related study of this aquifer (Tesoriero et al., 2004). As such, higher SiO_2 concentrations in the outer coastal plain setting indicate that residence times are longer in this setting than in the inner coastal plain setting.

Quartz and/or feldspar dissolution are possible sources of SiO_2 in the surficial aquifer system. While these minerals dissolve irreversibly at earth surface temperatures, calculating the saturation indices for these minerals will help to assess the likelihood that they are significant sources of SiO_2 in this system. While many factors control dissolution rates, minerals that are much more undersaturated (more negative saturation indices) tend to have higher dissolution rates than minerals near saturation (Hem, 1985). Silica concentrations in natural waters commonly are within a range defined by over-saturation with respect to quartz and undersaturation with respect to amorphous SiO_2, which indicates that some other mineral phase (e.g., clay minerals) controls SiO_2 concentrations (Hem, 1985). This is generally the case in samples collected for this study (Table 2). While both feldspars and quartz are possible sources of SiO_2,

feldspar dissolution is indicated in samples that are highly supersaturated with respect to quartz.

Possible mineral sources of alkalinity in coastal plain sediments include the dissolution of carbonates or feldspars. A 1:1 relation between alkalinity (as bicarbonate (HCO_3^-)) and sodium (Na) plus K results when alkalinity is the result of K- and Na-feldspar dissolution (Eq. (2)).

$$H_2CO_3 + (Na, K)AlSi_3O_8(albite, K\text{-}feldspar) + 4\frac{1}{2}H_2O$$
$$= Na^+(or\ K^+) + HCO_3^- + 2H_4SiO_4$$
$$+ \frac{1}{2}Al_2Si_2O_5(OH)_4(kaolinite) \qquad (2)$$

Similarly, a strong correlation between Na^+ and HCO_3^- in ground water has been presented as evidence that ion exchange of Ca^{2+} with Na^+ and K^+ adsorbed to clays is a major source of Na in ground water along deep flow paths (Back, 1966; Chapelle and Knobel, 1983; Speiran and Aucott, 1994). The relationship between Na^+ plus K^+ and alkalinity (as HCO_3^-) shows considerable scatter and is not well represented by the 1:1 relation that would be expected for the dissolution of Na- and K-feldspars

Table 1

Chemistry of shallow ground water in the inner and outer coastal plain settings of the ALBE basin. Concentrations are in mg/L

Parameter	Inner coastal plain			Outer coastal plain			p-value[b]
	10%[a]	50%	90%	10%	50%	90%	
pH	5.1	6.0	6.7	5.7	6.7	7.4	0.004
Dissolved O_2	0.2	2.0	5.6	0.1	0.5	4.0	0.04
Ca	2.9	10	43	5.8	38	130	0.005
Mg	1.0	2.1	5.8	2.0	6.2	24	0.004
K	0.5	2.1	7.4	0.6	1.5	10	0.74
Na	3.2	5.9	20	7.0	29	400	<0.001
Alkalinity (as HCO_3^-)	3	27	138	34	176	456	<0.001
Cl^-	4.5	12	18	8.2	27	710	<0.001
SO_4^{2-}	0.7	12	41	0.1	11	62	0.96
Fe	0.1	1.6	8.5	0.33	7.8	31	0.014
Mn	0.018	0.059	0.23	0.025	0.12	0.69	0.031
SiO_2	4.9	8.8	33	6.0	35	64	<0.001
NO_3^- (as N)	<0.05	0.38	9.2	<0.05	<0.05	1.1	<0.001
NH_4^+ (as N)	<0.01	0.04	0.17	0.04	0.23	2.7	<0.001
Dissolved inorganic C	7.9	28	47	26	55	101	<0.001
Dissolved organic C	<0.3	0.8	3.6	0.8	4.6	25	<0.001
P	<0.01	<0.01	0.43	<0.01	0.07	0.49	0.002
Well depth (m)	3.4	6.1	10.1	2.3	4.6	18.3	0.18
Depth to water level (m)	1.0	2.4	4.9	0.64	1.2	2.5	0.001

[a] 10th percentile. 50th and 90th percentiles are also reported.
[b] p-values refer to the χ^2 statistic of the Wilcoxon rank-sum test for significant differences between the inner and outer coastal plain.
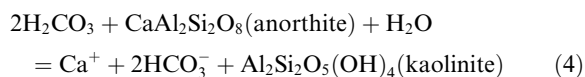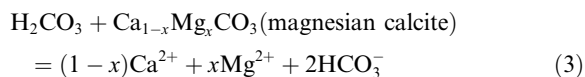
Table 2

Saturation indices for possible mineral phases in the inner and outer coastal plain settings of the ALBE basin. Saturation indices greater than zero indicate supersaturation; indices less than zero indicate undersaturation

Mineral Phase	Inner coastal plain			Outer coastal plain		
	10%[a]	50%	90%	10%	50%	90%
Quartz	−0.09	0.15	0.68	−0.04	0.68	0.99
SiO_2 (a)	−1.41	−1.17	−0.62	−1.32	−0.60	−0.32
K feldspar	−2.93	−1.41	−0.38	−3.49	−0.10	1.11
Albite	−5.36	−3.19	−2.13	−4.63	−1.10	−0.34
Anorthite	−8.69	−5.12	−3.57	−6.55	−3.70	−2.50
Calcite	−5.21	−3.06	−1.29	−3.40	−0.98	0.31
Aragonite	−5.36	−3.21	−1.44	−3.55	−1.13	0.16
Siderite	−3.71	−1.88	0.33	−1.42	0.10	1.07
Dolomite	−10.1	−6.53	−3.19	−6.82	−2.57	−0.06

[a] 10th percentile. 50th and 90th percentiles are also reported.

or from ion exchange with clays ($r^2 = 0.23$). Removing three high-concentration outliers (Na^+ in excess of 10 mM) does not improve this relation ($r^2 = 0.22$, Fig. 3).

Carbonates and Ca-feldspars also may be sources of alkalinity in this system. A 2:1 relation (slope = 2, intercept = 0) between HCO_3^- alkalinity and Ca^{2+} (plus Mg^{2+} for magnesian calcite) would be expected from the dissolution of Ca–Mg carbonates (Eq. (3)) or the dissolution of Ca-feldspar (Eq. (4)):

$$H_2CO_3 + Ca_{1-x}Mg_xCO_3 \text{(magnesian calcite)}$$
$$= (1-x)Ca^{2+} + xMg^{2+} + 2HCO_3^- \qquad (3)$$

$$2H_2CO_3 + CaAl_2Si_2O_8 \text{(anorthite)} + H_2O$$
$$= Ca^+ + 2HCO_3^- + Al_2Si_2O_5(OH)_4 \text{(kaolinite)} \qquad (4)$$

The relationship between alkalinity and Ca^{2+} plus Mg^{2+} closely approximates that expected for the dissolution of
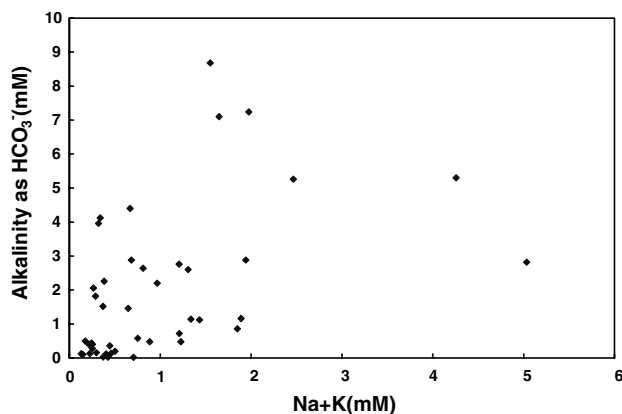
Fig. 3. The relation of alkalinity to the summation of Na and K. The 1:1 relation that would result if the dissolution of K- and Na-feldspars were responsible for alkalinity in ground water was not observed.

magnesian calcite (Fig. 4, slope $= 2.0 \pm 0.3$, intercept $= 0.0 \pm 0.4$, at 95% confidence intervals). The relationship between alkalinity and Ca^{2+} also is good ($r^2 = 0.79$). While the slope and intercept are higher than expected (slope $= 2.3 \pm 0.4$, intercept $= 0.21 \pm 0.4$) by the dissolution of feldspar (Eq. (4), slope $= 2$), it is within the range of uncertainty so feldspar dissolution cannot be discounted as an alkalinity source. While feldspars are more prevalent in the surficial aquifer, carbonates dissolve more readily and are common minor mineral phases, so either carbonates or Ca-feldspars are plausible sources of alkalinity in this system.

4.2. Redox reactions

Shallow unconfined aquifers tend to be oxygenated because the rate of recharge with oxic water exceeds the rate of microbial respiration in the aquifer. However, in spite of the shallow depth to water in both the inner and outer coastal plain settings, most ground-water samples contain low concentrations of dissolved O_2 (Table 1). The inner and outer coastal plain settings are favorable for anaerobic conditions as a result of several factors: (1) a gentle topography that results in largely horizontal flow paths, (2) high organic C content, particularly in the outer coastal plain soils, favors high rates of microbial respiration, and (3) low-permeability soils in many areas limit the rate of percolation through the soil zone, allowing for greater microbial respiration.

Given the high organic content of soils and waters in the coastal plain, it is expected that redox reactions involving the oxidation of organic matter are likely to have an important effect on the evolution of water chemistry. The oxidation of organic matter (Eq. (5)–(7)) and the dissolution of carbonates produce dissolved inorganic carbon (DIC). The amount of DIC derived from
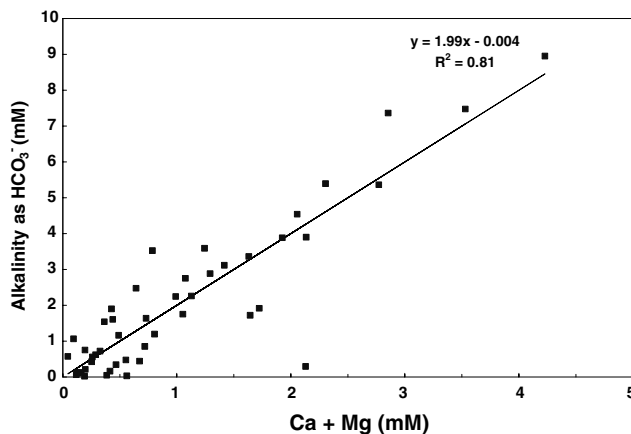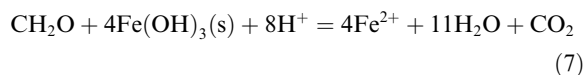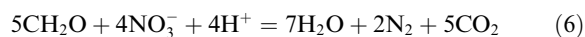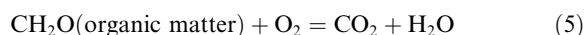

Fig. 4. The relation between alkalinity and the summation of Ca and Mg. Best fit line is also shown and closely approximates the 2:1 relation that results if the dissolution of magnesian calcite is responsible for alkalinity in ground water.

inorganic sources (carbonate dissolution) was estimated by assuming that all of the Ca and Mg in the samples was derived from carbonate dissolution and that none was removed from solution by precipitation. DIC derived from inorganic sources was estimated to be a small portion of the total DIC (15% and 26% in the inner and outer coastal plain settings, respectively), indicating that a large fraction of the DIC in this system is derived from the oxidation of organic C (in the saturated zone or from root-zone sources). Root- and soil-zone respiration often lead to significant supersaturation with respect to CO_2 (Holmes, 2000).

Organic matter oxidation often is coupled with the reduction of inorganic compounds. Thermodynamically, the sequence of reactions for the oxidation of organic matter should occur first by aerobic respiration (Eq. (5)). Once dissolved O_2 is consumed, organic matter oxidation typically is coupled with denitrification (Eq. (6)) followed by dissolution of Mn (IV) compounds (e.g., MnO_2) and Fe (III) compounds (e.g., Fe $(OH)_3$, Eq. (7)). Following Mn (IV) and Fe (III) reduction, when conditions become sufficiently reducing, SO_4^{2-} reduction and methanogenesis occur (Stumm and Morgan, 1996).

$$CH_2O(\text{organic matter}) + O_2 = CO_2 + H_2O \quad (5)$$

$$5CH_2O + 4NO_3^- + 4H^+ = 7H_2O + 2N_2 + 5CO_2 \quad (6)$$

$$CH_2O + 4Fe(OH)_3(s) + 8H^+ = 4Fe^{2+} + 11H_2O + CO_2 \quad (7)$$

While the concentrations of dissolved organic C are high in both settings, significantly higher levels can be found in the outer coastal plain setting. Not surprisingly, when the redox chemistry of ground water in the inner and outer coastal plain setting is compared, a consistent pattern emerges: ground water in the outer coastal plain setting is more chemically reducing than inner coastal plain ground water. While concentrations of oxidized forms of O (dissolved O_2) and N (NO_3^-) are greater in the inner coastal plain setting, reduced forms of N (i.e., NH_4^+) are greater in the outer coastal plain setting (Table 1). Furthermore, the higher levels of Fe and Mn in the outer coastal plain setting also indicate Fe- and Mn-reducing conditions, as the oxidized forms of these metals are only sparingly soluble.

Determining the dominant terminal electron-accepting process can provide an indication of the redox conditions of ground water and provide information on the stability of redox-active constituents (Chapelle et al., 1995). The dominant terminal electron-accepting process is commonly classified by using reactant consumption and final product accumulation. To a first approximation, water samples can be classified as aerobic (O_2-reducing) if concentrations of dissolved O_2

exceed 0.5 mg/L or NO_3^--reducing if concentrations of dissolved O_2 are less than 0.5 mg/L and NO_3^- concentrations exceed 0.5 mg/L. More reduced waters (including Fe and possibly SO_4^{2-}-reducing) have both dissolved O_2 and NO_3^- concentrations less than 0.5 mg/L. Using this methodology, most samples (16 of 21) were aerobic in the inner coastal plain setting; the remaining samples exhibited Fe-reducing conditions. In the outer coastal plain setting, nearly half (14 of 29) of the samples were aerobic, with one NO_3^--reducing sample, and the remainder were Fe-reducing. However, this is likely an underestimate of the prevalence of reducing conditions in this aquifer. Many of the aerobic ($O_2 > 0.5$ mg/L) samples, particularly in the outer coastal plain setting, had high levels of Fe and NH_4^+ and low levels of dissolved O_2. NH_4^+ may be generated by the mineralization of organic N but is readily oxidized to NO_3^- in the presence of O_2 (Eq. (8)), so its dominance as a N specie indicates anaerobic conditions. Similarly, because of the low solubility of Fe (III) oxyhydroxides, high levels of Fe are indicative of Fe-reducing conditions.

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \quad (8)$$
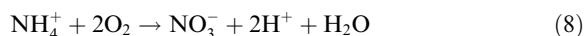
It is likely, therefore, that aerobic samples having high concentrations of Fe and NH_4^+ were collected across multiple redox zones or that small amounts of O_2 were introduced during sampling. (Exchange with the atmosphere during sampling was minimized by using flow cells, however only a small amount of O_2 would need to be introduced to affect its classification.) In any event, the prevalence of NH_4^+ and Fe in the outer coastal plain setting suggests that most samples in this part of the surficial aquifer are dominated by anaerobic conditions. In this system, the dominant form of N provides a useful indicator of the redox state of the system. NO_3^- is the dominant form of N in most inner coastal plain samples, whereas NH_4^+ is the dominant form in the outer coastal plain setting (Fig. 5). Many of the outer coastal plain samples also have a large organic N component (Fig. 5). This is consistent with mineralization of organic matter as the source of NH_4^+ and with high levels of dissolved organic C in these samples. It is hypothesized that dissolved O_2 is quickly consumed in most areas of the outer coastal plain setting by reaction with organic C. When organic matter is mineralized to form NH_4^+, there is insufficient O_2 to nitrify it to NO_3^-. Similarly, Fe (II) is not oxidized to form insoluble Fe (III) oxyhydroxides, resulting in high concentrations of dissolved Fe. Presumably, dissolution of Fe-bearing minerals continues until saturation with a Fe (II) phase is reached. Many outer coastal plain samples were at or near saturation with respect to siderite (Table 2). While siderite may control Fe (II) concentrations, a more detailed assessment of the min-
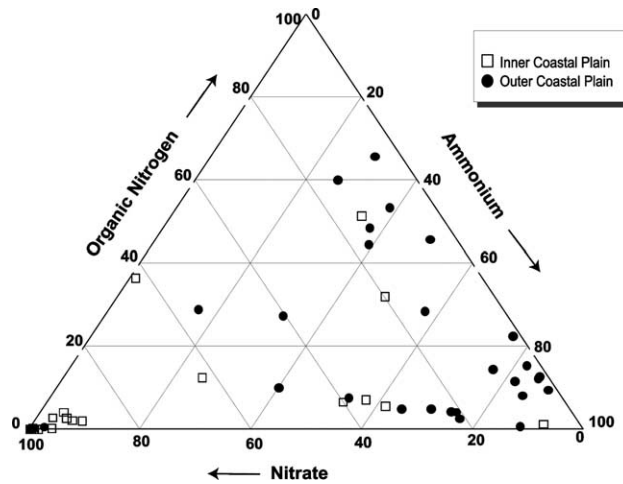
Fig. 5. Ternary diagram of the forms of N in shallow ground-water samples from the inner and outer coastal plain settings of the ALBE basin.

eralogy of these deposits is needed to more definitively assess mineralogical controls on Fe concentrations.

4.3. Pesticide occurrence in coastal plain settings

One or more pesticides were detected in water from more than a third of the wells sampled, but concentrations of pesticides were always less than 1 µg/L and typically less than 0.1 µg/L (Table 3, Fig. 6). Herbicides and herbicide-transformation products were the most frequently detected class of compounds. Atrazine, deethylatrazine, and metolachlor were detected significantly

($p < 0.1$) more often in the inner coastal plain setting. Conversely, alachlor and its transformation product 2,6-diethylaniline were detected only in the outer coastal plain setting. Environmental factors that influence pesticide fate include redox conditions and depth to the water table. The degradation of atrazine, alachlor, and many other herbicides occurs much more quickly under oxic conditions (e.g., Barbash and Resek, 1996). Alachlor degrades more rapidly than atrazine, with most of the degradation of atrazine and alachlor occurring in the top meter of the soil zone (Adams and Thurman, 1991; Clay et al., 1995; Potter and Carpenter, 1995). It has

Table 3

Range in concentrations and frequency of detection of pesticides above the method detection level for all samples. Concentrations are in µg/L

Compounds	Concentration range			Frequency of detection, in percent (%)			p-value[d]
	50%[a]	90%	Maximum	CP [b]	OCP [c]	All samples	
Atrazine	< 0.001	0.010	0.18	29	7	16	0.06
Deethylatrazine	< 0.002	0.006	0.14	29	3	14	0.03
Metolachlor	< 0.002	0.003	0.77	24	0	10	< 0.01
2,6-Diethylaniline	< 0.003	0.006	0.049	0	17	10	0.07
Alachlor	< 0.002	< 0.002	0.010	0	10	6	0.25
Diazinon	< 0.002	< 0.002	0.031	10	0	4	0.17
Dieldrin	< 0.001	< 0.001	0.026	5	0	2	0.42
Tebuthiuron	< 0.01	< 0.01	0.071	5	0	2	0.42
Carbofuran	< 0.003	< 0.003	0.034	0	3	2	0.99
Chlorpyrifos	< 0.004	< 0.004	0.006	0	4	2	0.58
One or more pesticides detected	NA [e]	NA	NA	48	27	36	0.23

[a] 10th percentile. 50th and 90th percentiles are also reported.
[b] ICP: inner coastal plain.
[c] OCP: outer coastal plain.
[d] p-values are for the Fisher 's exact test for a 2-way contingency table analysis of detection frequency between the ICP and OCP.
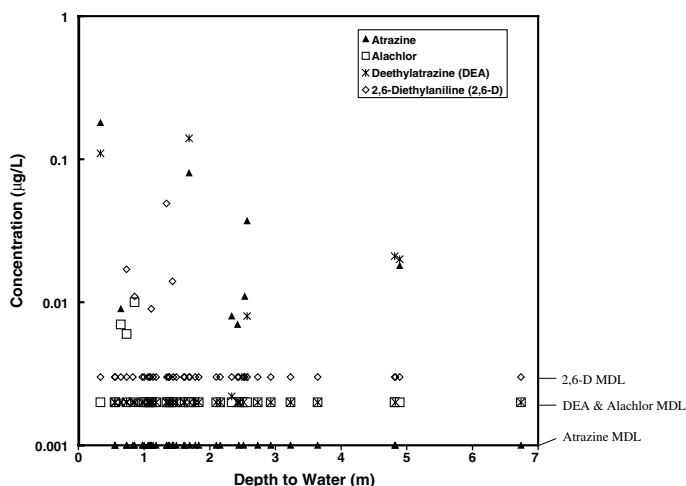[e] NA: not applicable.

Fig. 6. Relation of concentrations of selected pesticides to depth to the top of the water table. Values plotted at the method detection level (MDL) for a compound were not detected.

been suggested that degradation occurs primarily in the shallow soil zone rather than in deeper soil horizons due to the greater microbial populations, greater organic C content, and higher temperatures found in this zone (e.g., Adams and Thurman, 1991). The thicker unsaturated zone found in the inner coastal plain setting (Table 1) is a conducive environment for the degradation of alachlor and its transformation product, 2,6-diethylaniline and may be the cause of the nondetectable concentrations of this compound. Conversely, alachlor and 2,6-diethylaniline are less likely to degrade under the shallow water-table conditions in the outer coastal plain setting. In fact, all detections of alachlor and 2,6-diethylaniline were found in outer coastal plain samples with an unsaturated zone thickness of less than 1.5 m (Fig. 6). Atrazine and deethylatrazine were detected under both shallow and deep water-table conditions, perhaps due to the less reactive nature of these compounds (e.g., Clay et al., 1995).

5. Summary and conclusions

An evaluation of water-chemistry differences between two distinct coastal plain settings has determined that there are significant differences in the degree of mineral dissolution and in redox chemistry. In both inner and outer coastal plain environments, the oxidation of organic matter is likely an important source of inorganic C and electrons in the reduction of oxidized species. Carbon dioxide produced from the oxidation of organic matter aids in the dissolution of feldspars and carbonates, which are the sources of much of the SiO_2, Ca, Mg, and alkalinity found in the waters of these two environments. The degree of oxidation of organic matter and of mineral dissolution is greater in the outer coastal

plain setting; concentrations of most major ions, dissolved inorganic C, and dissolved organic C are significantly higher in this setting.

The stability of many contaminants in ground water is dependent on the redox conditions of the aquifer. As such, the susceptibility of an aquifer will be dependent, in part, on its redox condition. Aerobic conditions are more commonly found in the inner coastal plain setting, making this area more susceptible to contamination by NO_3^-. Conversely, NO_3^- concentrations are very low in the outer coastal plain, where redox conditions are more reducing. Herbicides were detected frequently in both settings but concentrations were generally low. The outer coastal plain setting has very shallow water table depths that may put these areas at an increased risk of contamination to pesticides that degrade rapidly in the unsaturated zone.

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