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Water Chemistry of Two Hydric Soils of Southern Louisiana

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ABSTRACT

Chemical composition of the shallow groundwater of two hydric soils in southern Louisiana was monitored for one year. Two sites were instrumented with nested wells (0.25, 0.50, 0.68 or 0.78, 1.00 and 2.00 m depth). One of the sites is located in Calcasieu Parish on a Brimstone soil (fine-silty, mixed, thermic Typic Natraqualfs) and the other one at Livingston Parish on a Verdun soil (fine-silty, mixed, thermic Glossic Natraqualfs). Electrical conductivity (EC), pH and cation and anion composition were determined for every water sample. Variations in the composition, EC and pH were attributed to differences in soil and parent materials, soil physical properties and groundwater flow. Brimstone soil is a typical hydric soil with a perched water table. The water is supplied by rainfall and lateral movement from the adjacent higher landscape with addition of NO_3 and leaching of Na and Cl. Na and Cl accumulate at short distances in depressional areas. Verdun soil has a morphology that would indicate that leaching of Na is a predominant process. However, presently the soil is undergoing secondary salinization produced by discharge from a permanent groundwater table. The discharging groundwater is brackish, of probable marine origin as indicated by the strong relationships Cl - Na (r^2 = 0.75, P > 0.01) and Cl - Na + Mg (r^2 = 0.89, P > 0.01).

Key Words: Wetland, aquic, groundwater, Natraqualfs, sodic

INTRODUCTION

Hydric soils are defined as soils that are saturated, flooded or ponded long enough during the growing season to develop anaerobic conditions in the upper part according to the National Technical Committee for Hydric Soil (NTCHS 1992). Therefore, seasonally wet soils that meet this definition are considered functional wetland soils. Two representative hydric soils in the Coastal Plain of Louisiana are the Deerford-Verdun Series (fine-silty, mixed, thermic Glossic Natraqualfs) in Livingston Parish (McDaniel 1991) and the Brimstone Series (fine-silty, mixed, thermic Typic Natraqualfs) in Calcasieu Parish (Roy and Midkiff 1988), which have also been correlated and mapped across other Parishes in the Coastal Plain (Amacher et al. 1988).

An important characteristic of these soils (Natraqualfs) is that they have natric horizons. A natric horizon is defined by its exchangeable sodium percentage or ESP which requires an increase in clay as an agrillic horizon and an ESP of ≥15% or sodium absorption ratio (SAR) of ≥13 in some subhorizon within a depth of 40 cm of the upper boundary of the agrillic horizon (Soil Survey Staff 1992). High ESP in soils affects

adversely several soil properties such as fertility, soil water availability for plants, permeability and workability.

Walthall et al. (1992) studied the occurrence of these soils in the Macon Ridge in Louisiana. They found that soils in swale positions that had a thinner loess mantle than soils in ridge positions also had natric horizons and hydric characteristics. The source of Na in soils with natric horizons in the Macon Ridge in Louisiana was the groundwater. The upward movement of NaCl was due to the discharge from a regional Tertiary aquifer containing saline water to the locally connected alluvium aquifer that underlines the loess mantle. This regional hydrologic system occupies much of the area beneath the Mississippi River floodplain (Payne, 1968). Interpretation of results obtained by Walthall et al. (1992) according to the recharge-discharge hydrologic systems for soil aquic conditions described by Richardson et al. (1992) would indicate the occurrence of a discharge wetland system with addition of NaCl to the soils by the groundwater.

Other Aqualfs in Louisiana that have appreciable ESP but do not fulfill the requirements of a natric horizon were investigated by McQuaid et al. (1987). They proposed a modification in the classification of those soils that had a deeper occurrence of exchangeable Na in their profiles by defining a solodic subgroup. The criteria proposed to recognize solodic subgroups are: i) an ESP ≥15 (SAR ≥13) in some subhorizon within 1.25 m below the soil surface or ii) an ESP ≥6 (SAR ≥5) and <15 (SAR < 13) within the upper 40 cm of the argillic horizon.

The morphology and physico-chemical properties of Natraqualfs and "solodic" Aqualfs in the Coastal Plain are the result of the continued leaching of the upper part of the former sodic soils (Solonetz) probably formed in the late Pleistocene (approximately 18,000 y BP) in a climate drier than at present (Suter et al. 1987). During the Holocene (about 7,000 y BP) in a humid climate documented by studies in Louisiana on changes of sea level by Coleman and Smith (1964), salt-affected soils were probably leached out (solodization) and evolved into the actual Natraqualfs and associated soils.

According to Fanning and Fanning (1989) sodic soils under continuous leaching become more acid with the development of A and E horizons, with a natric horizon moving deeper into the soil by eluviation-illuviation processes. According to Szabolcs (1989) this is the typical development of a solodized-solonetz when the groundwater is rarely or not at all linked with the upper soil layer; however, secondary salinization may occur by upward movement of saline groundwater.

The potential source of salt spray from the Gulf Coast is not taken into account in this study as an actual source of salinization. The reasons for this are: i) our study sites are located 40 and 60 miles from the coast line in Calcasieu and Livingston parishes respectively. ii) The annual precipitation-weighted means Cl ion concentrations for 1991 are 0.48 and 0.50 mg L^{-1}, while Na ion concentrations are 0.27 and 0.19 mg L^{-1} for New Iberia and Franklinton respectively, the two closest localities to our sites (National Atmospheric Deposition Program 1992). These values are similar to those reported for the Macon Ridge by Walthall et al. (1992).

The objective of this study is to investigate the relationship between the variation of the groundwater composition and the occurrence of seasonally wet saline and sodic soils as a consequence of their local hydrology and parent material properties. The hypothesis of Walthall et al. (1992) was used that the source of sodium is the groundwater and that the geochemistry of the wetland soils is a function of water movement through them according to the hydrological models of Richardson et al. (1992).

MATERIALS AND METHODS

Soils

The investigation was based on two soil series: Verdun silt loam (fine-silty, mixed, thermic Glossic Natraqualfs) and Brimstone silt loam (fine-silty, mixed, thermic Typic Natraqualfs) described by Hudnall et al. (1990). Both soils are part of an extensive network of monitoring sites constructed to investigate aquic conditions in the Coastal Plain of Louisiana and the list of hydric soils of the United States (National Technical Committee on Hydric Soils 1992). The location map and associated soil mapping units are presented in Figure 1.

Verdun and Brimstone soils were formed on deposits of the Prairie Formation or Terrace. The geomorphology of this formation is an extensive regional coast-trending terrace that extends across Louisiana (Snead and McCulloh 1984).

Verdun soils were formed in silty deposits of Pleistocene age. These soils are level, somewhat poorly drained, occupying broad flats on the terrace uplands in intermediate positions of the landscape and associated to the Deerford series in a complex mapping unit.

Brimstone soils are poorly drained, slowly permeable soils that formed in loamy sediments of late Pleistocene age. They are on nearly level to slightly depressional, broad flats on stream or marine terraces, with intermediate positions in the landscape. The profile used in this study is morphologically similar to Brimstone Series; however, it does not have a natric horizon. This soil was classified as fine-silty, siliceous, hyperthermic Typic Epiaqualfs (Soil Survey Staff 1992).

Selected analytical data are presented in Table 1 for Verdun and Brimstone profiles sampled next to the groundwater monitoring site.

Groundwater Sampling

Groundwater samples were taken from nested wells at 0.25, 0.50, 0.68 or 0.78, 1.00 and 2.00 m depth at least once a month from March 1991 to March 1992. The nested wells were installed in triplicate at each depth in a 10 x 10 m square plot (Hudnall and Wilding 1990).

Water Analysis

The pH of the water was measured in the field with a combination electrode. Electrical conductivity was measured in the laboratory at 25°C. Concentrations of Na, Mg, Ca and K were measured by inductively coupled plasma (ICP). Total alkalinity was measured titrimetrically (Chemetrics, VA, alkalinity field kit). Concentrations of Cl were measured with a Cl selective electrode. The SO_4 concentrations were estimated by multiplying S measurements by ICP by an empiric conversion factor, and NO_3 was measured with an autoanalyzer (Wescan Instruments Inc., Santa Barbara, CA) for the Verdun soil water samples. Concentrations of Cl, SO_4 and NO_3 were determined by ion chromatography (IC) for the Brimstone soil groundwater samples.

The overall reliability of the analyses was tested by charge balance calculations, following procedures in Bresler et al. (1982).

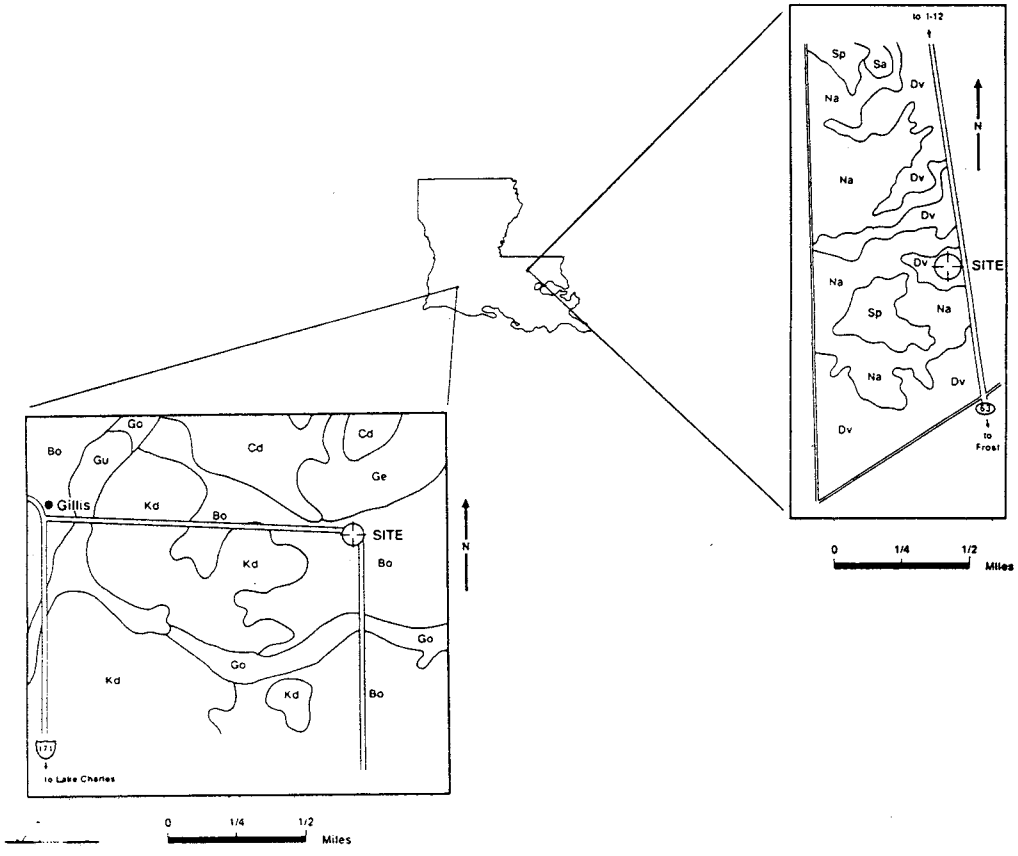

Figure 1. Site location for the Verdun and Brimstone soils and soil maps of the area adjacent to the sites.
Soil map **A**: Bo (Brimstone soils), Cd (Caddo - Messer soils), Ge (Glenmora soils), Go (Guyton occasionally flooded soils), Gu (Guyton frequently flooded soils), Kd (Kinder -Messer soils).
Soil map **B**: Dv (Deerford - Verdun soils), Na (Natalbany soils), Sa (Satsuma soils), Sp (Springfield soils).

Table 1. Selected analytical data for Verdun and Brimstone soils (Hudnall et al. 1990).

Soil/ Horizon	Depth cm	pH	Texture	Org. C %	Tot. N %	CEC cmol./kg	Base Sat. %	Bulk Dens. kg/m³
VERDUN								
Ap	0-13	4.2	SiL	1.73	0.092	6.6	30	1.36
Eg1	13-24	4.6	SiL	0.48	0.019	4.1	61	1.58
Eg2	24-45	4.4	SiL	0.41	0.015	6.8	60	1.54
Eg/Btg	45-71	4.7	SiL	0.21	0.015	10.6	95	1.61
Btng/Eg	71-103	6.5	SiCL	0.07	0.033	16.3	100	1.78
Btkng1	103-128	7.6	SiCL	0.04	-	15.3	100	1.85
Btkng2	128-170	7.5	SiCL	0.03	-	14.3	98	1.87
Btng1	170-215	7.5	SiC	0.02	-	17.1	100	1.84
Btng2	215-280	7.3	C	-	-	19.9	100	-
BCg	280-380	7.9	SL	0.01	-	15.2	98	-
2C	380-400	7.3	LS	0.02	-	9.6	100	-
BRIMSTONE								
Ap	0-15	4.6	SiL	0.80	0.071	5.0	54	1.54
Eg	15-33	6.6	SiL	0.20	0.017	6.2	91	1.76
E/Btng	33-60	6.6	SiL	0.16	0.024	9.3	93	1.73
Btng/E	60-81	6.4	SiCL	0.09	0.011	11.3	97	1.74
Btng1	81-147	6.9	SiCL	0.5	-	14.8	98	1.73
Btng2	147-190	6.6	SiCL	0.02	-	19.1	95	1.78
BCg	190-264	6.8	SiCL	0.02	-	22.5	95	1.96
Cg1	264-314	6.7	SiL	0.02	-	13.7	96	
Cg2	314-325	6.8	SiCL	0.02	-	27.5	97	
Cg3	325-360	6.9	SL	0.016	-	10.8	99	

Soil Analysis

Particle sized analysis was determined by the pipette method. SAR was calculated from analysis of saturated paste solution extract (Ca, Mg and Na measured by ICP) as $SAR = Na/[(Ca+Mg/2)]^{0.5}$. ESP was calculated by subtracting water soluble Na from extractable Na (extracted by displacement with 1N ammonium acetate) divided by the soil CEC (pH 7).

RESULTS AND DISCUSSION

Groundwater Chemistry

The ionic composition, pH and EC of the groundwater for the Brimstone and Verdun sites are given in Tables 2 and 3 respectively. In the same tables an indication of the variability of the water composition is illustrated by the coefficient of variation (CV) for each component. With the exception of pH the rest of the components have large coefficients of variations (CV > 20%). Some components such as K and NO_3 have very skewed distributions with values close to or below detection limits, which explains their CV >100%.

According to Pettijohn (1982), large CV for water quality can be expected in shallow and surficial aquifers due to chemical changes brought about by natural events occurring on the soil surface (e.g. wetting-drying cycles, development of cracks, etc.) or from human induced pollution (e.g. use of fertilizers).

Table 2. Mean ionic composition in mg L^{-1}, calculated total dissolved solids (TDS) in mg L^{-1}, electrical conductivity (EC) in dS m^{-1}, pH and coefficient of variation (CV) in % between parenthesis of the groundwater at the Verdun soil site

Ion	Depth (m)				
	0.25	0.50	0.68	1.00	2.00
Ca^{2+}	91	247	217	225	83
CV	(45)	(32)	(40)	(32)	(59)
Mg^{2+}	31	90	79	101	60
CV	(44)	(37)	(43)	(35)	(60)
Na^{+}	155	544	450	516	440
CV	(65)	(21)	(47)	(47)	(49)
K^{+}	1.9	7.0	3.5	9.4	3.1
CV	(240)	(264)	(283)	(143)	(274)
Cl^{-}	461	1344	1105	1332	848
CV	(73)	(28)	(49)	(31)	(42)
SO_4^{2-}	58	219	219	251	132
CV	(35)	(45)	(25)	(37)	(39)
NO_3^{-}*	0.1	0.1	0.1	0.1	0.1
CV	(96)	(129)	(98)	(182)	(148)
Alk**	63	65	54	75	49
CV	(34)	(45)	(31)	(32)	(39)
TDS	861	2516	2128	2510	1615
EC	2.3	3.9	4.0	4.5	2.9
CV	(34)	(32)	(44)	(21)	(25)
pH	7.1	6.9	6.9	6.8	6.9
CV	(3)	(3)	(3)	(4)	(4)

* NO_3 expressed as NO_3-N ** Alk is total alkalinity

The mean concentrations of every major constituent are different between the two groundwaters. When comparing values of Tables 2 and 3, the mean concentration of Cl, SO_4, Ca, Mg and Na are significantly different ($P > 0.01$) at any depth with the exception of pH and at 0.25 m depth where EC, NO_3 and Cl are the only ones significantly different.

The difference between the ionic concentrations of both soils is also expressed through their different EC. Since the EC has positive correlation with total dissolved solids (TDS) it is used as a simplified index to the total concentration of dissolved salts through the approximate relationship: TDS (mg L^{-1} ≈640 *EC (dSm^{-1}) according to the U.S. Salinity Laboratory Staff (1954). Groundwater from Verdun soil has a higher content of dissolved salts at any depth than Brimstone soil according to their EC. The estimation of TDS indicates that Verdun soil water is brackish (1,000 to 10,000 mg L^{-1}) while Brimstone soil

water is fresh to slightly brackish (< 1,000 mg L^{-1}) according to the classification of water based on TDS given by Bresler et al. (1982). This TDS estimation is consistent with TDS values calculated by adding up the ionic concentrations reported in Tables 2 and 3.

Table 3. Mean ionic composition in mg L^{-1}, calculated total dissolved solids (TDS) in mg L^{-1}, electrical conductivity (EC) in dS m^{-1}, pH and coefficient of variation (CV) in % (in parenthesis) of the groundwater at the Brimstone soil site

Ion	Depth (m)				
	0.25	0.50	0.78	1.00	2.00
Ca^{2+}	76	66	30	59	48
CV	(54)	(53)	(54)	(46)	(52)
Mg^{2+}	28	28	14	27	28
CV	(62)	(68)	(55)	(46)	(48)
Na^{+}	116	107	77	140	153
CV	(68)	(68)	(50)	(60)	(45)
K^{+}	3.5	1.2	0.4	1.2	5.9
CV	(136)	(134)	(142)	(116)	(339)
Cl^{+}	341	304	168	341	318
CV	(68)	(61)	(42)	(59)	(61)
SO_4^{2-}	8.7	7.7	6.7	10.1	8.
CV	(60)	(95)	(53)	(59)	(80)
NO_3-*	4.8	3.9	4.5	4.5	4.4
CV	(18)	(34)	(7)	(12)	(4)
Alk**	63	65	54	75	49
CV	(43)	(53)	(25)	(19)	(44)
TDS	657	596	370	673	360
EC	1.3	1.2	0.76	1.1	1.1
CV	(75)	(60)	(43)	(50)	(45)
pH	7.1	7.1	7.0	7.0	7.0
CV	(7)	(4)	(5)	(4)	(5)

* NO_3 expressed as NO_3-N ** Alk is total alkalinity

The dominant cation is Na and the dominant ion is Cl in both groundwaters (Tables 2 and 3). Na dominance is reflected by the calculated Na/Ca + Mg and Na/Ca molar charge ratios increase with depth (Figure 2). The Na/Ca + Mg and Na/Ca in the first 0.25 m of the Verdun site indicates the diluting effect of fresh water supplied by rainfall. The increase of these ratios with depth indicates an enrichment in the groundwater at 0.50,0.68 and 1.00 m depth due to leaching (solidization processes). The maximum Na/Ca + Mg and Na/Ca ratios are reached at 2.00 m depth. A relatively low Na/Ca ratio indicates that the Mg proportion increased at this depth where a permanent brackish groundwater occurs. The Brimstone site Na/Ca + Mg and Na/Ca are fairly constant at 0.25 and 0.50 m depth due to leaching processes. These ratios increase between 0.50 and 2.00 due to the presence of soil horizons rich in Na.

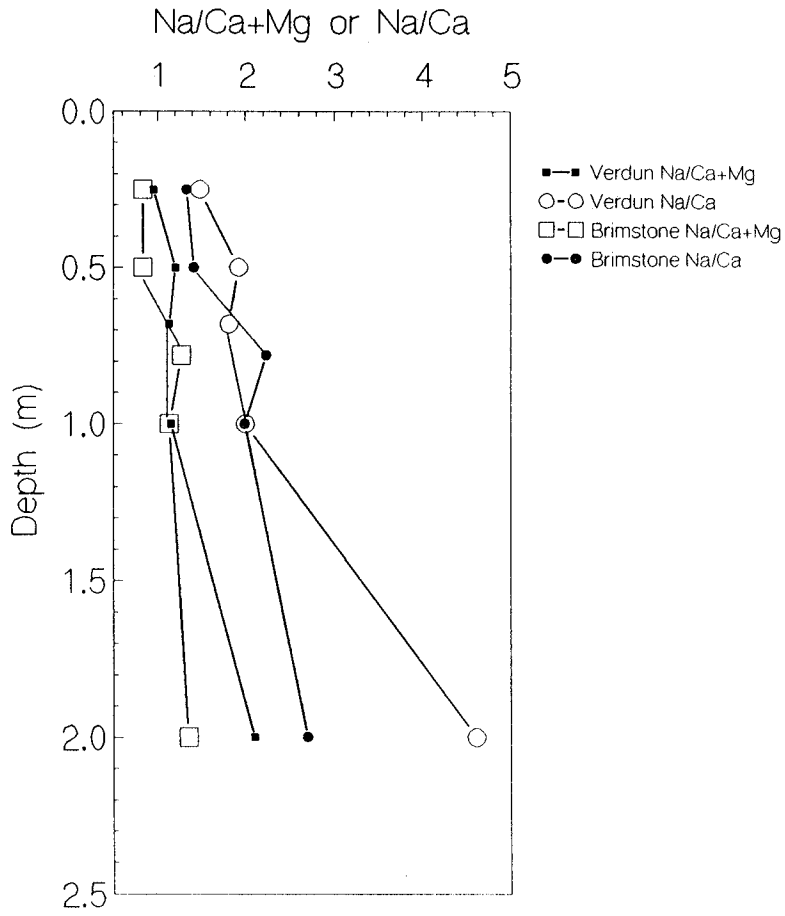

Figure 2. Na/Ca+Mg and Na/Ca molar charge ratios for Verdun and Brimstone groundwater.

Large differences exist between concentrations of NO_3 and SO_4 of the two groundwaters. A higher concentration of NO_3-N for Brimstone soil (Table 3) is the result of fertilization in this agricultural soil with N sources. These concentrations do not surpass the safety limit of 10 mgL^{-1} NO_3-N (US Environmental Protection Agency 1976), but they are high enough to render a poor water quality. The high concentration of this anion at any depth suggests that the groundwater flows laterally from higher parts of the landscape. For the Verdun soil we found very low concentrations of NO_3 (Table 2) because it is a forest soil where N fertilizers probably were never applied. Small amounts of NO_3 may be rapidly absorbed by plants or dinitrified when the soil is in anaerobic conditions.

Calculation of Cl/SO_4 molar charge ratio < 9.7 from Table 2 data indicates that the proportions of SO_4 are higher than in seawater (Drever 1988) at any depth except at 0.25 m depth for the Verdun soil. These ratios may indicate the combined effect of the brackish groundwater with soil parent materials already rich in sulfates. For the Brimstone site, Cl/SO_4 ratios are high (34 to 54) indicating that the soil materials and water are low in SO_4.

Total alkalinity concentrations are similar in both groundwaters and in the range of concentrations (10^{-3} to 10^{-2} $mol_c L^{-1}$) given by van Beek and van Breeman (1973) at pH 7 for a poorly aerated subsoil.

Soil and Parent Materials

The particle size distribution with depth for Verdun and Brimstone soils are shown in Figure 3. These two soils developed in silty materials, originated from locally retransported loess in a fluviatile-deltaic environment, underlain by sandy braided stream deposits (Hudnall et al. 1992). Processes operative during and after deposition of these materials have resulted in a diffuse, gradational contact between the upper mantle and the underlying unit called basal mixing zone (BMZ) that we consider analogous to the BMZ defined for loess soils by Miller et al. (1986). The BMZ is mainly determined by changes in texture and color (Schumacher et al.1988). The thickness of the BMZ is inversely related to loess thickness (Rehage 1980). Walthall et al. (1992) found that Natraqualfs affected by saline groundwater occurred in thin loess (< 3 m thick).

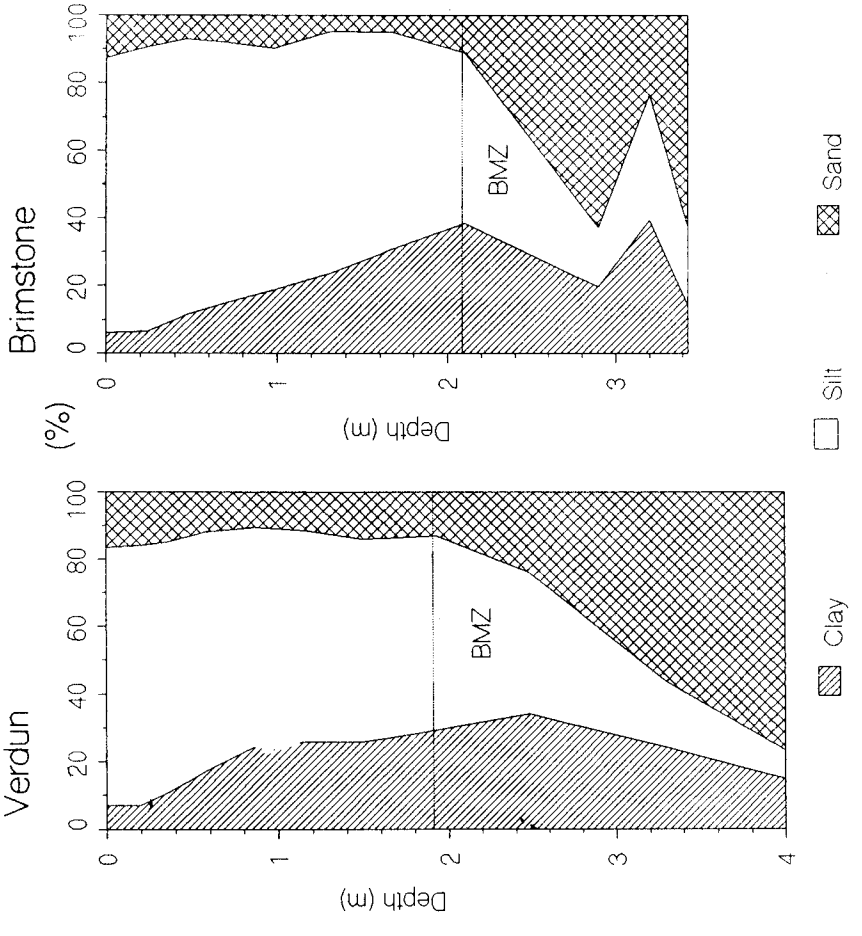

Figure 3. Particle size distribution depth function for Verdun and Brimstone soil. BMZ indicates the basal mixing zone.

BMZ's are delineated in Figure 3 for Verdun and Brimstone soils at the depth where a particle size change occurs. The particle size distribution indicates that the silty material has almost the same thickness in both soils (about 2 m). However, the BMZ's are different. The Verdun soil has a characteristic BMZ with an steady increase in sand below 2.15 m depth. For a thin silty mantle, as in the case of the Verdun, salinization occurs by upward saturated flow. The Brimstone soil has an irregular BMZ because of the presence of maximum content of clay with an oven dry bulk density reported by Hudnall et al. (1990) of 1.96 kg m^{-3} at the top of the BMZ between 1.90 and 2.30 m depth and a deeper clay layer between 3.15 and 3.25 m depth. These dense impermeable layers may confine the groundwater to the underlying deeper sandy aquifer and prevent its upward flow. The soil water must then be supplied by rainwater or lateral flow. Therefore, these differences in soil material properties must be reflected by differences in water quality. SAR and ESP are water and soil parameters that relate the solution chemistry to colloidal soil properties. Depth functions of the SAR and ESP are found in Figure 4. The ESP and SAR for Verdun soil meets the natric horizons criteria. The same does not apply for the Brimstone profile because it does not reach the maximum SAR or ESP values to qualify as Natraqualf. However, its morphology (Hudnall et al. 1990) indicates that this soil as well as the Verdun soil are or were under solodization processes. Therefore, the Brimstone profile would be in a solodic subgroup as proposed by McQuaid et al. (1987).

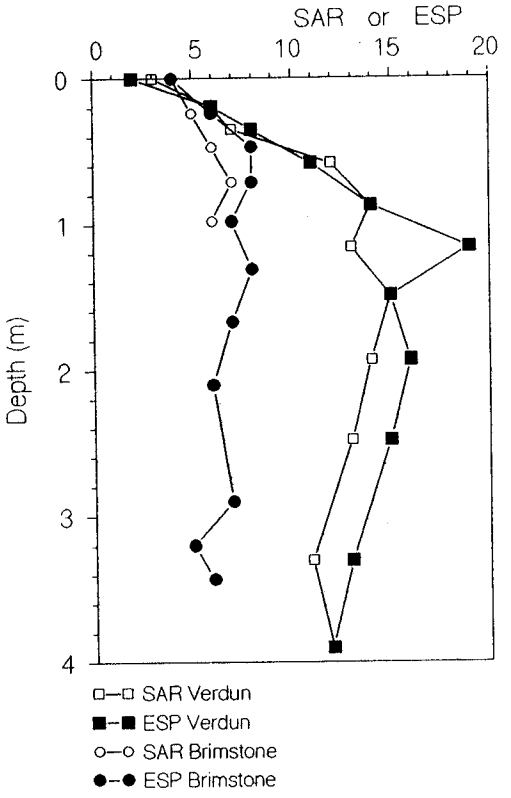

Figure 4. SAR and ESP depth functions for Verdun and Brimstone soils.

Sodium Sources

A strong relationship was found for Verdun soil between Cl and Na in the groundwater (r^2 = 0.75, slope = 0.58, n = 45, P > 0.01) that indicates the saline origin of Na. It also indicates a limited removal of Cl due to the very poor drainage conditions of this soil. The correlation between Cl and Na in Brimstone soil groundwater was weaker than for Verdun (r^2 = 0.44, slope = 0.32, n = 50, P > 0.01) and indicates that additions of NaCl are not made by the groundwater and probably Cl is being leached out. The trend between Na and Cl is found in Figure 5. Generally the lowest concentrations in Cl and Na comes from samples at 0.25 m depth supplied by rainfall. An even stronger relationship was found when Cl and Na+Mg in the groundwater were correlated for the Verdun soil (r^2 = 0.89, slope = 0.88, n = 40, P > 0.01) while the same relationship was extremely weak for Brimstone soil (r^2 = 0.12, slope = 0.61, n = 0.45, P < 0.01). The trend between Cl and Na + Mg is found in Figure 6, with data plotted only for the Verdun site. This significative correlation reinforces the hypothesis of the marine origin of the groundwater, since the slope and observed values are close to the sea water (Na + Mg)/Cl ratio calculated from sea water concentrations given by Drever (1988).

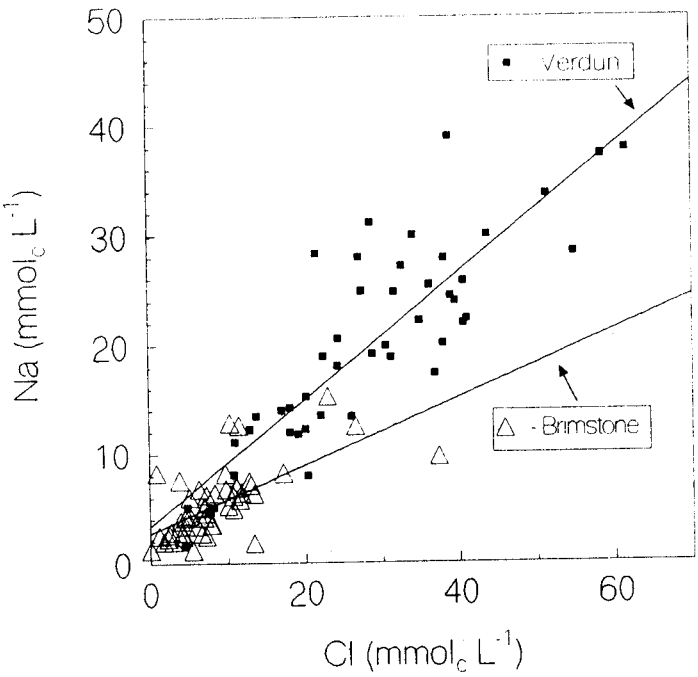

Figure 5. Relationship between Na and Cl in the groundwater of Verdun and Brimstone soils.

Brimstone soil was a former sodic soil where Na and Cl moved out of the profile under continuous leaching by fresh water. However, we have evidence that Na and Cl moved laterally over short distances. The mean EC and concentrations of Na and Cl were consistently as high as for Verdun site groundwater in one of the 1.00 m depth nested wells of the Brimstone site. The causes of accumulation of salts at short distances and the

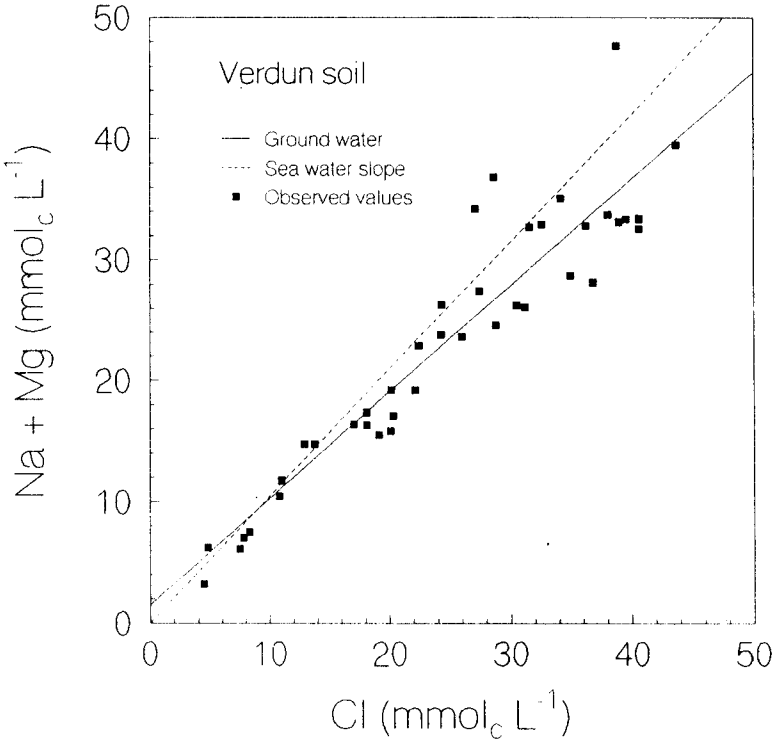

Figure 6. Relationship between (Na + Mg) and Cl in the ground water of Verdun soil.

occurrence of profiles with and without natric horizons in the Brimstone soil unit may be explained by: i) faunal pedoturbation and ii) low local relief. Intense activity of crawfish (*Procambarus clarkii)* can mix soil materials and induces preferential flow of water through freshly open burrows, which induces large spatial variability and accumulation of salts in microsites. According to Toth (1962), under extended flat areas, groundwater movement is retarded, and the low groundwater system is not well defined with characteristic discharge and recharge areas. Under these circumstances groundwater is discharged by evapotranspiration. Discharge of this type results in waterlogged areas. Since the flow velocity is low, those areas will have high concentrations of salts. Salts move to and accumulate in these areas which, usually are depressions in the microrelief of the terrain as described by Richardson et al. (1992) for the mound-intermound distances in soils of the Coastal Plain of Texas. The horizontal mound-intermound distances can be short (15 m) and the difference in elevation as much as 0.5 m (Carty et al. 1988). The Typic Epiaqualf that was sampled as the Brimstone Series in one side of the monitoring plot occupies microhigh areas of the landscape where recharge occurs. The true Brimstone Series is probably in the centre of the monitoring plot, which is also the centre of a microdepression about 15 to 20 m away from the sampling pit where we placed the well that yielded samples with higher salt concentrations than the adjacent ones.

CONCLUSIONS

The Verdun soil is a hydric soil with a well developed natric profile. Its morphology would indicate that leaching of Na was sometime a predominant process in the soil. However, presently the soil is undergoing secondary salinization. The discharging groundwater is brackish, of probable marine origin as indicated by the strong relationships Cl - Na and Cl - Na + Mg. According to models of Richardson et al. (1992), we describe this case as a seasonal discharge wetland with addition of materials to the soil.

The particle size distribution of Brimstone soil suggests that the water flows very slowly laterally. The irregular BMZ with high oven dry bulk density influences the direction of the flow locally by creating a perched water table characteristic of hydric soils. The origin of the water is not saline groundwater but infiltrating rain water as demonstrated by the weak relationship between Cl and Na. According to the models of Richardson et al. (1992), the Brimstone site could be the case of a seasonal flow through wetland. It receives water from the adjacent landscape with addition of NO_3, as well as it yields water to the shallow groundwater system (Na and Cl are leached out).

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