Equilibrium Concentrations of Major Cations and Total Alkalinity in Laboratory Soil-Water Systems

by

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Abstract

Three kinds of soils and four kinds of water were used to prepare laboratory soil-water mesocosms. Soil-water mesocosms were prepared containing 5-cm deep layers of soil and 21 L of water from each of the four sources. Water pH, conductivity, major cations and alkalinity were measured at intervals for 200 days. The Coastal Plain and Blackland Prairie soils caused greater increase in intensities of variables in rain and stream water than did the Piedmont Plateau soils, while conductivity, calcium, sodium, and total alkalinity in rain and stream water increased more in mesocosms with Blackland Prairie soil; magnesium increased more in the mesocosms with Coastal Plain soil. In saline water and seawater mesocosms, the Blackland Priarie soil caused significant changes in all measured variables in well water except pH and conductivity. In sea water, only calcium, magnesium and potassium in the mesocosm water were significantly different from the original source water.

A shaker experiment revealed equilibrium concentration of water quality variables increased as the ratio of soil to water increased. Concentrations of nutrients increased rapidly for some variables for the first 2 days. However, attainment of equilibrium might require more than 9 days. Findings of this study suggest that water quality of the soil-water systems can be predicted from source water chemical composition and soil properties. However, because of the wide variation in soil characteristics and in the quality of source water, neither the mesocosm technique nor the shaker procedure seems to provide a highly reliable way of predicting water quality in a pond.

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INTRODUCTION

Aquaculture ponds are constructed in soils with a wide variation in physical and chemical properties. For instance, the Blackland Prairie of Alabama tends to have fertile, heavy clay soils with a high cation exchange capacity (CEC) and free calcium carbonate, while the Piedmont Plateau soil in Alabama is low in natural fertility and organic matter. The Piedmont Plateau soil does not contain free calcium carbonate and the concentration of exchangeable ions is low (Boyd 2000).

Rain water, the ultimate source of water for ponds has low concentrations of dissolved substances and does not vary in composition very much from place to place (Boyd 1990). However, rain water that becomes runoff or groundwater contacts soils and minerals that dissolve to increase the degree of mineralization of water, and evaporation concentrates dissolved substances. Thus, climate and geology have a great effect on water quality. Concentrations of ions in sea water are much greater than fresh water. Concentrations of minerals for stream water vary greatly with location, and it might be different even for the same location at different season.

The major cations and total alkalinity of pond water are determined by composition of source water and properties of bottom soil. There is equilibrium of substance between pond water and bottom soil. Pond water derives many dissoved and suspended solids from bottom soil. On the other hand, bottom soils are a storehouse for organic matter from uneaten feed, fish excrement, and dead plankton (Boyd 1990).

Information on relationships among water quality variables and soil physical and chemical characteristics will be attained by using laboratory soil-water mesocosms. These data will then be evaluated to determine if laboratory studies can generate data useful in predicting the water quality variable in aquacuture ponds from source water compositions and bottom soil properties.

LITERATURE REVIEW

The major ions in natural waters are bicarbonate, carbonate, sulfate, chloride, calcium, magnesium, sodium, and potassium. However, the concentrations and proportions of these ions in natural waters are extremely varied as illustrated (Table 1) with data from Boyd (1990).

Table 1. Chemical composition of water from lakes and rivers. Sodium and potassium concentrations were combined for samples C and G.

	mg/L						
Analysis	A	B	C	D	E	F	G
Bicarbonate…………	26.2	121	14.6	2.7	136	20	154
Sulfate………………	8.5	28	7.7	5.4	28	3.1	968
Chloride……………..	1.0	17	75.5	5.2	29	1.4	378
Calcium……………....	9.0	39	6.4	0.5	41	3.8	186
Magnesium………….	3.6	8.7	6.9	3.2	9.1	1.2	3.5
Sodium………………	3.8	8.2		0.6	22	2.5	
			39.5				544
Potassium…………....	_	1.4		_	1.2	1.0	
Total dissolved solids	56.6	227	163	19.9	277	43.3	2,260

A. Lake Nipissing at North Bay, Ontario. Canadian Shield.

B. Lake Erie at Huron, Ohio. Sedimentary rocks.

C. Dalvary Pond, Dalvay, Prince Edward Island. Near Ocean.

D. Mean of 9 lakes in Halifax County, Nova Scotia. Slate or quartzite.

E. Lake Okeechobee near Clewiston, Florida.

F. Etowah River near Cartersville, Georgia.

G. Fort Stockton Lake, Pecos County, Texas.

Concentrations and proportions of major ions vary greatly among samples. Samples A, D and F had low levels of all measured ions and total dissolved solids. Samples A and D were from regions where the rocks and soils of the earth's surface were quite insolube, while sample F was from the regions where soils were highly leached. Sample C had a higher concentration of alkali metals, chloride and total dissolved solids because it was collected from a pond near the coast. Samples B and E were from lakes in regions of soluble, sedimentary rocks. Sample G was collected from an area with low rainfall and high evaporation. Both samples B, E and G had relatively higher concentration of ions.

Total alkalinity and total hardness of water are two extremely important variables in pond aquaculture. Total alkalinity is a measure of the total concentration of titrable bases in water expressed in terms of equivalent calcium carbonate. Common bases in water are bicarbonate, carbonate, hydroxide, and ammonia, but in most ponds, total alkalinity is primarily from bicarbonate (Boyd 2000). Of course, as pH rises above 8.3 in response to photosynthetic activity in ponds, some bicarbonate is transformed to carbonate. Total hardness is the total concentration of divalent cations in water also expressed in terms of equivalent calcium carbonate. The two major cations contributing hardness to pond waters are calcium and magnesium (Boyd 2000).

The major source of total alkalinity and total hardness in many waters is the dissolution of limestone (Wetzel 2001). Limestone exists in several forms, but it is a mixture of calcium carbonate and magnesium carbonate in different proportions. Limestone with nearly equal proportions of calcium and magnesium carbonates is called dolomitic limestone (Hutchinson 1957). Limestone is acted upon by carbon dioxide and water, and upon dissolution contributes both alkalinity and hardness as illustrated using dolomitic limestone:

$$CaCO_3 \cdot MgCO_3 + 2CO_2 + 2H_2O = Ca^{2+} + Mg^{2+} + 4HCO_3^-$$

In acidic soils, weathering of feldspars can contribute alkalinity but not hardness (Garrels and Christ 1965). The major source of alkalinity and hardness in water that does not contain free calcium and magnesium carbonates is the weathering of calcium silicate (Ittekkot 2003) by the following equation:

$$CaSiO_3 + 2CO_2 + 3H_2O = Ca^{2+} + 2HCO_3^- + H_4SiO_4.$$

Weathering of feldspar can contribute alkalinity but not hardness to water (Boyd 1990).

Sea water is high in concentration of most of the major ions (Boyd 2000). Saline ground water used for culturing marine white shrimp in West Alabama has low potassium and magnesium concentrations, while calcium and bicarbonate concentrations are greater than expected for seawater diluted to same salinity (Boyd and Thunjai 2003). Concentrations of minerals usually are small for rain water. Boyd (2000) reported the concentrations of major cations in rain water of the Central United States as follows: 0.33 mg/L sodium, 0.31 mg/L potassium, 2.18 mg/l calcium, and no detectable magnesium. Stream water has more opportunity for greater mineralization because of relatively long contacting with soil. However, the ionic compostion of water from streams varies from place to place and concentrations of ionic constituents in the water reflect geological and climatic condition within that area (Boyd 2000).

Soils from the Blackland Prairie area were typically smectite clay containing free calcium carbonate. The soils were typically alkaline with high cation exchange capacity (CEC). The major exchangeable cation in the soils was calcium, while exchangeable magnesium concentration is relatively low compared to calcium (Pine and Boyd 2010; Boyd et al. 2007b; Dixon and Nash 1968). The Piedmont Plateau soils developed from the oldest surface rock in Alabama. This soil is low in natural fertility and in content of organic matter. It is an acid soil with low CEC (Arce and Boyd 1980; United States Department of Agriculture USDA, Natural Resources Conservation Service NRCS, Soil Survey Staff Website). Soils in the Coastal Plains tend to be sandier than those of the Piedmont Plateau and they seldom developed in limestone (Arce and Boyd 1980).

Complicated reactions occur in water and at the soil-water interface in ponds. By studying the total alkalinity and hardness of surface waters in Alabama and Mississippi, Boyd and Walley (1975) found that water from streams in sandy soils has less than 20 mg/L total alkalinity, while in calcareous areas, stream water can have total alkalinity higher than 100 mg/L. Arce and Boyd (1980) did a study about the water chemistry of Alabama ponds and pointed out that the average concentrations of total ions in waters of Alabama ponds differed among soil areas. The waters of the Blackland Prairie had greated concentrations of ions than the waters from the Piedmont Plateau and Coastal Plains. In aquaculture pond, the sediment is different from original soil. Uneaten feed, application of liming materials and fertilizer, dead plankton, and fish excrement are sources of organic matter and tend to accumulate slowly in pond bottoms (Munsiri et.al. 1995; Boyd 1990). Nevertheless, most ponds have organic carbon concentration less than 3% and there is no strong correlation between pond age and sediment organic matter concentraion (Thunjai et al. 2004; Wudtisin and Boyd 2006). Pond soils have distinct horizons, with the upper 4 to 6 cm having the strongest influence on water quality. Total carbon concentration and microbial respiration were greater for the upper 0.5-cm or 1.0-cm sediment layers (Munsiri et.al. 1995; Sonnenholzner and Boyd 2000).

Soil is a major factor in pond aquaculture; however, few data are available on relationships among soil chemical and physical properties, water quality, and aquatic animal production. Concentrations of nutrients and phytoplankton productivity in pond waters are related to pH and nutrient concentrations in soils (Boyd 1995). Boyd and Munsiri (1997) measured the water quality in laboratory soil-water microcosms with soils from many areas in Thailand and these findings suggested that different soils caused wide variation in composition of waters. Differences in water quality caused by interactions with soils may affect aquatic animal production.

An early study suggested that fish yields were better in ponds located on fertile soil than on infertile soil in extensive aquaculture production (Toth and Smith 1960). Banerjea (1967) was able to identify desirable ranges of soil pH, organic carbon, nitrogen, and phosphorus for high fish production by studying 80 ponds in India. Because shrimp spend most of their time on the bottom, pond bottom conditions are more critical for them. Under laboratory conditions, growth of *Litopenaeus vannamei* was significantly affected by soil (Ritvo et al. 1998a). A significant positive correlation between the pH of the sediment surface and the shrimp osmotic pressure was detected, and shrimp tend to undergo more stress under the lower pH conditions (Lemonnier et al., 2004).

Different ions may react differently with respect to exchange between soil and water. For example, loss of potassium from the water of shrimp ponds to the bottom soil was a result of both the cation exchangeable process and fixation with interlayers of clay micelles by a non-exchangeable process (Boyd et al. 2007b). However, nearly all of the magnesium lost from the water was the result of cation exchange with the bottom soils (Pine and Boyd 2010). Although equilibrium exists between the concentration of a substance in the soil and its concentration in the water (Boyd 1995), the ability of soil to adsorb some substances decreases over time as the concentration of these substances increase. For example, potasium, magnesium and copper decreases over time upon repeated exposure to water of high potasium, magnesium and copper, respectively (Silapajarn et al. 2006; Boyd et al. 2007b; Pine and Boyd 2010). In aquculture ponds, several years might be needed for pond soil to become saturated with potassium (Boyd et al. 2007b). However, a study in the laboratory soil-water microcosms showed that concentrations of nutrients did not increase after the second day of the trial (Boyd and Munsiri 1997). Silapajarn and Boyd (2006) demonstrated that copper adsorption by bottom soil was positively correlated with increasing soil pH and organic concentration and negatively correlated with increasing concentration of dilute acid-extractable copper. They also point out that sandy soil would be more likely to become copper saturated.

Pine and Boyd (2010) found that proportions and concentrations of the exchangeable cations in water and on cation exchange sites in bottom soil would affect the equilibrium magnesium.

MATERIALS AND METHODS

A soil sample was collected from each of the Blackland Prairie, Coastal Plain, and Piedmont Plateau regions of Alabama, USA in November 2008. The Blackland Prairie soil was collected from the surface of a soybean field near Boligee, Alabama. Soils in this region are mainly represented by three official series: Leeper, Sumter, and Trinity. The Leeper (inceptisols) and Trinity (vertisols) are soils of very slowly permeable that formed in clayey alluvium, while the Sumter series is a carbonatic (>40% carbonate) inceptisols containing smectite clay (USDA, NRCS, Soil Survey Staff Website). Coastal Plain soil was attained from the surface (0-30 cm layer) of an abandoned field near Notasulga, Macon County, Alabama. Soils in this region are mainly represented by three official series: Marvyn, Cowarts and Uchee. These Ultisols normally have a sandy surface layer, and loamy and clayey subsoil (USDA, NRCS, Soil Survey Staff Website). Piedmont Plateau soil was collected from the surface of a denuded area at a construction site on the E.W. Shell Fisheries Center Auburn, Alabama. This area is mainly represented by two official series: Pacolet and Cecil. The Pacolet (Ultisols) and Cecil (Ultisols) have a loamy surface and dominantly clayed subsoil (USDA, NRCS, Soil Survey Staff Website).

Four kinds of water, stream water, rain water, low salinity well water, and sea water, were used in this study. The stream water was collected from the Little Loblockee Creek on U.S. Highway 280 N near Opelika, Alabama; artificial rain water was made by dissolving salts in water to achive a concentation of major ions equal to the average composition (Boyd 2000). Low salinity well water was collected from the Greene Prairie Aquafarm located on Alabama Highway 43 near Forkland, Alabama; sea water was dipped from a pier in the Gulf of Mexico near the Mississippi Coast Coliseum and Convention Center, Biloxi, Mississippi.

Soil-water mesocosms were made in quadruplicate by putting a 5-cm deep layer of soil over the bottom of an aquarium (30×30×30) and adding 21 L of water from one of the four sources. The moisture content of each soil sample was determined (Gardner 1986). So that the amount of dry soil put into each aquarium could be determined. Tops of aquaria were covered with clear plastic wrap to reduce evaporation. Water in aquaria was gently and continuously mixed using air stones that were suspended above the soil surface to prevent suspension of particles and attached by polyethylene tubing to small aquarium pumps.

Water samples were collected after 2, 4, 8, 12, 16, 24, 32, 48, 64, 96, 128 and 200 days between 13 December 2008 and 1 July 2009. Conductivity was measured using a YSI 556 multi-parameter system equipped with a conductivity-salinity probe (Yellow Springs Instrument Company, Yellow Springs, Ohio, USA). A glass, combination electrode and electrionic pH meter were used to measure pH. Total hardness (TH) was determined by EDTA titration to the eriochrome black – T endpoint, while calcium harness (CaH) was measured by EDTA titration to the murexide endpoint (Boyd and Tucker 1992). Calcium (Ca) and magnesium (Mg) concentrations were then estimated as follows:

Ca = CaH/2.5

Magnesium hardness (MgH) = TH – CaH

Mg = MgH/4.2

Total alkalinity concentration was determined by sulfuric acid titration to the methyl orange end point. Sodium and potassium were measured by flame spectrometry using a Cole-Parmer Model 2655-00 flame photometer.

Subsamples of soils were taken from each of the three sources.The samples were dried at 60°C in a mechanical convection oven. Dry samples were pulverized and analyzed by methods described by Boyd and Tucker (1992) for the following variables: pH, particle size distribution (sand, silt, and clay content), organic carbon. Basic exchangeable cations (calcium, magnesium, sodium, and potassium) were extracted with neutral, 1N ammonium acetate and determined by atomic absorption spectrophotometry. To determine cation exchange capacity (CEC), the exchangeable acidity was measured and added to the sum of basic exchangeable cations (Boyd and Tucker 1998).

Another experiment was set up to see how different soil: water ratios affected equilibrium in the soil-water microcosoms. Samples of Blackland Prairie soil weighing 100 g, 50 g, 33.3 g, 25 g, 12.5 g and 6.25 g were put into 500-ml Erlenmeyer flasks with 400 ml stream water to give soil: water ratios of 1:4, 1:8, 1:12, 1:16, 1:32 and 1:64.

Flasks were placed on a rotating shaker table at 150 rpm. Conductivity was measured every 6 hr at the beginning, then daily, every other day, and every 3 days for the last two sampling periods. On day 11, water samples were collected and pH, conductivity, total alkalinity, calcium, magnesium, potassium, and sodium were measured.

A third experiment was prepared in quadruplicate for each soil and water combination by adding 25 g of pulverized soil and 400 ml water to 500-ml Erlenmeyer flasks. Flasks were placed on a rotating shaker table (150 rpm). Conductivity was measured every 6 hr at the beginning, then on the daily basis, and finally every other day to ascertain when the equilibrium conductivity was reached. On day 9, water samples were collected and pH, conductivity, total alkalinty, calcium, magnesium, potassium, and sodium were measured.

Microsoft Excel 2007 and SAS (version 9.1) were used for data analysis.

RESULTS AND DISCUSSION

Freshwater Mesocosms

Concentrations of dissolved substances, conductivity and pH were quite different in the four water sources (Table 2). Artificial rain water was near neutral in pH and had low concentrations of major cations and total alkalinity. Stream water was near neutral in pH with considerably greater concentrations of cations and total alkalinity. Saline well water was basic. It had about tenfold more calcium, magnesium, and potasium than stream water, was high in sodium and total alkalinity concentrations.The sea water sample was higher in concentrations of all major ions than the saline well water, but lower in total alkalinity. The sea water sample had a composition very nearly the same as average seawater which has the following composition: pH of 8.1, 400 mg/L calcium, 1,350 mg/L magnesium, 380 mg/L potassium, 10,500 mg/L sodium, 122 mg/L total alkalinity, and a conductivity of about 50,000 µmhos/cm (Boyd 2000).

The soil samples also differed considerably in composition (Table 6). The Piedmont Plateau soil was highly acidic with low cation exchange capacity (CEC), and low concentrations of organic matter and major cations. It was clay in texture. The Coastal Plain soil had a high pH but a low CEC and organic matter concentration. Calcium and magnesium concentrations were much higher for the Coastal Plain soil than for the Piedmont Plateau soil, but the Coastal Plain soil was similar to the Piedmont Plateau soil with respect to potassium concentration. However, the Coastal Plain soil was very low in sodium. The texture class of the Coastal Plain soil was sandy clay loam. The Blackland Prairie soil was slightly neutral in pH and contained free calcium carbonate. It was very high in CEC and in concentrations of calcium, potassium, and sodium with respect to the other two soils, but it had a lower magnesium concentration than the Coastal Plain soil. The Blackland Prairie soil was clay in texture.

In the mesocosms with Piedmont soil, stream water was buffered well enough by its alkalinity to maintain a relatively constant pH (Fig.1); rain water decreased slightly in pH because of the effect of the acidic soil. In mesocosms with alkaline Coastal Plain and Blackland Prairie soils, the basic nature of the soil had a stronger influence on water quality in the mesocosms than did the initial chemical composition of the water, and pH increased in both rain water and stream water.

The acidity of the Piedmont Plateau soil caused a decline in the total alkalinity of stream water, but total alkalinity of the rain water remained essentially unchanged (Fig. 2). Both Coastal Plain and Blackland Prairie soils apperently contained free calcium carbonate, and dissolution of the carbonate caused alkalintiy to increase. Soils from the Blackland Prairie often contain free calcium carbonate (Hajek et al. 1975), but Coastal Plain soils normally do not contain free calcium carbonate (McNutt 1981).The most likely explanation is that agricultural limestone had been applied to the field from which the Coastal Plain soil was obtained, but this possibility could not be verified.

Calcium concentration increased moderately in both rain water and stream water in the mesocosms with Piedmont Plateau soil (Fig. 3). There was a marked increase in calcium concentration in both rain water and stream water in the mesocosms with Coastal Plain and Blackland Prairie soils. The main source of the calcium no doubt was dissolution of free calcium carbonate in the soils.

Magnesium concentration increased slightly in rain water and decreased slightly in stream water in mesocosms with Piedmont Plateau soils (Fig. 4). This was likely the result of ion exchange between soil and water, but the soil was too lower in magnesium to cause a substantial increase in magnesium in rain water and too low in CEC to remove much magnesium from the stream water. The Coastal Plain soil caused a larger increase in magnesium in both rain water and stream water. As mentioned above, it was suspected that the Coastal Plain soil had been limed, and if the agricultural limestone had been dolomitic, i.e., $CaCO_3$ and $MgCO_3$, both calcium and magnesium concentration would have increased. The Blackland Prairie soil did not contain much magnesium relative to calcium, as is typical for these soils which formed in an area where limestone deposits are low in magnesium (calcitic limestone) (Boyd et al. 2007a). Thus, the magnesium concentration increased only slightly in rain water and stream water in mesocosms with Blackland Prairie soil.

Potassium concentration in both rain water and stream water remained rather constant in mesocosms with Piedmont Plateau soil (Fig. 5). Moreover, concentrations of potassium in both water sources increased only slightly in mesocosms with the other two soils.The Coastal Plain and Piedmont Plateau soils were rather low in potassium, so the failure of potassium to increase in the water is not surprising. The Blackland Prairie soil had a much higher potassium concentration, but much of the potassium in Blackland Prairie soils is fixed within the interlayer of the smectic clay contained in their soils (Dixon and Nash 1968). The fixed potassium is not readily available to waters through cation exchange processes (Boyd et al. 2007a)

There were slight to moderate decreases in sodium concentration in both waters in the mesocosms with Piedmont Plateau soil (Fig. 6). In the mesocosm with Coastal Plain soil, sodium concentration remained fairly constant in stream water, but declined in rain water. There was an increase in sodium concentration in both waters in the mesocosms with Blackland Prairie soil. These are fairly consistent with the concentrations of sodium in the three soils.

The soils caused an increase in conductivity of both waters in all mesocosms. However, the increase in conductivity was much greater in the mesocosms with Coastal Plain and Blackland Prairie soil than that in those with Piedmont Plateau soil (Fig. 7). This also is consistent with the observation that the Coastal Plain and Blackland Prairie soils were higher than the Piedmont Plateau soils in concentrations of major ions.

The pH of water in mesocosms did not change appreciably after 30 to 60 days. However, equilibration of other measured variable between soil and water occurred more slowly. In the mesocosms with Piedmont Plateau and Blackland Prairie soils, conductivity, major cations, and total alkalinity appeared to have reached an equilibrium concentration by day 120 to day 200. However, in the mesocosms with Coastal Plain soil, total alkalinity, calcium, magnesium, and potassium appeared to still be slowly increasing when the experiment was terminated after 200 days.

The final concentrations of measured variables after 200 days were compared statistically in two manners. The concentrations of each variable in original source water (no soil contact) and in source waters after standing in contact with soil in mesocosms (Table 3) were compared with a multiple range test. This comparision revealed whether or not there were differences related to soil effects. The results can be summaried as follows:

1. Soils caused an increase in pH, conductivity, and concentrations of other measured variables in rain water with only two exceptions - sodium and total alkalinity did not increase in rain water exposed to Piedmont Plateau soil.
2. Both the Coastal Plain and Blackland Prairie soils caused greater increase in intensities of variables in rain water than did the Piedmont Plateau soils. However, there were differences between Coastal Plain and Blackland Prairie soils. Conductivity, calcium, sodium, and total alkalinity in rain water increase more in mesocosms with Blackland Prairie soil; magnesium increased more in the mesocosms with Coastal Plain soil.
3. The levels of only conductivity and calcium increased in stream water with Piedmont Plateau soils, while that of sodium decreased.
4. The Coastal Plain soil caused an increase in the levels of all variables other than sodium in stream water, while the Blackland Prairie soil caused intensities of all variables to increase in stream water. However, when these two soils are

compared, the Blackland Prairie soil caused greater conductivity and higher concentrations of calcium, sodium and total alkalinity while the Coastal Plain soils caused larger concentrations of magnesium and potassium.

The data were then arranged to use a t-test to determine if there were differences in concentrations of variables in rain water and stream water exposed to the same soil (Table 4). In the case of Piedmont soil, the mesocosms with stream water were higher in pH and concentrations of other variables than were the mesocosms with rain water, and except for pH, the same was true in mesocosms with Coastal Plain soil. However, there was only one variable - sodium, exhibiting different concentrations between rain water and stream water in mesocosms with Blackland Prairie soil.

Saline Water and Sea Water Mesocosms

The pH of saline well water declined slowly over time in mesocosms, while that of sea water remained relatively constant; after 200 days, the pH was the same for both the two waters (Fig. 8).

The saline well water had a high total alkalinity concentration initially, but upon equilibrium with atmospheric carbon dioxide, the total alkalinity concentration declined from 269.7 mg/L to about 142.6 mg/L by day 30 (Fig. 8).The decline was caused by precipitation of calcium carbonate, a process that does not involve soil interaction. By the end of the mesocosm study, concentrations of total alkalinity were similar in the two waters.

Potassium concentration was low, 8.6 mg/L in the saline well water and it decreased to 4.6 mg/L in the mesocosms after 200 days. The sea water had a potassium concentration of 365 mg/L, much higher than the well water, but its concentration also decreased by about half in the mesocosms after 200 days (Fig. 9). The Blackland Prairie soil had high clay content (Table 6) of 69%, and most of the clay in Blackland Prairie soil is smectite (Dixon and Nash 1968). Smectite clay can sequester potassium between the interlayers of the clay minerals and render it unavailable (Sparks 2000; Yuan et al. 1976). Boyd et al. (2007 a, b) demonstrated that bottom soils from ponds for inland culture of marine shrimp in the Blackland Prairie had a high capacity to sequester potassium added to pond waters in muriate of potash to increase potassium concentrations to levels needed by shrimp.

Calcium concentration increased slightly in the mesocosms with saline well water despite of the decline in total alkalinity through calcium carbonate precipitation (Figure 9). The calcium apparent entered the water from the soil via exchage for soil calcium.The increase in calcium in the mesocosms with sea water apparently was also the results of exchange for soil calcium.

Magnesium concentration remained relatively constant in the mesocosms with saline well water. However, magnesium concentration declined in the mesocosms containing sea water (Figure 9). Pine and Boyd (2010) demonstrated that bottom soil in inland shrimp ponds in the Blackland Prairie removed magnesium applied to pond waters through cation exchange of calcium for magnesium rather than by fixation between interlayer of clay minerals. They also suggested that a high magnesium concentration in the water would lead to greater exchange of soil calcium for magnesium in the water, this apparently happened in the mesocosms.

Sodium concentration remained relatively stable in waters of the mesocosms (Figure 9). The conductivity of water in the mesocosms also remained constant (Figure 8). Conductivity, pH, and concentrations of major ions in water of the saline well water and sea water mesocosms are presented (Table 5). A t-test was used to see whether there were differences between water quality in original source water (no soil contact) and in waters after standing in contact with soil in mesocosms. The Blackland Priarie soil caused significant changes in all measured variables in well water except pH and conductivity. In sea water, only calcium, magnesium and potassium in the mesocosm water were significantly different from the original source water. The mesocosm water was higher in calcium but lower in potassium and magnesium than the original sea water.

Shaker Experiment

The ability to predict concentrations of water quality variables that will occur in water of ponds to be constructed at particular sites obviously would be advantageous. However, results reported above suggest that using mesocosms, it would require 200 days or more to estimate water quality concentrations. Moreover, it is not known if the ratio of soil to water affects equilibrium concentrations of water quality variables

The trial in which flasks containing different soil: water ratios were agitated on a shaker table and conductivity measured at intervals revealed that equilibrium had not been fully reached after 264 h of shaking (Fig.10). Moreover, conductivity declined as the soil: water ratio decreased; e.g. conductivity was over 500 µmhos/cm in the 1:4 soil: water ratio but only about 200 µmhos/cm in the 1:64 soil to water ratio after 264 h. In the mesocosm, the combination of stream water and Blackland Prarie soil used in the shaker study gave a conductivity of 400 µmhos/cm after 200 days. Concentrations of other water quality variables also declined as the soil: water ratio decreased (Table 7). The 1:4 soils: water ratio tended to agree best with the results from the mesocosms study. Thus, shaking the samples of soil with stream water for 264 h gave similar concentrations of water quality variables as those observed in the mesocosms containing stream water and Blackland Prairie soil.

Although the 1:4 soil: water ratio gave the best results, water in flask with this ratio was highly turbid after shaking, making analysis very difficult. Thus, it was decided for practical purposes to use a 1:16 soil: water ratio in the trial using all three soils with the different water sources (Table 8). The results, however, did not agree well with those obtained for the same soil: water combinations used in the mesocosms.

Data on conductivity and concentrations of total alkalinity and major cations are available from a study of the chemistry of pond waters in the different physiographic province of Alabama (Arce and Boyd 1980). There was a wide range in concentrations of all variables within each of these physiographic provinces that are of interest in this study (Table 9).

All ponds sampled in the study by Arce and Boyd (1980) were watershed ponds filled by runoff. Thus, the results of the soil - water mesocosms and the shaker test (1:16 soil: water ratio) for the three soils and rain water were included in Table 8 for comparision. The shaker tests results agreed almost as well as the mesocosm results with coverage concentrations for the ponds. However, there was a wide range in variables in the ponds. Also, the Coastal Plain soil used in this study was atypical in that it apparently contained limestone.

Conclusions

The results of this study reveal the following:

(1) It requires a long time, more than 200 days for some variables, for equilibrium to be attained between dissolved ions (conductivity), major ions, and total alkalinity. However, pH reaches equilibrium much faster.

(2) Depending upon chemical properties, either the soil or the source water may be the dominating factor determing the equilibrium concentration of the dissolved substances measured in this study.

(3) Because of the wide variation in soil characteristics and quality of source water, neither the mesocosm technique nor the shaker procedure seems to provide a highly reliable way of predicting water quality in a pond.

Table 2. Source water quality.

Source	pH	Conductivity (µmhos/cm)	Major Cations (mg/L) Ca^{2+}	Mg^{2+}	K^+	Na^+	Total Alkalinity (mg/L as $CaCO_3$)
Rain	7.19	17	1.4	0.1	0.4	0.5	4.5
Stream	7.34	79	5.4	3.6	1.0	7.9	28.7
Well	8.23	6,048	33.1	14.3	8.4	1,208	269.7
Sea	8.11	52,117	388	1,341	418	12,030	121.3

Table 3. Comparison of concentration of water quality variables between source water (no soil contact) and source water after it stood in contact with each of three different soils in mesocosms for 200 days [1].

				Major Cations (mg/L)				
Water	Soil [2]	pH	Conductivity (µmhos/cm)	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Total Alkalinity (mg/L of $CaCO_3$)
Rain	None	7.19^{a}	17^{a}	1.4^{a}	0.1^{a}	0.4^{a}	0.5^{a}	4.5^{a}
	PP	5.82^{b}	59^{b}	4.7^{b}	2.1^{b}	0.6^{b}	0.5^{a}	4.4^{a}
	CP	8.56^{c}	241^{c}	23.2^{c}	14.5^{c}	2.0^{c}	1.0^{b}	116.9^{b}
	BP	8.57^{c}	374^{d}	60.6^{d}	3.8^{d}	2.1^{c}	9.4^{c}	179.5^{c}
Stream	None	7.34^{a}	79^{a}	5.4^{a}	3.6^{a}	1.0^{a}	7.9^{a}	28.7^{a}
	PP	7.36^{a}	115^{b}	9.4^{b}	3.2^{a}	1.2^{a}	4.9^{b}	13.2^{a}
	CP	8.57^{b}	273^{c}	25.3^{c}	15.4^{b}	2.5^{b}	6.3^{c}	129.0^{b}
	BP	8.49^{b}	408^{d}	64.1^{d}	5.0^{c}	1.8^{c}	13.1^{d}	191.9^{c}

1. Entries indicated by the same letter (vertical comparision only) did not differ at p=0.05 as determined by the Duncan’s multiple range test.
2. PP = Piedmont Plateau; CP = Coastal Plain; BP = Blackland Prairie.

Table 4. Comparison of water quality variables between waters of two sources that stood in contact with each of three different soils in mesocosms for 200 days.

				Major Cations (mg/L)				Total alkalinity
Soil [2]	Water	pH	Conductivity (µmhos/cm)	Ca^{2+}	Mg^{2+}	K^+	Na^+	(mg/L of $CaCO_3$)
PP	Rain	5.82*	59*	4.7*	2.1*	0.6*	0.5*	4.4*
	Stream	7.36	115	9.4	3.2	1.2	4.9	13.2
CP	Rain	8.56	241*	23.2*	14.5*	2.0*	1.0*	116.9*
	Stream	8.57	273	25.3	15.4	2.5	6.3	129.0
BP	Rain	8.57	374	60.6	3.8	2.1	9.4*	179.5
	Stream	8.49	408	64.1	5.0	1.8	13.1	191.9

1. For each soil, an asterisk beside the rain water entry (vertical comparision only) indicates that the rain water and stream water entries differ at p=0.05 as determined by t-test.
2. PP = Piedmont Plateau; CP = Coastal Plain; BP = Blackland Prairie.

Table 5. Comparison of concentration of water quality variables between source water (no soil contact) and source water after it stood in contact with Blackland Prairie soil in mesocosms for 200 days [1].

				Major Cations (mg/L)				Total alkalinity
Water	Soil [2]	pH	Conductivity (µmhos/cm)	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	(mg/L of CaCO$_3$)
			Saline Well Water					
	None	8.23	6,048	33.1*	14.3*	8.4*	1,208*	269.7*
	BP	8.09	6,145	234.8	21.2	4.6	1,069	142.6
			Sea Water					
	None	8.11	52,117	388*	1,341*	418*	12,030	121.3
	BP	8.08	47,140	1,472	910	147	10,403	105.7

1. For each water, an asterisk beside the source water entry (vertical comparision only) indicates that the source water and source water after it stood in contact with the soil in mesocosoms for 200 days differ at p=0.05 as determined by t-test.
2. BP= Blackland Prairie.

Table 6. Composition of soils.

Soil	pH	Organic Carbon (%)	Silt (%)	Clay (%)	Sand (%)	Ion concentration (mg/kg)				CEC (meq/100g)
						Ca^{2+}	K^{+}	Mg^{2+}	Na^{+}	
Blackland Prairie	7.44	1.92±0.03	26.00	69.04	4.96	9390.03	188.23	90.60	126.51	50.22
Coastal Plain	8.17	0.63±0.02	22.84	25.17	51.99	701.37	33.22	239.84	0.48	6.11
Piedmont Plateau	4.99	0.59±0.02	24.29	52.39	23.31	233.43	49.96	91.30	33.98	4.56

Table 7. Water quality in flasks at the end of the trial (Blackland Prairie soil and stream water with different soil water ratios).

			Ion Concentration (mg/L)				
Ratio	pH	Conductivity (µmhos/cm)	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Total Alkalinity (mg/L of $CaCO_3$)
1:4	8.46±0.07	529±24	87.53±4.44	5.30±1.54	3.59±0.17	13.38±0.49	223.28±10.87
1:8	8.56±0.22	369±9	59±1.14	3.11±0.63	3.09±0.05	10.46±0.29	148.79±3.49
1:12	8.35±0.22	323±8	51.30±1.64	2.13±0.19	2.45±0.03	9.32±0.25	128.09±4.81
1:16	8.52±0.27	295±3	46.29±0.49	1.75±0.30	2.20±0.13	9.06±0.05	113.58±2.58
1:32	8.31±0.20	261±2	39.07±0.42	2.08±0.34	1.98±0.03	8.65±0.49	95.98±2.82
1:64	8.42±0.25	209±5	29.79±1.11	1.94±0.52	1.59±0.05	7.96±0.00	75.80±1.48

Table 8. Water quality in flasks at the end of the trial (different water and soil combinations with soil: water ratio of 1:16).

Abbreviations see Figure 1 and Figure 8.

			Ion Concentration (mg/L)				
Sample	pH	Conductivity (µmhos/cm)	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Total Alkalinity (mg/L $CaCO_3$)
BR	8.47±0.10	254±5	42.41±0.86	2.06±0.52	1.92±0.05	3.90±0.06	92.34±20.69
CR	6.98±0.09	86±4	7.76±0	4.47±0.27	0.91±0.05	0.75±0.14	31.96±0.78
PR	5.89±0.11	45±1	1.22±0.12	0.55±0.19	1.34±0	2.98±0.14	4.02±0.19
Bstr	8.10±0.11	273±12	39.75±1.25	2.23±0.36	1.92±0.10	9.29±0.05	101.12±5.40
Cstr	7.77±0.05	125±1	9.03±0.27	5.50±0.29	1.49±0.06	7.49±0.06	42.15±0.77
Pstr	7.10±0.11	81±1	2.23±0.19	1.47±0.12	1.29±0.06	8.66±0.08	6.64±0.54
BW	8.31±0.07	5676±14	124.60±1.00	8.57±0.59	5.57±0.05	1068.41±3.80	187.85±4.90
BS	7.65±0.02	55520±34	794.79±5.82	1259.69±3.53	354.46±0	12869.90±70	98.41±10.19

Table 9. Comparison of conductivity and concentratons of total alkalinity and major cations in pond waters and soil-water systems.

System	Conductivity (μmhos/cm)	Major Cations (mg/L)				Total Alkalinity (mg/L of $CaCO_3$)
		Ca^{2+}	Mg^{2+}	K^+	Na^+	
		Piedmont Plateau				
Ponds[1]	40	2.7	1.4	1.4	2.6	11.6
Mesocosms	59	4.7	2.1	0.6	0.5	4.4
Shaker	45	1.2	0.55	1.3	3.0	4.0
		Coastal Plain				
Ponds[1]	48	3.4	1.1	2.8	2.9	13.2
Mesocosms	241	23.2	14.5	2.0	1.0	116.9
Shaker	86	7.8	4.5	0.9	0.8	32
		Blackland Prairie				
Ponds[1]	161	19.7	1.5	1.5	4.3	51.1
Mesocosms	374	60.6	3.8	2.1	9.4	179.5
Shaker	254	42	2.1	1.9	3.9	92.3

1. Source: Arce and Boyd (1980).

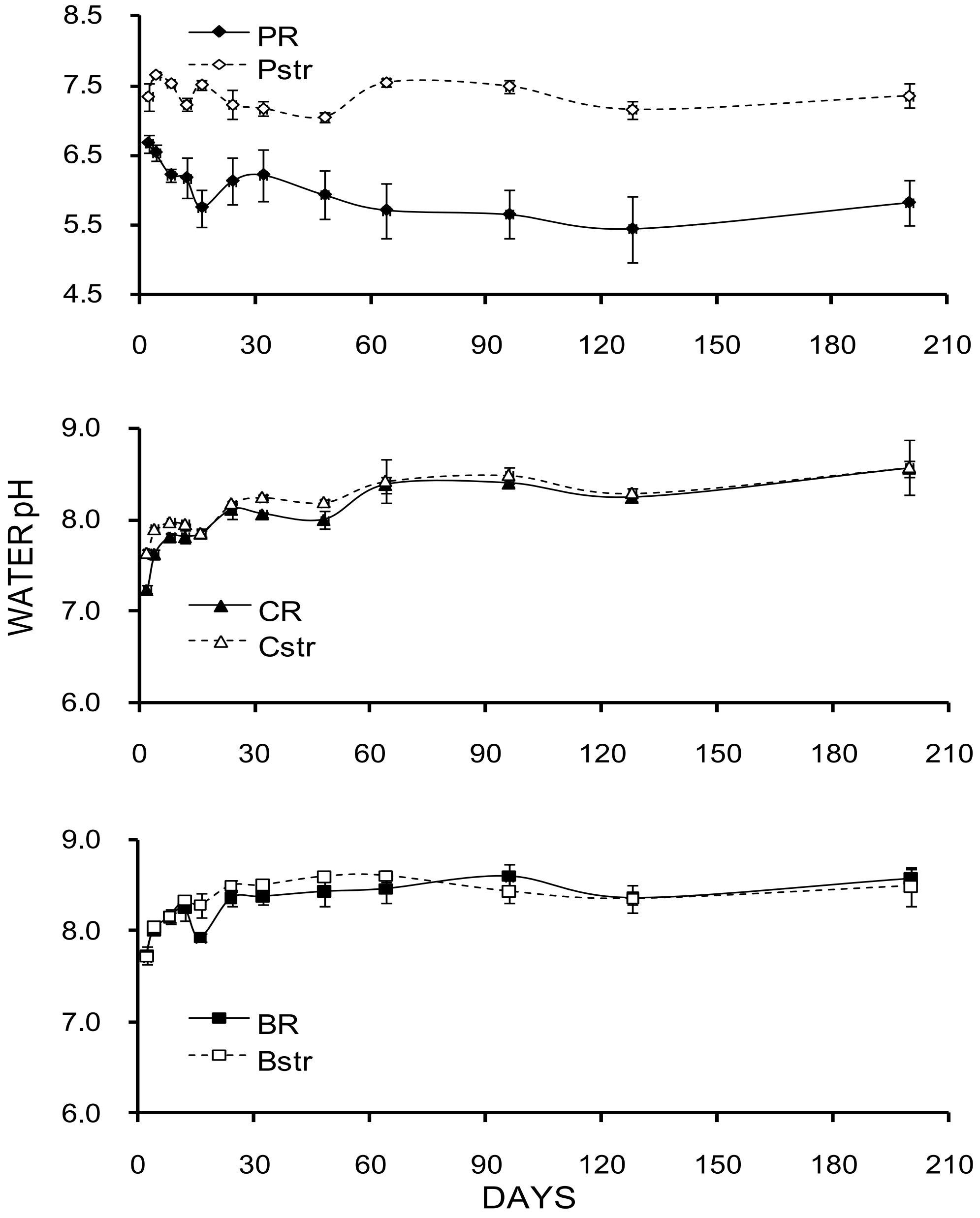

Figure 1. Water pH in different soil-water systems from December 2008 through July 2009. PR=Piedmont Plateau soil and rain water; Pstr=Piedmont Plateau and stream water; CR=Coastal Plain soil and rain water; Cstr=Coastal Plain soil and stream water; BR=Blackland Priarie soil and rain water; Bstr=Blackland Priarie soil and stream water.

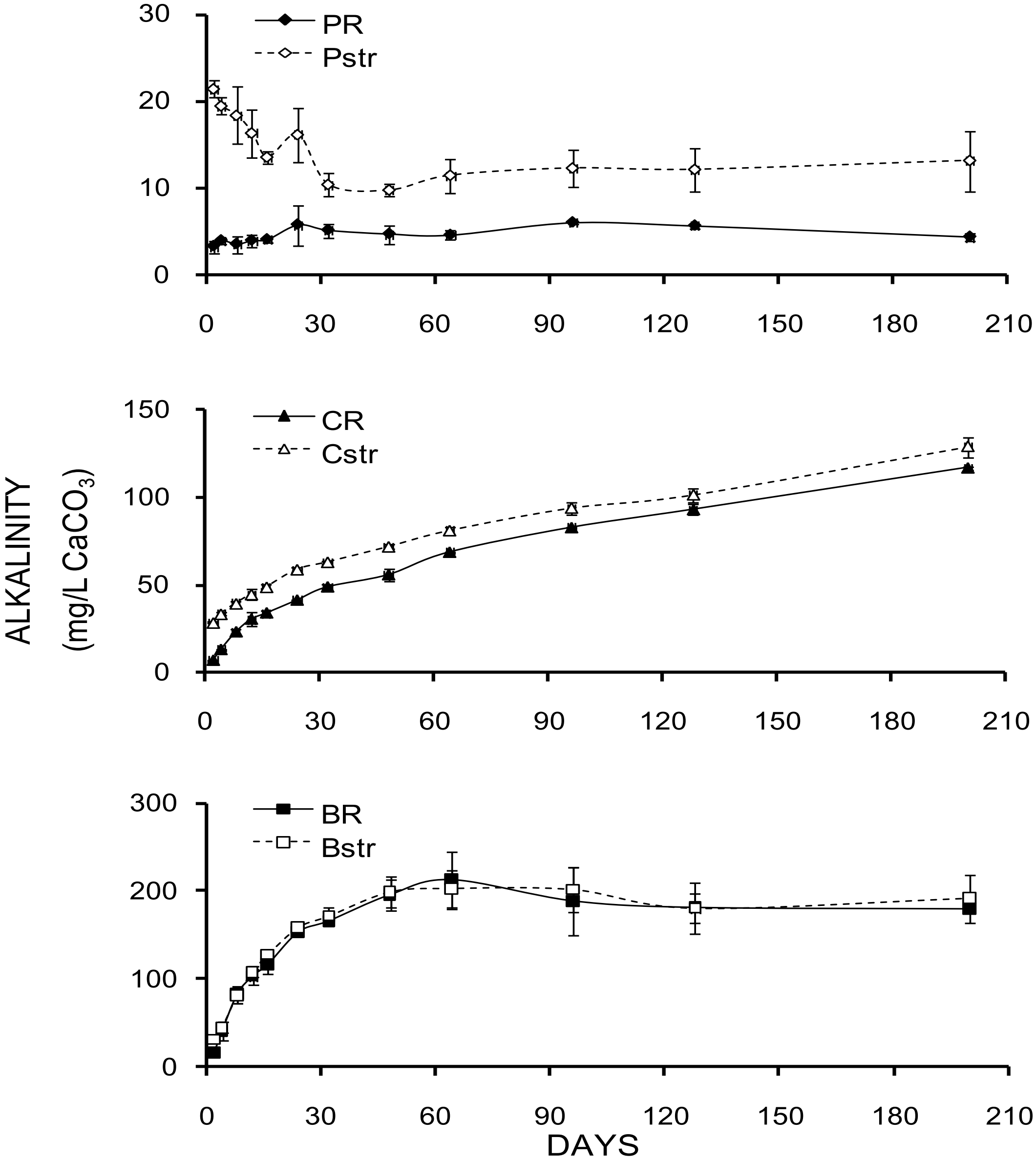

Figure 2. Alkalinity in different soil-water systems from December 2008 through July 2009. Abbreviations see Figure 1.

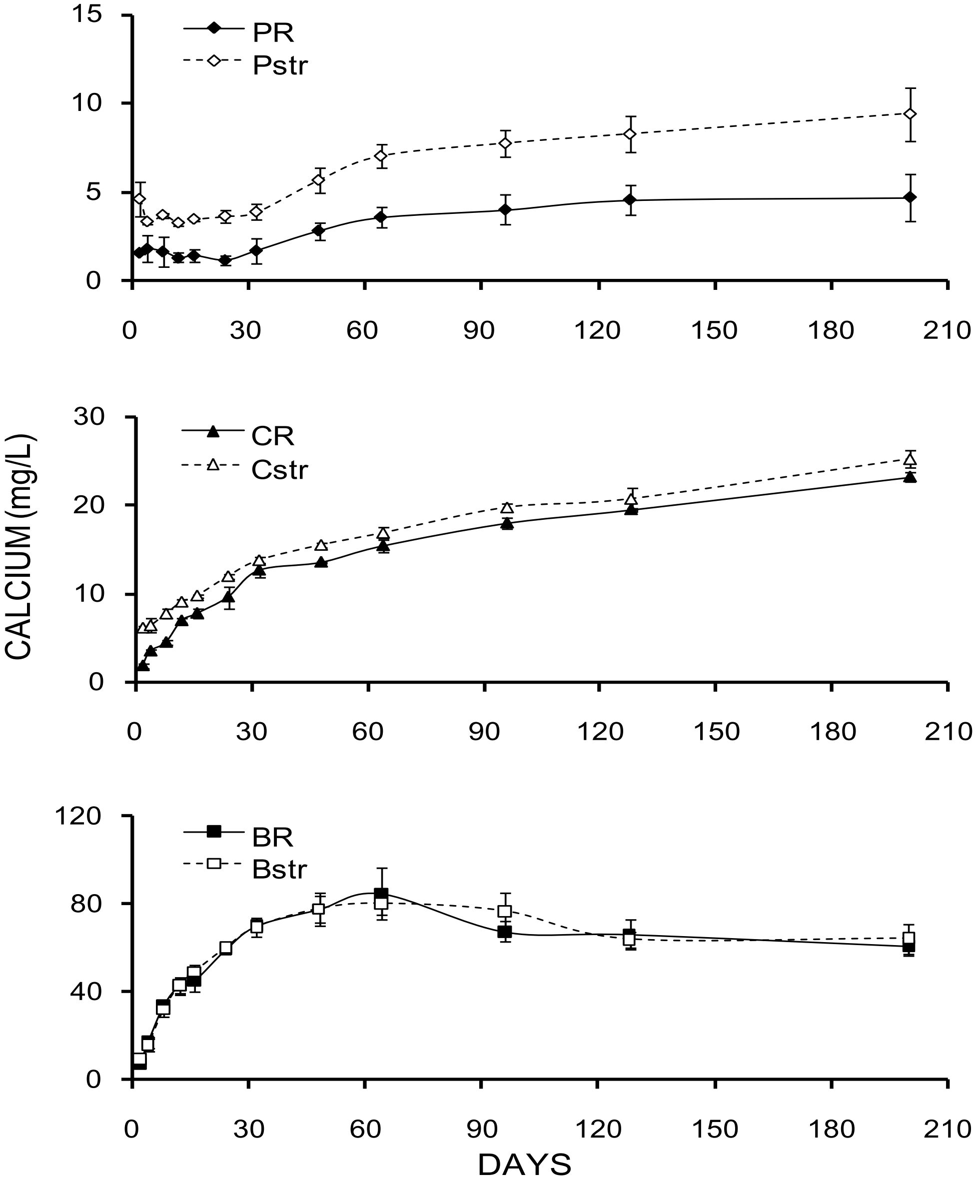

Figure 3. Calcium concentrations in different soil-water systems from December 2008 through July 2009. Abbreviations see Figure 1.

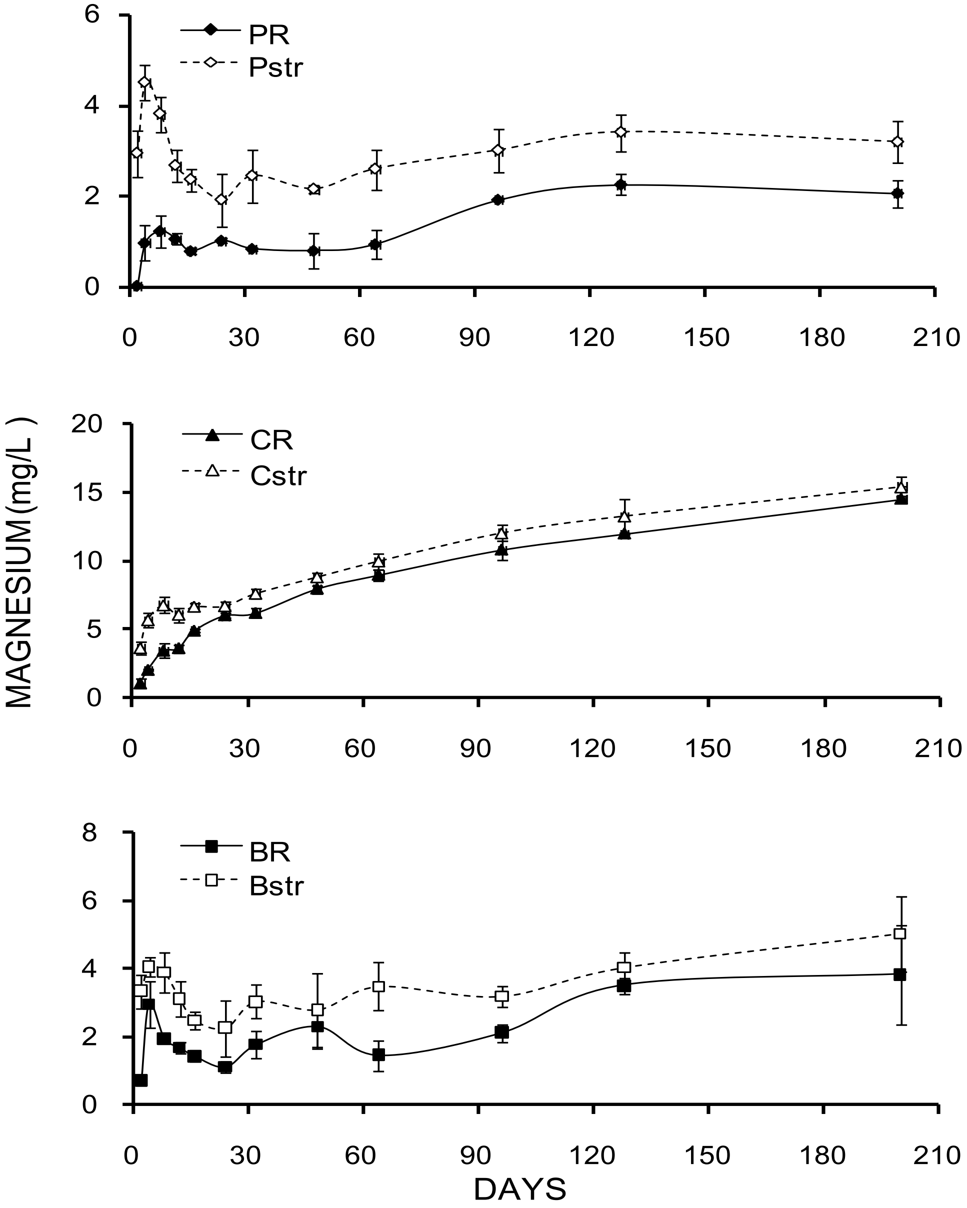

Figure 4. Magnesium concentrations in different soil-water systems from December 2008 through July 2009. Abbreviations see Figure 1.

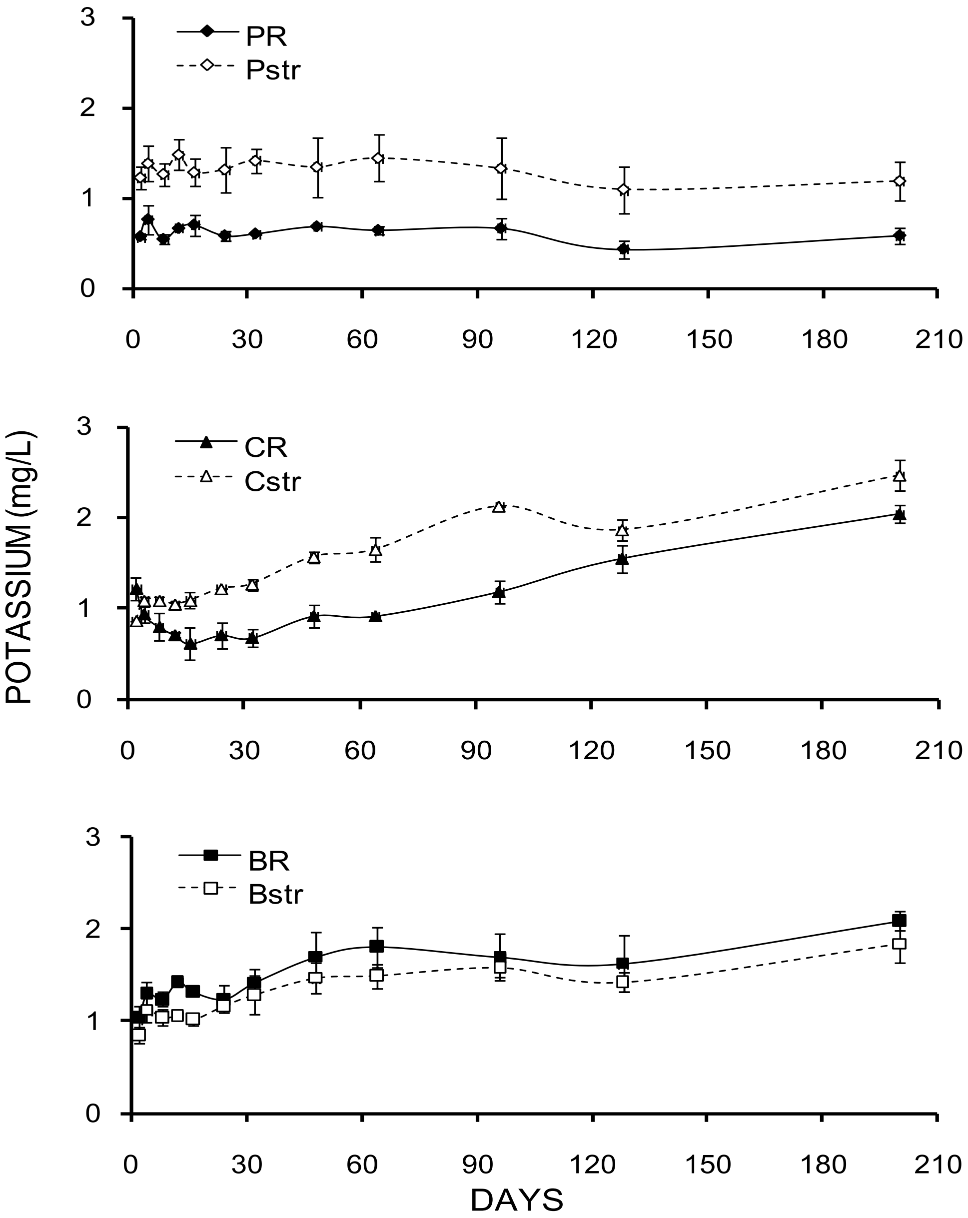

Figure 5. Potassium concentrations in different soil-water systems from December 2008 through July 2009. Abbreviations see Figure 1.

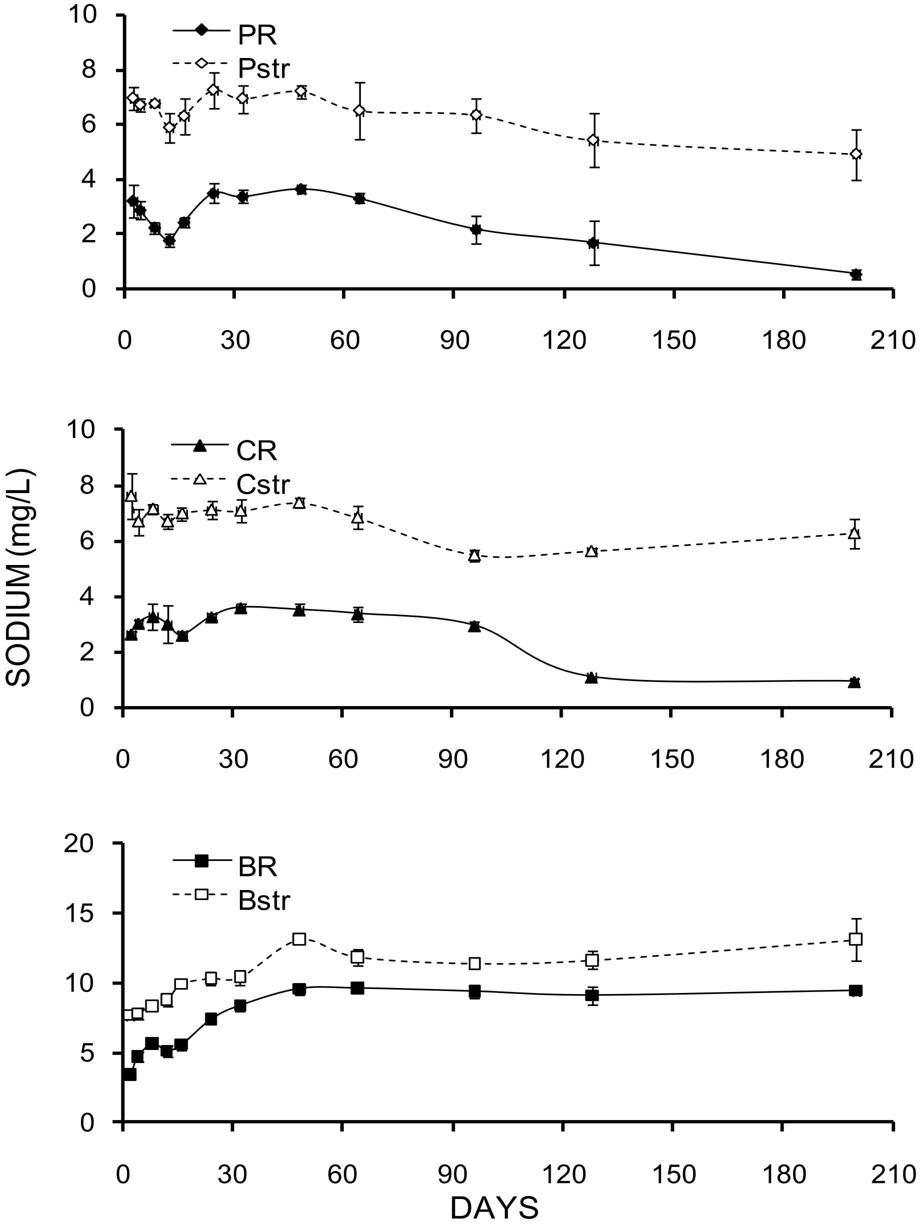

Figure 6. Sodium concentrations in different soil-water systems from December 2008 through July 2009. Abbreviations see Figure 1.

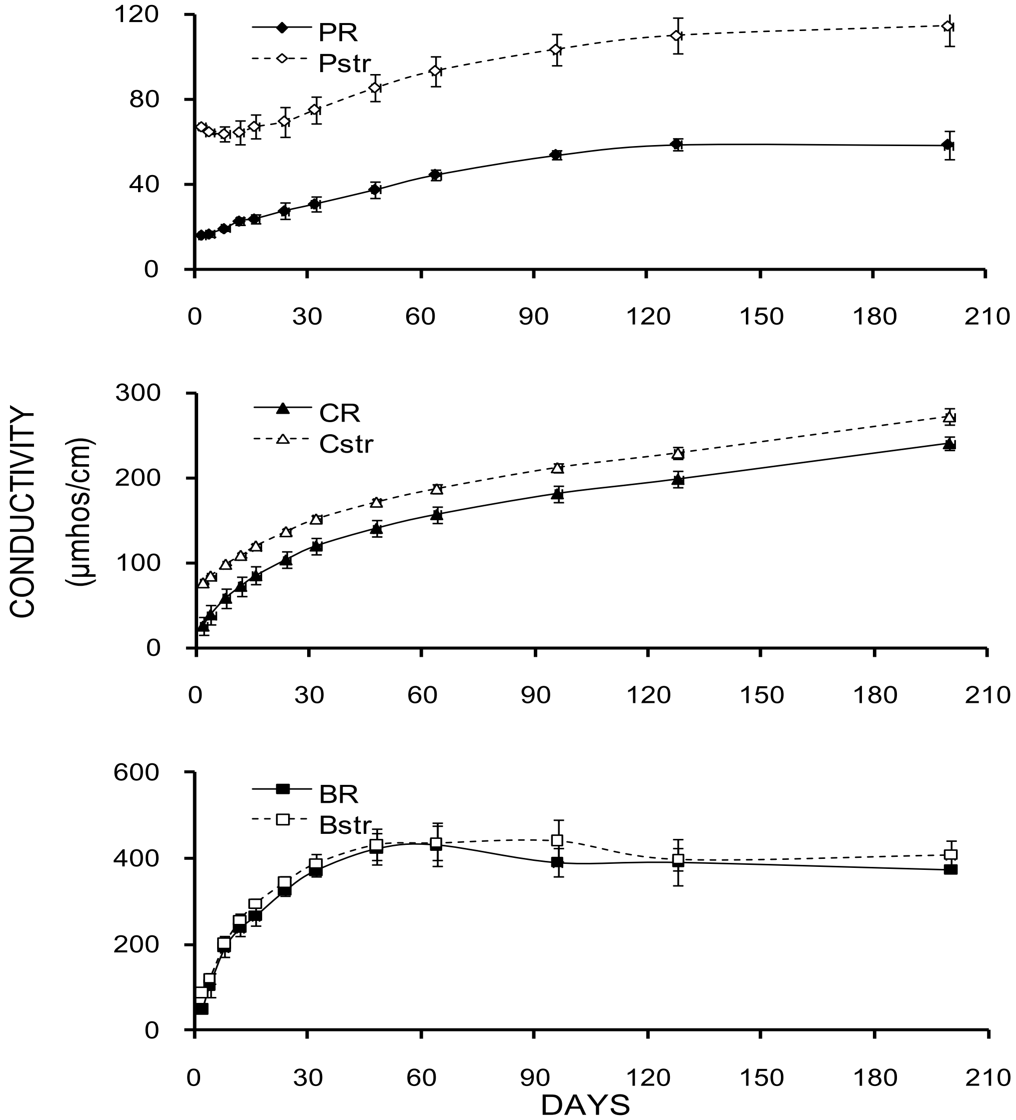

Figure 7. Conductivity in different soil-water systems from December 2008 through July 2009. Abbreviations see Figure 1.

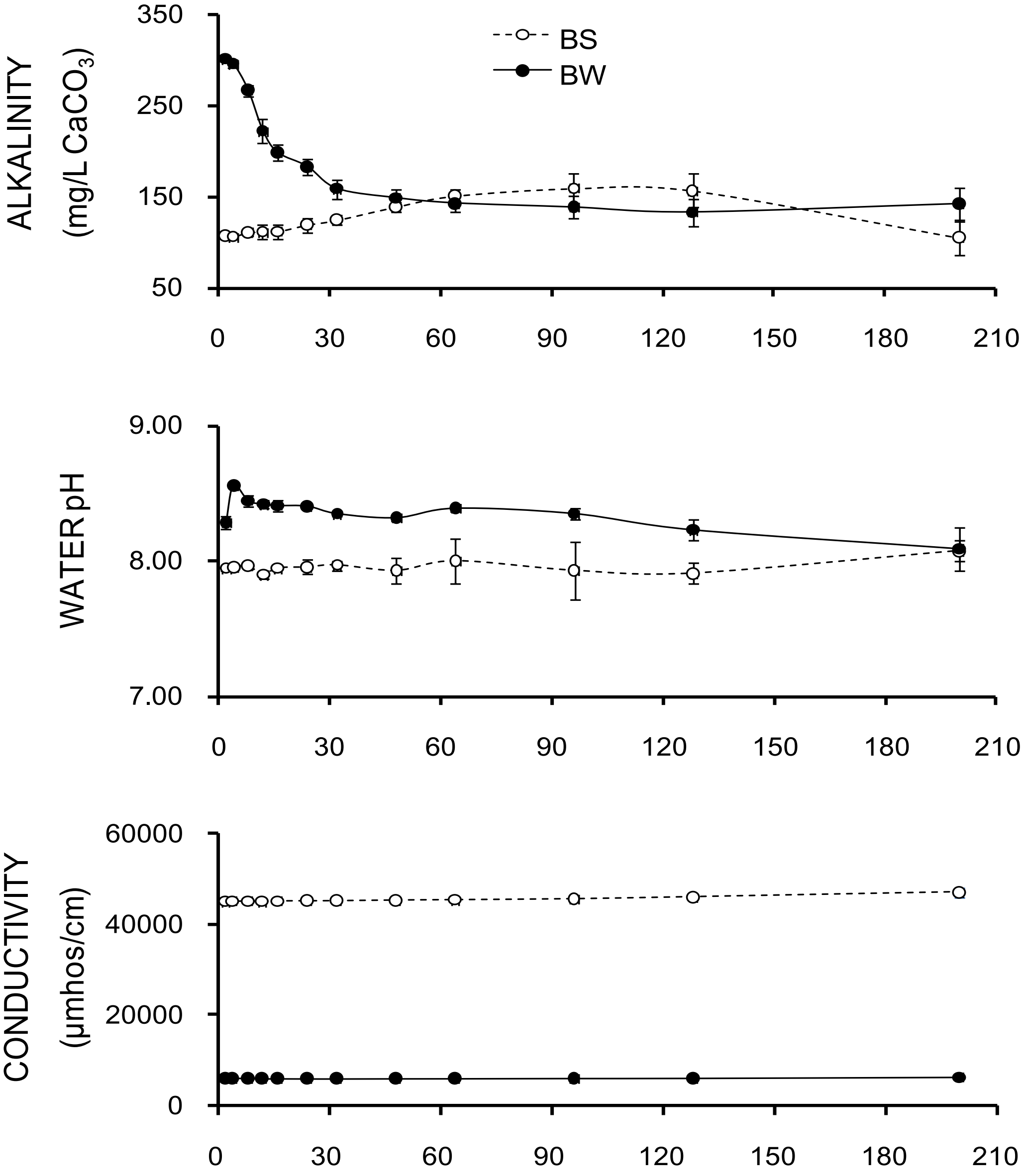

Figure 8. Alkalinity, conductivity and pH in saline well water and sea water which stood in contact with Blackland Prairie soil in the mesocosms from December 2008 through July 2009. BS=Blackland Prairie soil and sea water; BW=Blackland Prairie soil and well water.

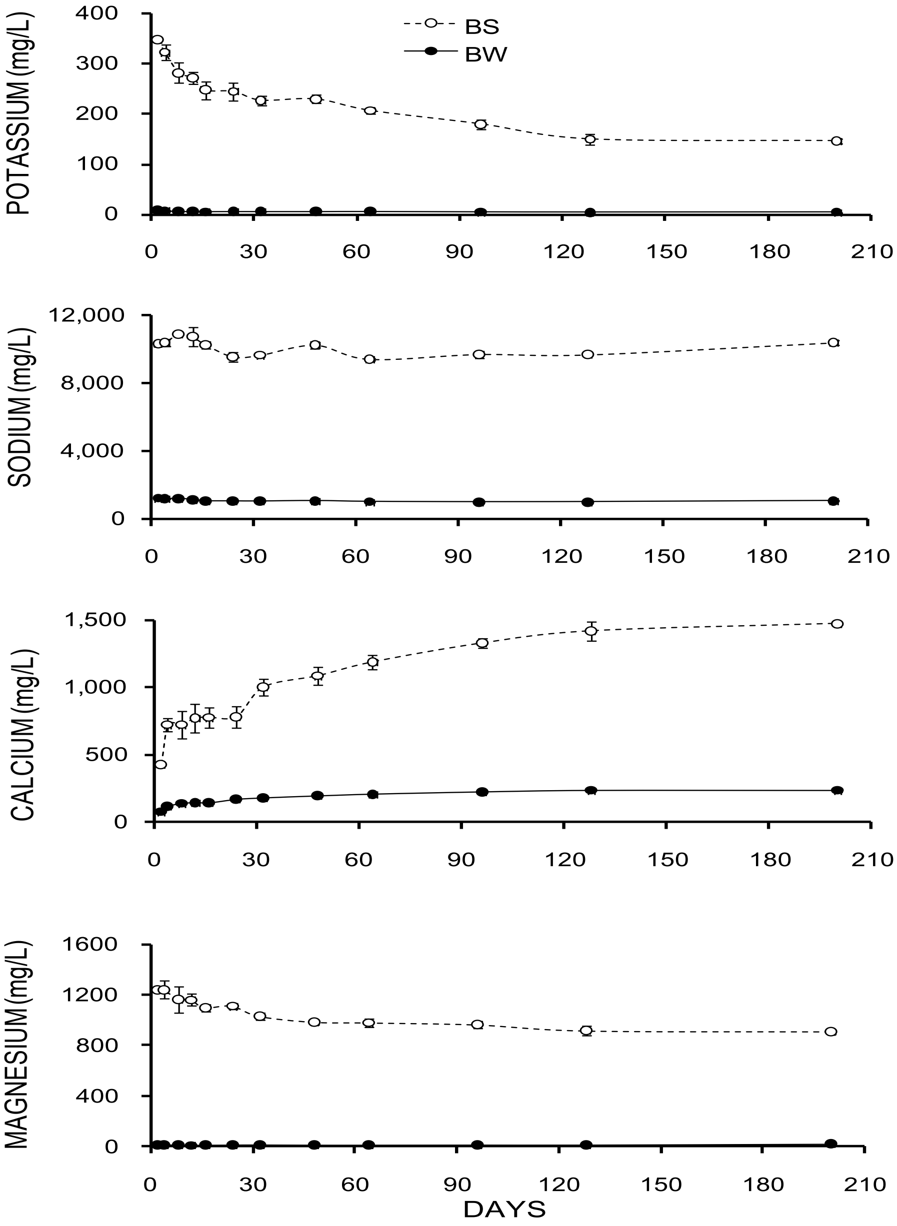

Figure 9. Potassium, sodium, calcium and magnesium concentrations in saline well water and sea water which stood in contact with Blackland Prairie soil in the mesocosms from December 2008 through July 2009. Abbreviations see Figure 8.

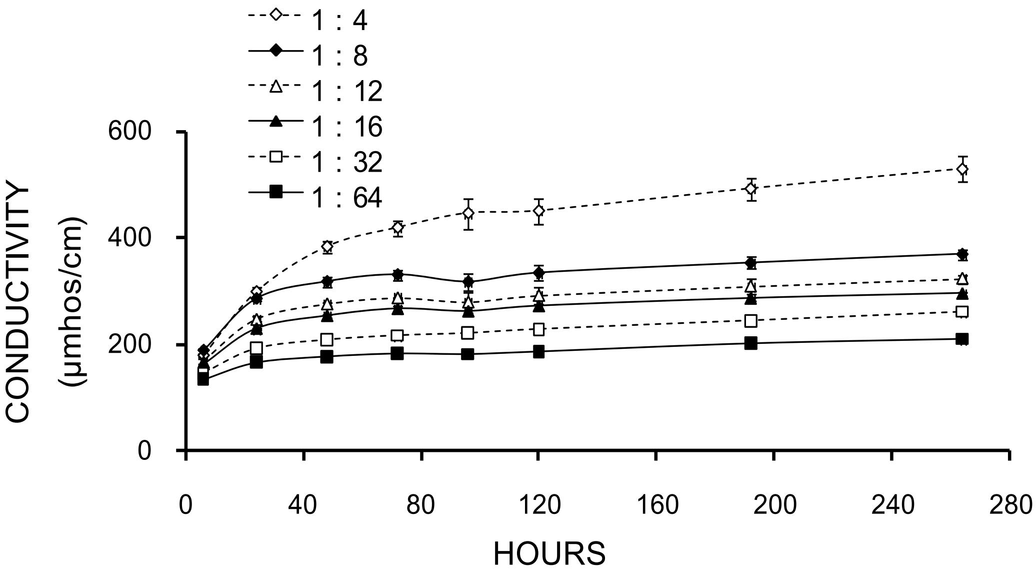

Figure 10. Conductivity of the stream water exposed to Blackland prairie soil with different soil: water ratios agitated on the table shaker for 264 hours.

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