FINAL REPORT

Integrative Approach to Understanding the Causes of Salt Marsh Dieback: Experimental Manipulations of Hydrology and Soil Biogeochemistry (Task II.2)

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Abstract

The purpose of this study was to simulate the effects of increased drought, caused by both decreased frequency of tides and lack of rainfall, on biogeochemical properties across clay, organic and sandy salt marsh soils. Strong patterns were observed for some soil characteristics, but they were inconsistent across soil type, tidal frequency, and influence of precipitation. But there was a distinct pattern of decreased marsh biomass as tidal frequency and precipitation decreased, indicative of increased stress with drought conditions. Based on this observation, it is assumed that some soil characteristics associated with changes in hydroperiod across clay, organic and sandy soil types are linked to ecological response.

1) The organic soils exhibited lower soil salinity than clay and sandy soils, yet all three types demonstrated that reduced tidal exchange and lack of rain could increase soil salinity. The effect of tidal inundation frequency can increase soil salinity as predicted in our conceptual model of drought effects on vegetation; however, these salinities were not in the range sufficient to cause salt marsh mortality.
2) Redox values did increase with decrease in tidal inundation and no rainfall, suggesting that soils oxidation was enhanced with this hydroperiod condition associated with drought.
3) There were examples of soil fertility from decreased tidal frequency and more oxidized environment including elevated nitrates in sandy soil due apparently to nitrification; and the spike of ammonium in soils with less tidal inundation demonstrates the stimulation of ammonification linked to increased oxidation of soils..
4) The degree of oxidation in clay and organic soils under less frequent tidal inundations and no precipitation resulted in decreased levels of pyrite and higher concentrations of iron, all supporting the pyrite oxidation hypothesis associated with the drought of 2000.
5) Salinity increased and pH decreased as the tidal frequency was reduced from daily to monthly occurrences along with absence of precipitation. Yet the salinity peak occurred in the sandy soils, whereas the lowest pH values occurred in the clay soils. pH was more sensitive to treatments than salinity; and there was more response in the clay and organic soils for pH and none in sandy. In contrast, there was little change in salinity across hydroperiod treatments for clay and organic soils, compared to sandy soils.
6) Sulfide has strongest signal in 7-day tidal treatment while the strongest pH signal was in the 30-day tidal treatment. Yet the soil difference is consistent for both pH and hydrogen sulfide, with the strongest signal in the clay soils.
7) The patterns of manganese and zinc fit the oxidation hypothesis that under less frequent tidal inundation and no rain there would be reduced pH and more soluble ions. Lower pH values in clay, and to a degree in organic soils, resulted in increased solubility of Mn and Zn demonstrating that this could particularly be a mechanism of marsh stress in the field.
8) Sandy soils did not exhibit such a strong shift in pH or change in metal concentration with increased soil oxidation; yet it had the highest increase in soil salinity with decreased tidal inundation and rain frequency.
9) The rain effect could be reducing the oxidation potential by filling pore space in between the tidal occurrences, thus reducing the negative effects of decrease in tidal frequency.
10) The greenhouse studies confirm that soil biogeochemistry can be strongly controlled by the degree of water deficits driven by decreased tidal inundation frequency and precipitation inputs, which increases soil oxidation potential.

Introduction

Restoration ecology includes the development of diagnostic capabilities for ecological systems that are based on ecological theory of succession and ecosystem development. These diagnostic capabilities are presently limited by the ability of scientists and managers to: 1) anticipate ecological responses of ecosystems to specific manipulations or site conditions; 2) monitor responses of ecosystems at sufficient space and time scales to validate these responses; and 3) modify operations of rehabilitation projects according to the response of ecosystems to obtain specific goals. One of the most difficult tasks in restoring ecological systems is to first perform diagnostics as to what factors are responsible for deteriorating conditions (or health) of the ecosystem. Better early diagnostics would allow managers to select the proper set of conditions for site manipulations necessary to rehabilitate habitats toward a specifically defined goal. Thus, a fundamental need of restoration ecology is cause and effect research leading to development of diagnostic tools that can be used to predict, monitor, and validate the response of ecosystems to rehabilitation criteria. This report focused on what caused the dieback of salt marsh communities in the Barataria-Terrebonne estuary known as 'brown marsh' phenomenon.

There was widespread dieback of salt marsh in coastal Louisiana in spring and summer of 2000 with estimations of nearly 100,000 acres of severely damaged area. An integrated science program was initiated to support wetland restoration objectives and goals, with the purpose of testing the mechanisms that were proposed as responsible for the brown marsh phenomenon. Marsh damage during the severe drought over the last 12 months suggests that water levels have been below average in the coastal zone of Louisiana (Fig. 1). Land use changes that alter regional and local hydrology can lead to significant changes in flooding patterns (water logging stress), freshwater/saltwater imbalances (saltwater intrusion), and soil biogeochemical processes. These forcing functions negatively affect plant vigor and organic matter accumulation, leading to reduced soil formation in coastal wetlands. There are limited data available to evaluate the impact of water deficits brought about by a combination of drought and low river flow to changes in hydroperiod and biogeochemistry of coastal wetland soils. It is not understood how these types of dry conditions associated with La Niña climate disturbances can cause plant stress and wetland loss. This is somewhat due to our lack of basic information on the tolerance of salt marsh plants to a combination of potential stressors. Salt-water intrusion associated with the inland movement of isohalines to locations that seldom experience even low salinity conditions can explain diebacks in fresh water and intermediate marshes. But the unique trend in the brown marsh condition observed in summer 2000 was the stress to higher salinity vegetation in the salt marsh zone suggesting additional mechanisms beyond salinity stress. Brown marsh was unexpectedly most evident in Fourleague Bay, which is connected to discharge from the Atchafalaya River. And the most prominent trend is for the damage to first appear in more inland areas of the marsh, with less damage observed to fringe salt marsh zone.

The goal of the manipulative greenhouse experiments described in this report was to develop parameters that are needed to develop the HYMAR model that describes hydrology in coastal marsh wetlands to simulate the impacts of changes in river flow and precipitation on marsh die back. We examined selected soil biogeochemical processes and their responses to changes in marsh hydrology. The implications of these impacts to marsh elevation and long-term stability were evaluated relative to rehabilitation efforts. Mesocosm studies were used to optimize for both controllability and realism to distinguish between the complex interactions of hydroperiod (soil water deficits) and soil biogeochemical changes on marsh productivity (above and below ground) and stability (marsh elevation).

Conceptual Model of Brown Marsh Event

There have been several periods of distinctly low water levels occurring in coastal Louisiana since 1980/1981. Most recently such low water levels were observed in 1995/1996 and during January to August in 2000 based on monthly mean water levels at Bayou Rigaud, near Grand Isle in Barataria Basin, and Atchafalaya Bay at the Amerada Hess platform show (Fig. 1). A detailed comparison of monthly mean water levels, river discharge, precipitation/drought and mineral soil conditions for 1995/1996, 1999/2000 and the 10-year mean is shown in Figure 1. From October to February, monthly mean water levels at Bayou Rigaud near Grand Isle were similar for 1995/1996 and 1999/2000, but much lower than the long-term average. After February, mean water levels were lower in 1995/96 than in 1999/2000. The same pattern held at the Amerada Hess platform. Through April, river discharge was lower than the long-term mean but comparable for the two years. However, in 1996, discharge for May and June was quite high. Precipitation was lower than average for both 1995/1996 and 1999/2000. While the cumulative rainfall through June was comparable for the two water years, the pattern of rainfall was not. In 1999/2000 more than 80% of the rain between October and June fell in three major episodes, with almost no rain in the intervening time period. In 1995/1996 rain fell intermittently, and in small amounts through the similar time frame (Fig. 4).

In 1995/1996 water levels along the Louisiana Gulf Coast were lower for longer periods than in 1999/2000. No widespread die-back of the salt marsh was noted. This suggests that low coastal water levels by themselves did not contribute to the current die-back during the summer of 2000. Similarly, the absolute (cumulative deficit) amount of rainfall from October of one year to mid-summer of the next did not appear to contribute by itself to the die-back, again as evidenced by comparing 1995/1996 with 1999/2000. The most pronounced difference between the two time frames in terms of rain was that most rain during the die-back year occurred in a few, large events. In 1995/1996 there were more frequent rain events of shorter duration. This pattern shows up in the soil moisture deficit, calculated as the difference between Potential Evaporation and Actual Evaporation. When there is not enough soil moisture to meet demands of the potential evaporation, a soil moisture deficit can occur (Fig. 2). Taken as indicators of moisture stress only, and not as actual numbers, the deficit is greater in May, July and August of 2000 than in 1996.

Hydrology data measured in Old Oyster Bayou provides a data set to better understand water levels in an interior marsh site during summer 2000 (Fig. 3). Through this effort, we observed that marsh water levels since May 2000 are highly correlated with prolonged drawdowns occurring in response to westerly and northerly winds. The most extreme drawdown instance measured (-18 cm) lasted for several weeks, contributing to the stress of marsh vegetation due to lack of easily extractable water (Fig. 3). Preliminary analysis of the marsh water level data also suggest that water level decreases are in large part due to high rates of evapotranspiration (ET) with a slight recharge of groundwater during the nighttime hours.

Based on these observations, we propose the following a possible scenarios that were tested in the greenhouse mesocosm study:

1. Unusually high salinity water flooded the marsh. In the soil this salinity was concentrated/amplified to levels that were toxic because there were only three rainfall events of any significance. Without higher than average surface water salinities dieback would not have occurred even with the observed pattern of precipitation. The higher than usual salinities could have come from low river discharge, overall lack of rain and/or coastal upwelling.
2. Rainfall events in 1999/2000 were too far apart to sustain normal soil moisture or to provide recharge of water deficits associated with evapotranspiration. The lack of water may have caused plant stress, regardless whether soil salinities increased; and/or the lack of infiltrating rainwater allowed soil salinities to build up. The latter would have occurred even if surface water salinities had not been unusually high this year.
3. Drought induced changes in marsh hydrology caused normally anaerobic and reduced soils to become aerobic and oxidizing. Oxidation of pyrite (FeS_2) and other reduced metal sulfides lowers pH (increased acidity) and elevates levels of soluble metals especially Fe, Mn, and Al. These changes in soil biogeochemistry may have been significant enough to cause plant mortality.

This project focused on integrating hydrologic and biogeochemical processes that could potentially affect marsh productivity, and are likely to be modified by restoration and rehabilitation of coastal environments. Restoring geophysical processes is a key factor associated with site criteria to rehabilitate marsh ecosystems in coastal environments. We have identified geophysical processes associated with regional drought and low river flow as key site criteria that are responsible for brown marsh phenomenon. Thus the key forcing functions that will formulate the hypotheses of how biogeochemical processes maintain marsh stability (succession) include soil water deficits (change in hydroperiod), in concert with abiotic stressors (e.g. salinity, pH, metals, etc.). We tested how these biogeochemical processes, driven by changes in hydrology, could contribute to patterns of brown marsh.

Benthic animals play an important role in the oxidation of marsh soils, and also function in the breakdown of organic matter, the cycling of nutrients as well as toxicants, and enhance sediment deposition (e.g. Gunnarsson et al. 1999; Klerks et al. 1996; Klerks et al. 1997). The activities of these organisms also affect sediment and pore-water characteristics, such as sediment redox conditions and sediment organic content (e.g. Nates and Felder 1998). These benthic animals tend to be very abundant in marsh ecosystems, making bioturbation (the organisms' reworking and transport of detritus, sediment and water) a major process shaping environmental conditions for marsh plants. Therefore an accurate picture of the how redox reactions and soil biogeochemistry may influence the health of marsh vegetation must include the role of bioturbators. The proposed research will therefore have a component that investigates the interplay between specific hydrologic drivers, bioturbators, and the generation of plant stressors.

The HYMAN hydrology model that was originally developed for mangrove wetlands will be used to simulate marsh hydrology conditions of summer 2000 (Fig. 4, Twilley and Chen 1998).

This is a hydrology model that simulates the mass balance of freshwater and tidal inputs, and calculates porewater and surface salinity. The model explicitly includes transpiration and evaporation to better account for daily water loss. We used the HYMAN model to describe the sensitivity of soil water levels in inland wetlands associated with climate change scenarios in precipitation or evapotranspiration for the Gulf Coast region (Fig 4, right panel). There are several key forcings that control the accumulation of salt in the more inland areas of coastal wetlands (see conceptual model in Fig. 2). The first is the generation of water deficits caused by ET greater than recharge. Recharge can be supplied by three major sources: precipitation, upland seepage, or tidal inundation. The first one adds no salt to the marsh soil, thus existing salts are diluted. The second source usually is much lower in salinity, and thus adds minor salt to the wetland soil. The latter process can add additional salts to the hydrology budget, thus increasing soil salinities. The salinity of flood tides determines the amount of salt loading that will occur during the recharge event. In combination, water deficits followed by soil oxidation can also cause pH changes in porewaters during recharge. This model can also track the amount of oxidation of wetland soil by using porosity and water levels to calculate the amount of soil exposed to the atmosphere.

Under natural hydrology, the biogeochemistry of salt marsh systems is dominated by the anaerobic and reduced chemical condition of the soil. Sulfides are stable as long as the chemical environment is reduced, however these minerals are readily oxidized as described above. Both pyrite oxidation and jarosite formation yield large quantities of acidity, which if not buffered within the soil system, result in low pH's (<4) typical of acid sulfate soils. The lowering of water tables in die-back areas in response to the drought would provide an opportunity for these oxidation reactions to occur. However, the amount of acidity influencing the marsh plants is a function of both the amount of pyrite oxidized and the acid neutralization capacity of the soil. Therefore, the effects of hydrologic drivers on these soil characteristics were established in soils of different mineral composition.

METHODS

Experimental Approach:

Greenhouse studies were established to simulate different hydrologic functions that test the response of soil parameters to hydrologic drivers. Greenhouse marsh-tidal mesocosms simulated water drawdown and recharge to test the scenarios of marsh drought conditions. Scenarios were established to simulate different degrees of water deficits followed by different sources of recharge (either precipitation or tidal). Tidal recharge and precipitation were done following different durations of water deficits.

Three different soil types were tested (based on relative organic and mineral content) to characterize clay, organic and sandy characteristics. Buckets of intact sediment and plant sods were sampled from three different field locations to simulate the desired soil textures. Clay soil was represented by sods from Bay Junop (N 29 12' 15.9" N and W 91 03' 56.2") sampled on February 14, 2002; organic soil was represented by sods from Lake Felicity (N 29 20' 59.0" and W 90 24' 48.3") sampled on February 19, 2002; and sandy soil was represented by sods from

Elmer Island (N 29 17' 80.0" and W 90 06' 83.3") sampled on February 21, 2002. Buckets of sod were brought directly back to the experimental greenhouse facility at the UL Lafayette Center for Ecology and Environmental Technology (CEET). A mesocosm system was developed to control salinity and hydroperiod manipulations to test more specific scenarios on factors that contributed to brown marsh and to assist in model calibration. This mesocosm facility, which is a cooperative effort between UL Lafayette and USGS NWRC, provides a unique marsh/wetland greenhouse capability. Approximately 1 ha is enclosed in two large greenhouse-structures.

Mesocoms consisted of tidal platforms that simulated different hydroperiods in three soil types at two salinity ranges. These platforms contained buckets (23 L, 48 cm deep) situated on top of a 190 L-reservoir. Seawater was pumped from the reservoir to individual buckets using a splitter. Tidal amplitude was controlled independently in each bucket by two concentric pipes that drained water back to the reservoir once the pumps were turned off. The depth of saturation was controlled by the depth of holes in this central drain pipe. Timers controlled inundation frequency and duration by turning on and off the pumps on a daily pattern. Air temperatures in the greenhouse were maintained above 8 C and within 2 C of the high summer temperatures. Light within the greenhouse was 53% of the ambient solar energy.

This tidal microcosm system was designed to study different durations of lowered water levels and source of pore water recharge. Water levels were lowered to –20 cm in each bucket and duration treatments consisted of one-day deficit (control), recharge after 7 day-deficits, and recharge after 30 day-deficits to simulate varying strength of drought conditions. At the end of each period, the 7-day and 30-day tidal treatments were recharged either by precipitation (freshwater), or tide (saltwater at salinity treatment level). These duration and recharge treatments were operated at two salinities: 15 and 30 g/kg. Three types of marsh soil covering the range of soil types identified in brown marsh areas were tested including sandy mineral, clayey mineral, and organic. This three by two by two by three factorial design was replicated three times for a total of 108 experimental units.

The mesocosm study was operational by 23 April 2002, with nearly one month of acclimation as salinity adjustments were made at a rate of 10 g/kg per week. Sampling dates of greenhouse study included 21 May, 18 June, 16 July, 13 August, and 23 September 2002. Results are the means of these five sampling dates. This experimental design tracked changes in soil biogeochemical parameters (redox, regulators, resources, and metals) under different scenarios of soil water deficits and recharge in three contrasting soil types. These parameters were selected as the most relevant drivers associated with the summer 2000 drought. Routine parameters monitored in the soils of each treatment included pore water salinity and nutrients (NH_4, NOx, SRP, Si), soil redox, pH, water levels, We measured soluble levels of iron, manganese, and aluminum in each bucket, along with copper, zinc, cadmium, lead, nickel, chromium, calcium, and magnesium. We also measured two other extractable forms of iron (oxalate extractable and citrate-dithionite extractable iron) that may reveal current, or in the case of on-site measurements, past changes in pyrite chemistry affecting pH and the chemistry of three abundant soil metals (iron, manganese, and aluminum) that can become phytotoxic under certain conditions. In addition, we examined treatment effects on possible changes in the levels of two iron minerals, pyrite and jarosite. Measures of plant response included above and below ground biomass.

Bioturbation Experiment

Since bioturbation by itself is not a plant stressor (bioturbation is intense in healthy marsh ecosystems), the extent to which bioturbation or lack thereof contributes to the generation of plant stressors was not tested by itself but only in combination with the other experimental variables. Since it was not feasible to assess the influence of bioturbation for the full set of treatments (2 bioturbation regimes, 3 drought durations, 2 salinities, 2 recharge rates and 3 soil types), this experiment was limited to 5 of the treatments used in the main part of the research. The experiment used 2 bioturbation levels (1 fiddler crab, *Uca pugnax*, added per microcosms or no crab added). The experimental set-up will otherwise be the same as for the other experiments. Microcosms were carefully checked before the start of the experiment to make sure that no other large bioturbators were present in the microcosms, and were checked at 3-day intervals to verify continued presence of *U. pugnax*. Crabs were replaced with new ones if crab mortality occurred. Experimental endpoints were the same as those used in the rests of the project.

Analytical Methods:

A permanently installed tube was placed to 5 and 15 cm depth in each mesocosm (bucket). The top of the sampling tube was sealed when not in use to prevent gaseous oxygen from diffusing down into the marsh soil. The outside diameter of the rigid, inert (plastic) tube is about 5 mm. The lower end was sealed, then, many small holes were drilled into the side of the tube over the bottom 2 cm. Two or three layers of cheesecloth were wrapped over these holes and then a layer of fine mesh nylon (as in nylon hose) was tied over the cheesecloth. The sampling tube was permanently installed by pushing the lower end to the desired depth in the marsh soil. The tube permitted pore water sampling in a saturated zone. To collect a sample, a 50-ml plastic syringe was connected to the upper end of the tube and a short dowel stick used to keep the plunger pulled back in the syringe created a partial vacuum in the sampling tube. Soil pore water from the saturated zone was drawn into the tube and collected in the syringe barrel. The nylon and cheesecloth prevented most soil solids from being drawn into the tube, and the turbidity in the sample was easily removed by filtering the sample through a disposable 0.45-micron filter attached to the syringe. Forcing the sample through the filter resulted in a clear sample for salinity, metals, nutrient and hydrogen sulfide analyses.

For the "Control" hydrology treatment, these measurements were made weekly. Thus 4 measurements were made per month. For the "7-day drawdown" treatment (drainage, or simulated water table lowering), these measurements were made from fluid collected from the saturated zone one day before the reflooding event, and then repeated two days after the reflooding event. Thus 8 measurements were made per month or 28-day cycle. For the "28 or 30 day-drawdown" treatment, measurements were made weekly during drawdown, except one day before and two-days after a reflooding event.

Soils were sampled twice during the study to encompass the annual extremes in relatively more reducing and more oxidizing conditions resulting in changes in soil acidity (Feijtel et al., 1988). Sulfur fractions, particularly acid volatile sulfides and pyrite, were quantified in the 0-10-cm and 20-30-cm depths following the technique of Nriagu and Soon (1985). Oxalate extractable and citrate-dithionite extractable iron was also quantified at the same depths using standard methods (Wieder and Lang, 1986). Soil alkalinity and their acid neutralizing capacity were also determined. Electron microscopy and x-ray diffraction were used to identify pyrite and jarosite minerals in the soil. Interstitial waters were sampled at 4-week intervals for soluble Fe, Mn and Al, Cu, Zn, Cd, Pb, Ni, Cr, Ca, Mg, and pH using standard methods (American Public Health Association, 1992). Data were collected at the same two depth intervals Eh was measured with Pt electrodes at 5 cm and 20 cm.

Sulfide concentrations were assayed with a LAZAR Model IS-146 sulfide-sensing electrode. Salinity was determined using a portable Labcomp Instruments model SCT (salinity, conductivity, and temperature) analyzer. Inorganic nutrients from pore waters were assayed on a LACHAT autoanalyzer. Phosphate contents were determined by colormetric analysis using the molybdate test (USEPA 1982). Nitrate and ammonium were measured using methods of the American Public Health Association (1992).

Dried soil samples were ground with a Wiley Mill through a 40-mesh stainless steel screen and stored in air-tight containers. Total P in sediment subsamples were analyzed colormetrically (U.S. Environmental Protection Agency 1982) following acid digestion with H_2O_2 and H_2SO_4 (Allen et al. 1974). Carbon and N were determined with Carla-Erba CHN-2400 elemental analyzer. Samples were combusted at 950 °C converting all forms of carbon and nitrogen to carbon dioxide and nitrogen gas, respectively. Organic content was determined by combusting each sample at 375 C for 24 h (Allen et al. 1974).

RESULTS

Pore Water Regulators

Salinity

Salinity values ranged from 8 to 22 g/kg among hydroperiod treatments in the 15g/kg salinity mesocosms, and results were similar between the 5 and 20 cm depths (Figs. 6 and 7). At 5 cm there was a strong difference among soil treatments with lower salinities in organic soils (clay and sand had similar salinities), slight reduction in salinities with daily tidal inundations, but no effect from rainfall. There were no effects among the interactions, indicating that the trends with soil treatments were consistent across hydroperiods. Salinities in organic soils were slightly lower at 20 cm, there was greater tidal effect, but the most significant difference at deeper horizons was the reduced salinities with rainfall treatments, particularly for the clay soils. The difference between the rain and no rain treatments resulted in nearly 10 g/kg difference in salinity in clay and organic soils, particularly in the 7 and 30 day tidal treatments. And this difference was due to salinities increasing with lack of rain above those in the daily tidal system, and not due to reductions in rain that may dilute salt content. In summary, the most apparent treatment effects of soils and hydroperiod in the low salinity treatment were observed at the 7 and 30 day tides in both the clay and organic soils. Yet all salinities in this lower salinity treatment remained below 20 g/kg during the study.

Trends in porewater salinity in the higher salinity treatment (30 g/kg) exhibited a larger range of values from 21 to 42 g/kg (Figs. 6 and 7). Patterns between 5 and 20 cm were similar, but more pronounced in the latter. Based on measures at 20 cm, peak salinity occurred in the sandy soils with 30-day tides and no rain. Within the other two soil types, this treatment combination caused the highest soil salinity, and significant difference to paired treatment with rainfall (the latter treatment remained near 20 g/kg). As observed for the lower salinity treatment, organic soils in the higher salinity treatment generally had lower values in the rainfall treatments.

Redox

Trends in redox measures are based on flooded conditions following the reintroduction of tidal water following the respective tidal frequency treatments (eg. Following 30 days without a tide). This reflects the conditions at which the other porewater samples were taken and described below. Measurements were also taken while buckets were being drained following this tide and after the soils had been drained (results not reported here). None of these redox values have been standardized for pH 7.

All mean redox values for salinity, hydroperiod and soil treatments were above zero. There was a distinct pattern of elevated redox conditions in the buckets without precipitation as the frequency of tides decreased (Fig. 8). This was particularly true for the clay soils in both the low and high salinity experiments. The difference in redox among the precipitation treatments was highest in the clay soils during the 7-day tidal treatment, compared to the 30-day tides in the organic soils. Sandy soils did not exhibit this difference in redox between the precipitation treatments among the 7 and 30-day tidal treatments, with the exception of the 30-day tide in the low salinity treatment. In most cases, there was not significant difference in redox between the precipitation treatments in the 1-day tide experiments.

pH

Porewater pH values in the low salinity treatment ranged from 8.3 to 4.5 at 5 cm measurements compared to a range of 8.0 to 3.4 at 20 cm depth (Figs. 9 and 10). At both depths there was a basic trend of little variation in pH in sandy soils among hydroperiod treatments, and minimum pH in the 30-day tidal treatment with no rainfall input. At 5 cm depth, the 1 and 7 day tides had similar pH among the two rain treatments, compared to 20 cm depth where both the 7-day treatment exhibited the same effects on pH as the 30-day effect in absence of rain. Daily tidal inundation exhibited little difference in pH with or without rain, yet there was a strong difference in pH across soil types for this combination of rainfall treatments at daily tidal regimes, particularly at 20 cm. At this depth, clay soils with daily tidal inundation had pH of about 5.5 compared to 6.2 for organic soils and 7.8 for sandy soils. Again, given a 30-day tide and no rain these reference pH values dropped by 2 pH units in organic clay soils, nearly 3 pH units in organic soils, compared to no significant change in sandy soils.

The higher salinity treatment, 30 g/kg, had similar patterns in pH as observed for the lower salinity treatment. pH values were generally higher at 5 cm depth than 20 cm; and there was very little change in pH in sandy soils among the treatments. There were some more pronounced changes in pH in the clay and organic soils among the 7 and 30-day tidal treatments with different rainfall events at 20 cm. At this depth, the daily tidal treatments in both clay and organic soils had pH of about 6.4, compared to 7.8 in sandy soils. Both the 7 and 30-day tidal frequency without rain caused pH to drop to 3.4 in clay soils and 4.3 in the organic soils. The pH of rain treatments for the 30-day tide was <5.0 in both the clay and organic soils.

Sulfide

Sulfide concentrations were very low (near limits of detection) in nearly all of the samples taken at 5 cm for both the low and high salinity treatments across all of the soil types and hydroperiods (Figs. 11 and 12). In contrast, there were several significant concentrations of hydrogen sulfide measured at 20 cm in both the 15 and 30 g/kg salinity treatments. In the 15 g/kg treatment, sulfide ranged from nearly undetectable to 8 ppm, with peak concentrations occurring in the 7-day tidal frequency with rain in both the clay and organic soils. Sulfide in sandy soils did not exceed 2 ppm during any of the hydroperiod treatments. The 30-day tidal treatments, with and without rain, had sulfide concentrations below 2 ppm, and were thus similar to the 1-day tidal treatment in sulfide concentrations. The 30 g/kg salinity treatment exhibited the same general pattern, with highest sulfide concentrations occurring in the 7-day tidal treatments with rain, although without rainfall treatment also had higher concentrations than the other hydroperiod treatments. Sulfides were <2 ppm in all the hydroperiod treatments in sandy soil. The difference was lower sulfide concentrations in clay soils with 7-day treatment (this was highest concentration in the 15 g/kg treatment), and higher concentrations in the 1-day tidal treatment in the clay and organic soils than observed in the 15 g/kg treatment. This was particularly true for the no-rain treatment in the 1-day tidal treatment, with sulfide concentrations nearly 4 ppm compared to concentrations <2.5 in the 15 g/kg treatment.

<u>Pore Water Nutrients</u>

Nitrate

Nitrate concentrations were generally higher at 5 cm than 20 cm depth in the 15 g/kg salinity treatment across all the hydroperiods (Figs. 13 and 14). Most concentrations near the surface ranged from 40 to 60 µmol/L, which is high for most saltmarsh pore waters. At 20 cm, concentrations ranged from 15 to 100 µmol/L, with most concentrations <40 µmol/L in contrast to the surface samples. There was a distinct pattern at 20 cm that was not observed in surface samples, with elevated concentrations occurring in the 30-day tidal treatment without rain, particularly in the clay and sandy soils, although this pattern was also noticed in the organic soils. There was a three-fold difference in nitrate concentrations between rain and no-rain treatments in the 30-day tidal regimes for both clay and sandy soils. At the 30 g/kg salinity treatment, this pattern between the rain treatments with low tidal frequency was observed in some cases, such as clay and organic soils at both 5 and 20 cm depth, but not as strong a difference as observed at 20 cm in the 15 g/kg treatment. With one exception, nitrate concentrations in all the soil and hydroperiod treatments at both 5 and 20 cm were < 40 µmol/L, which was distinct from that observed at 5 cm in the 15 g/kg treatment.

Ammonium

Ammonium concentrations were generally <50 µmol/L for most of the soils across all hydroperiod treatmens in both 15 and 30 g/kg salinity regimes, with an exception to the no-rain treatments at specific conditions (Figs. 15 and 16). The no-rain treatment had peak concentrations of ammonium, at times reaching >150 µmol/L, under both 7 and 30-day tidal regimes in both the clay and organic soils. These high concentrations were not observed in the sandy soils for any of the salinity or hydroperiod treatments at neither the 5 nor the 20 cm depths. When peak concentrations occurred, they were similar in magnitude in both the 15 and 30 g/kg treatments,

Phosphate

Soluble reactive phosphorus (SRP) concentrations were generally <2 µmol/L for both the clay and organic soils across all hydroperiod treatments for both the 15 and 30 g/kg salinity treatments (Figs. 17 and 18). This is in contrast to the sandy soils, where concentrations generally exceeded 3 µmol/L in both salinity treatments, particularly the daily tidal regime (with and without rain). There was no consistent effect of rainfall among the sandy soil hydroperiod treatments.

Porewater phosphorus was also evaluated based on conductivity measures and patterns in Figs. 19 and 20 were different compared to results based on soluble assays that are reactive to molybdate in Figs. 16 and 17. The conductivity concentrations are within the same range as the chemically reactive forms (0.31 ppm is about 10 µmol/L), but the ranges among the soils in the 15 g/kg experiment are not significantly different (Figs. 19 and 20). There is no significant effect of soil, tide or rain treatments on either the 15 or 30 g/kg experiments.

Calcium

Calcium concentrations range from 200 to 300 ppm at 5 cm depth in 15 g/kg salinity treatment, with no pattern among soil or hydroperiod treatments (Figs. 21 and 22). Concentrations are more variable at 20 cm, with some concentrations reaching >400 ppm, particularly in the less frequent tides without rain. This pattern is more apparent in the 30 g/kg salinity experiments, where concentrations are higher (>300 ppm), and the 7 and 30-day tides with no rain have elevated concentrations, particularly at 20 cm in the sandy soil. Under 30-day tide with no rain, the mean calcium concentration in sandy soil was 900 ppm, nearly double the value in the treatments with rain. There is very significant effect of tide and rain treatments on calcium concentrations.

Magnesium

As expected, magnesium concentrations were higher with the higher salinity treatment. In the 15 g/kg treatment, there was some slight indication based on 5 cm deep samples of a pattern in magnesium concentrations with hydroperiod treatments in clay and organic soils. This pattern, with reduced concentrations in rain treatments with decreasing tidal frequency was significant based on 20 cm samples. This effect of rain associated with lower magnesium concentrations was most significant in the 30-day tidal event (both rain and tide had significant effects on concentration), particularly in the clay and organic soils, but also observed in the sandy soils. There was a slight increase in the treatments with no rain compared to daily tidal treatments; but the threefold difference with concentrations between the rain treatments was due to a decrease in magnesium concentration. This same pattern was observed in the 20 cm deep samples in the 30 g/kg experiment, yet the difference between rain treatments was much less (25% difference compared to 300% in the 15 g/kg experiment), and only rain had a significant effect compared to no effect from tide. Thus the longer duration among tides did not reduce magnesium concentration in this experiment as observed in the lower salinity experiment.

Porewater Metals

Iron

Iron concentrations were <2 ppm at 5 cm depth for both the 15 and 30 g/kg salinity experiments, and there was no pattern among treatments, with the exception of a slight spike in concentration in the 30-day tidal treatment in the clay soils (Fig. 25). Iron at 20 cm in both salinity experiments exhibited wide range in concentrations in clay and organic soils and lower concentrations in sandy soils (Fig. 26). The pattern in iron concentrations was not consistent among hydroperiod treatments in either the clay or the organic soils in both salinity experiments. In nine instances when there was a significant effect of rain within a tidal treatment, three exhibited lower concentrations with rain, whereas six had higher concentrations with rain. In the clay soils, higher iron concentrations occurred during the 7-day tidal event, whereas in the organic soil iron was higher in the 30-day tidal treatment. Iron exhibited the least consistent pattern among treatments of soil, tide and precipitation compared to other soil characteristics measured in this study.

Manganese

Concentrations of manganese were <0.5 ppm at 5 cm depth for organic and sandy soils in both the 15 and the 30 g/kg experiments (Fig. 27). Concentrations were higher in the clay soils, by a factor of three in some cases. Both salinity experiments had a repeated pattern with elevated concentrations in the 30-day tidal treatment, and within that treatment those soils without rain had higher concentrations than those with rain. This pattern was more evident at 20 cm depth for both salinity experiments, with very similar concentrations per treatment for both salinity regimes. The most prominent pattern in manganese concentration occurred in the clay soils, and again higher concentrations were observed in the 7-day and 30-day tidal treatments, and peak concentrations with both tidal treatments occurred in absence of precipitation input. In the clay soils the peak concentrations under the 30-day tidal treatment was 350% and 400% compared to the rain treatment for 15 and 30 g/kg salinity experiments, respectively. This pattern among hydroperiod treatments was observed in organic soils, but concentrations were much lower and similar to the sandy soils.

Copper

Ranges in copper concentrations were similar for the 5 and 20 cm depths for both the 15 and 30 g/kg salinity treatments across all three soils types (Figs. 29 and 30). There really was no significant pattern among the treatments of either salinity experiment, nor was there any significant difference among soil types. With few exceptions, concentrations were < 0.05 ppm.

Zinc

Zinc concentrations were generally lower at 5 cm (0.05-0.38 ppm) than at 20 cm (0.05-0.93 ppm) for both salinity experiments, and there was little discernable pattern within the more shallow depth (Figs. 31 and 32). At 20 cm, concentrations between the two salinity experiments were similar for each soil type, and concentrations were generally higher in the clay soils. In the clay and organic soils, zinc concentrations increased with less frequent tidal inundation for both the clay and organic soils, most striking in the former soil type. And within each tidal treatment, the soils without precipitation had higher concentrations than those with rain (Fig. 32). This pattern was particularly true for the 30-day tidal treatment in the clay soils where there was a four-fold difference in zinc concentrations between the two rain treatments, for both salinity experiments. Sandy soils had lower concentrations and there were no patterns across hydroperiod treatments.

Iron Extractions

Oxalate extractable iron (Fig. 33): There was an effect of tidal and rainfall treatments on the concentrations of oxalate extractable iron in the clay and organic soils in both salinity experiments; but no pattern was distinct in the sandy soils (Fig. 33). Of the eight pairs of rainfall treatments among the 7 and 30-day tidal treatments for the low and high salinity treatments, all but one showed a higher concentration in the no-rain treatment compared to soils with rain; but only four of those were significant, yet both of the 30-day effects were significant in the organic soils. Thus while there seems to be a trend for increased iron in the longer duration between tides with no rain, this is only particularly true for organic soils with 30-day durations.

The same trend was even more apparent for the citrate-dithionite extractable iron, again for only the clay and organic soils (Fig. 34). As described for the oxalate extractable form of iron, if we compared the eight pairs of rain treatments among the 7 and 30-day tides in the clay and organic soils for the low and high salinity treatments, we see that the no-rain treatment has a significantly higher concentration in six pairs, and in all pairs with 30-day duration between tides. The difference is stronger in the higher salinity treatment in both the clay and organic soils. Again there is no pattern in the sandy soils, yet concentrations are similar to range found in the clay and organic soils.

There are no significant patterns in the ratio of the oxalate and dithionite fractions of iron for either of the soils across salinity or hydroperiod treatments (Fig. 35). In fact, nearly all mean ratios are about 0.6 in the low salinity experiment and 0.4 in the higher salinity, except ratios in the latter are about 0.6 in the sandy soils. Thus sandy soils have very similar ratios for both salinity experiments.

There was a significant pattern in pyrite concentrations among the different types of soils across hydroperiod treatments in both salinity experiments (Fig. 36). The pattern was most obvious in the lower salinity treatment (15g/kg) with lower pyrite concentrations occurring as tidal frequency decreased and without precipitation across all three soil types. Pyrite was about 6.8 mg/g and 6.5 mg/g in the daily tidal treatments of the clay and organic soils, respectively, compared to about 3.8 mg/g in sandy soils. With tides occurring only once in 30 days and with no rain, pyrite concentrations decreased to 1.7 and 0.6 mg/g in the clay and organic soils, respectively, and to 2 mg/g in the sandy soil. This represented about a four-fold decrease in pyrite with increased oxidation potential of clay and organic soils, compared to only two-fold decrease in sandy soils. Pyrite concentrations were less in the daily tidal treatments of the clay and organic soils in the 30 g/kg salinity experiment; and while the decrease in pyrite with decreased frequency of tidal inundation and no rain was observed, the reductions were not as significant as observed in the lower salinity experiment. The lowest concentration in all three soil types across all hydroperiod treatments was about 2.5 mg/g, observed in the sandy soil in the 7-day tidal and no-rain treatment.

The degree of pyritization followed the pattern described for pyrite concentration: decreased values with decreased frequency of tidal inundation and no precipitation, particularly in the clay and organic soils in the lower salinity experiment (Fig. 37). There was a similar trend in sandy soils, but the differences among tidal and precipitation treatments were not significant.

<u>Biomass</u>

The biomass results reported here (Fig. 38) was part of a separate contract with DNR directed by Drs. Karen McKee of USGS NWRC and Irv Mendelssohn of LSU (personal communication). Results are reported here to complement the response of biogeochemistry patterns from salinity, soil and hydroperiod manipulations, and are preliminary interpretations to that effect.

Biomass was generally higher in the clay soils, followed by the organic soils and significantly less in the sandy soils following the six months of salinity and hydroperiod treatments (Fig. 38). In the 15 g/kg salinity experiment, there was a general trend of decreasing biomass with decreased frequency of tides, but this was not significant until the 30-day treatment in both the clay and organic soils. In that less frequent tidal inundation, there was also a significant effect of no rain associated with lower biomass levels. This was more evident in the organic than the clay soils. Biomass levels in the 30-day tidal treatment without precipitation in the organic soils were similar to biomass in all hydroperiod treatments of the sandy soil (about 15 g/pot).

Biomass patterns were similar in the higher salinity treatment. Biomass in the clay soils subjected to 1-day tidal treatment was similar between the two precipitation treatments at about 65 g/pot. And this was similar to results in the 15 g/kg salinity experiment for same combination of treatments. A significant difference was observed in the 30-day tidal treatment in the clay soils where the presence of rain resulted in biomass of about 80 g/pot, compared to only 10 g/pot in the treatment without precipitation. This eight-fold difference in biomass between precipitation treatments was the highest recorded among the tidal, salinity, and soil combinations. Organic soils also exhibited a significant decrease in biomass in the absence of precipitation with 30-day tidal frequencies, at levels similar to clay soils under same combination of tidal and precipitation treatments. Again, these lower biomass values in the clay and organic soils were similar to the values observed in the sandy soils. While biomass in sandy soils was generally lower than the clay or organic, there was a significant reduction in biomass in treatments without precipitation when subjected to 7 and 30-day tidal frequencies, in the higher salinity experiment.

DISCUSSION

The purpose of this study was to simulate, monitor and analyze the effects of increased drought, caused by both decreased frequency of tides and lack of rainfall, on biogeochemical properties across different types of salt marsh soils. Strong patterns were observed for some soil characteristics, but they were inconsistent across soil type, tidal frequency, and influence of precipitation. But there was a distinct pattern of decreased marsh biomass as tidal frequency and precipitation decreased, indicative of increased stress with drought conditions. Based on this observation, it is assumed that some soil characteristics associated with changes in hydroperiod across clay, organic and sandy soil types are linked to ecological response. Plant biomass in clay and organic soils decreased under drought conditions (no precipitation) as tidal frequency decreased to once per month. Under more frequent tidal inundations, or under presence of precipitation, these plant stress conditions were not observed. The most stressed condition, measured based on the deflection of biomass from reference conditions in daily tidal treatments was in the 30-day tidal treatment with no precipitation in clay soils. The challenge is to associate these changes in biomass, and degree of plant stress, to biogeochemical processes linked to hydroperiod conditions of tides and precipitation.

One of the hypotheses tested in this greenhouse simulation was that decreased frequency of tidal inundation, over several months, would concentrate salts and increase soil salinity. The organic soils exhibited lower soil salinity than clay and sandy soils, yet all three types demonstrated that reduced tidal exchange and lack of rain could increase soil salinity. The most pronounced effect was 30 days duration between tides without a rainfall event. This monthly frequency in tides amplified salinity of pore waters relative to salinity of tidal waters by 1.4 (30 g/kg increased to 42 g/kg), particularly in sandy soils. Thus the effect of tides and inundation frequency can increase soil salinity as predicted in our conceptual model of drought effects on vegetation. However, these salinities were not in the range sufficient to cause salt marsh mortality. It has been argued that measurements of soil salinity after reflooding the buckets following the duration of a water deficit period were not indicative of salinity conditions around the rhizosphere. This may be an artifact of our study to accurately measure the salinity that actually influences the physiology of salt marsh vegetation, as is presently evaluated in most wetland studies. Tissue analysis of ionic balance may be a better indicator of whether the plants experience salt stress in the different hydroperiod treatments.

The other hypothesis was that decreased tidal frequency along with absence of rainfall would increase the redox conditions of marsh soils. Redox values did increase with decrease in tidal inundation and no rainfall, suggesting that soils oxidation was enhanced with this hydroperiod condition associated with drought. Yet it should be noted that redox values for all reference conditions, daily tides with and without rainfall, were about 200 mv. Redox conditions were most sensitive to changes in hydroperiod in clay soils and very little difference in sandy soils. This may be related to effects of porosity on the degree of oxygen transport among the different soils types as tidal frequency decreases. It was apparent that the presence of rain had strong influence on transport of oxygen, or oxidation processes, by filling up pore space even in the absence of tides.

Soil Hydroperiod-Fertility Effects

One of the hypotheses in this greenhouse simulation of hydroperiod effects on soil biogeochemistry is that organic matter oxidation is enhanced with draining the soil pore spaces. The diffusion of oxygen in these pore space can promote the remineralization of organic matter and other chemical compounds. This could lead to fertility effect of the soil, by enhancing nutrient regeneration and other oxygen dependant processes. Nitrification is one of those soil processes that requires oxygen, and nitrate concentrations were highest in the low salinity experiments with less frequent tidal inundation. Elevated nitrates, at concentrations that are unusual for salt marsh soils, was observed in sandy soil that has increased porosity and thus air space for oxygen to diffuse. This spike in nitrate could result from nitrification, since in long tidal deficit with no rain there are conditions for oxygen to stimulate the conversion of ammonium to nitrate. This spike was observed in the clay and sandy soils, but not in the organic soils, which could be due to lack of available oxygen (organics consuming oxygen transported). This explanation would follow that the highest concentrations of nitrate should occur in sandy soils. But it is not apparent why this spike did not occur in the higher salinity treatment under long duration tidal and precipitation conditions. .

The spike of ammonium in soils with less tidal inundation demonstrates the stimulation of ammonification linked to increased oxidation of soils. Yet the soils with the highest nitrate concentrations had the lowest ammonium concentrations. Ammonification reflected by presence of ammonium in soils was in the organic soils, which represents a source of organic nitrogen. Sandy soils, with low concentrations of organic matter, had low ammonium even with the possibility of higher oxygen concentration. Yet where is the ammonium to drive the nitrification described above. So the ammonium values track the degree of organic remineralization in these soils – which is accelerated by the tide deficit and absence of rain. In absence of organic matter in sandy soils, this oxidation potential does not affect the biogeochemistry of soils. But the tidal deficit in absence of rain does elevate soil fertility in clay and organic soils, as reflected by the significant increase in ammonium concentration, and in sandy soil by presence of nitrate.

Patterns for phosphate in soils across the hydroperiod treatments does not support the oxidation of organic matter providing a pulse of nutrients to soils. In fact, the opposite was true – the sandy soil with the lowest ammonium has the highest phosphorus, as observed for nitrate. So the presence of organic matter and deficit of tidal water promoting oxidation potential holds for ammonium but not for phosphorus. This may be evidence that rainwater was enriched in phosphorus, since no-rain treatments had higher concentrations on several occasions. Yet independent measures of water source used for rainwater do not confirm this possibility.

Calcium and magnesium also had higher concentrations in soils with less frequent tidal inundations, but differed in the effects of precipitation. But like inorganic nitrogen, there was an opposite pattern for magnesium than calcium. The reference concentration, with daily tides and no rain, is the point that should be compared to determine source and sink term effects of hydroperiod conditions. For example, longer duration among tides and no precipitation, associated with increased oxidation of soils, was associated with an increase in nitrate and ammonium, as was observed for calcium. Thus there is some process that is representing a source in soil pore waters. For magnesium, concentrations under these tidal conditions were similar to the reference concentrations, but with rain and long tidal durations there was a decrease in concentration, opposite than observed in nitrogen and calcium. This sink term could be due to dilution of salts with little replacement from less tides and pore space occupied proportionally more by rainwater. In the daily tidal treatment with no rain the concentrations were about 1300 ppm. Yet as tides decreased in frequency, the concentration of magnesium remained >1000 ppm in absence of rain. In presence of rain, the concentration decreased, and this dilution was stronger with decreased frequency of tidal influence.

Soil Hydroperiod-Acidity/Pyrite Effects

Under natural hydrology, the biogeochemistry of salt marsh systems is dominated by anaerobic and reduced chemical condition of the soil. High plant productivity provides sufficient organic matter for facultative and obligate anaerobes to use Fe, Mn, and SO_4 as alternate electron acceptors during respiration. The reduction of sulfate to sulfide in the presence of metals produces a variety of reduced metal sulfides. Most salt marsh sulfides are dominated by pyrite (FeS_2) and mackinawite (FeS) (Pons et al., 1982). Sulfides are stable as long as the chemical environment is reduced, however these minerals are readily oxidized via an initiation reaction [1.1] and a propagation or catalytic reaction [1.2] (Singer and Stumm 1970):

$$FeS_2 + (7/2)O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad 1.1$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad 1.2$$

Subsequent reactions in high sulfate environments such as salt marshes can produce characteristic yellow mottle of jarosite :

$$6Fe_2(SO_4)_3 + 4OH^- + 4K^+ + 20H_2O \rightarrow 4KFe_3(SO_4)_2OH_6 + 10H_2SO_4 \quad 1.3$$

Note that both the pyrite oxidation and jarosite formation yield large quantities of acidity. If this acidity is not buffered in some way within the soil system, then low pH's (<4) typical of acid sulfate soils can develop. The lowering of water tables in die-back areas in response to the drought would provide an opportunity for these oxidation reactions to occur.

The degree of oxidation in clay and organic soils under less frequent tidal inundations and no precipitation resulted in decreased levels of pyrite and higher concentrations of iron, all supporting the pyrite oxidation hypothesis associated with the drought of 2000. The iron concentrations were higher in the higher salinity treatments and nearly equal between the clay and organic soils; yet the degree of pyrite oxidation seems to be much less in the higher salinity experiment and in the clay soils. Levels of pyrite were higher in the clay and organic soils compared to sandy soils, as expected, yet all three soils had pyrite oxidation potentials.

The response of pH to the hydroperiod treatments across each soil type support the occurrence of the processes described above under both high and low salinity experiments. Salinity increased and pH decreased as the tidal frequency was reduced from daily to monthly occurrences along with absence of precipitation. Yet the salinity peak occurred in the sandy soils, whereas the lowest pH values occurred in the clay soils. pH was more sensitive to treatments than salinity; and there was more response in the clay and organic soils for pH and none in sandy. In contrast, there was little change in salinity across hydroperiod treatments for clay and organic soils, compared to sandy soils.

Sulfide has strongest signal in 7-day tidal treatment while the strongest pH signal was in the 30-day tidal treatment. Yet the soil difference is consistent for both pH and hydrogen sulfide, with the strongest signal in the clay soils. So why does salinity, pH and sulfide all respond to combinations of tidal and precipitation effects, and thus degrees of drought, that are inconsistent among the three soil types. The difference in porosity among the soils, particularly the higher values in sand, could affect storage capacity of water and thus salinity. The organic content of soils can influence the pH capacity. And clay soils with higher concentration of pyrite may explain the difference in pH and sulfide production. These soil characteristics may also explain why the 7-day treatment had the highest hydrogen sulfide concentrations, while the 30-day treatment had the lowest pH. One explanation may be the continuous oxidation of soils during 30 days converted sulfide to elemental sulfur. These patterns suggest that 30-day tidal frequency has strong influence on salinity and pH effects, but actually minimizes the sulfide effects.

Soil Hydroperiod-Metal Behavior

The behavior of metals in the oxidation of soils associated with drought described above was also a key hypothesis tested using our soil mesocosm system. Metals may have played a role in the mass mortality of *Spartina alterniflora* during the 2000 drought. This role of metals may be direct (such as via metal toxicity) or indirect (for example, an effect of metals on sulfide behavior and thus sulfide toxicity, or an effect on nutrient availability). Metals could either be a sole factor in marsh die-off, though it is probably more likely that metals are among a variety of interacting stress factors. There are several potential mechanisms for metals to be involved in marsh vegetation mortality. Changes in salinity, pH and especially redox potential of marsh soil can change metal speciation and metal bioavailability.

In general, an increased salinity will result in a decreased uptake of metals as a result of an increased competition among elements at uptake sites. An increase in pH will generally lead to decreased metal uptake, as metals are less mobilized and less bioavailable under basic conditions. Sandy soils had the greatest increase in salinity, pH above 7 in all hydroperiod treatments. Clay soils, on the other hand, had strongest changes in pH and less change in salinity. The influence of changes in soil redox potential on metal bioavailability is rather complex, with the behavior of many metals being redox sensitive, effects of the redox potential not being unidirectional over the range of redox conditions, and effects differing among metals.

Iron and manganese are the elements whose behavior and speciation is most intimately tied to the redox potential of marsh soil (as reviewed in Ernst, 1990). Reactions involving these elements (as well as sulfur) have in turn a large influence on the behavior of other elements such as cadmium, copper, nickel and zinc. Various changes can occur as a function of changes in redox potential. E.g., both Fe and Mn will be more bioavailable to plants during periods with a low redox potential; Mn (IV) changes to the more bioavailable Mn(II), while the insoluble ferric form of iron (FeIII) will be reduced to the very mobile Fe(II) form. However, at very low redox levels, Fe (together with some Mn) will precipitate in the form of pyrite, resulting in a lowered

Fe and Mn bioavailability (Brennan and Lindsay, 1996). Other metals such as Zn, Cd and Pb tend to be present as carbonates or associated with Fe and Mn oxyhydroxides under oxic conditions, but these metals will precipitate as sulfides (and be less bioavailable) under anoxic conditions, while their solubility might again increase if conditions become even more anoxic and the solubility come under control by pyrite (Brennan and Lindsay, 1996). In soils collected from salt marshes, both Cu and Ni were found to be mainly associated with the pyrite phase, while Zn and Cr were mainly associated with the reactive and organic fractions. Under suboxic conditions, Cr, Ni, Zn, and Cu were associated with Fe and Mn hydroxides (Otero et al., 2000). These findings demonstrate that changes in redox potential can have drastic consequences for metal bioavailability.

Various metals may be responsible for the stress on *S. alterniflora*. Iron and manganese are logical choices because small changes in redox conditions can have a large influence on their bioavailability. Furthermore, manganese and especially iron can be found in close association with *S.alterniflora*, in the form of deposits on the plant's roots. These deposits, believed to be iron oxyhydroxides, also contain some Mn (Mendelssohn and Postek, 1982). Other research has shown that such deposits of iron oxides (at least in the case of *S. maritima*) are also enriched in other metals such as cadmium, copper, lead and zinc (Sundby et al., 1998). In addition to the perceived importance of iron and manganese, zinc, chromium and nickel are very common elements, and even under relatively pristine conditions can be present at levels not far below levels where toxicity can occur. Furthermore, speciation of chromium is strongly influenced by redox conditions and has a very pronounced effect on chromium toxicity (with Cr(VI) being much more toxic than Cr(III)). Selenium may also play a role in the marsh die-off. While selenium toxicity is generally associated with irrigation-water evaporation ponds and arid wetlands (Lemly et al., 1993), the extensive drought in Louisiana might well have created similar circumstances. There is recent evidence that *S. alterniflora* may be able to detoxify selenium by transforming inorganic selenium into dimethylselenoniopropionate, the latter being a precursor for the volatilization of the relatively nontoxic dimethylselenide (Ansede et al., 1999). However, the same study reported that high selenium levels could be toxic to *S. alterniflora*, especially when sulfate levels are low (Ansede et al., 1999).

The most compelling evidence for soil acidification and possible involvement in *Spartina* mortality is from the field where soils from dieback areas acidified upon oxidation, whereas those from control sites did not. The acidification phase in early spring could have been prolonged or exaggerated by drought conditions sufficiently to affect plants, either by acidity *per se* or by toxic metals released at low pH. Solubility of Fe, Mn, and Al increases several fold with decreases in pH, and may reach toxic levels (Gambrell and Patrick, 1978). Concentrations of pyrite and acid-extractable Fe and Al were higher in dieback soils compared to control soils, but were not different across zones within dieback marshes. This pattern suggests that if acidification and/or toxic metals caused plant mortality, hydrology or an associated factor ameliorated effects along shorelines where plants were frequently inundated by tides. Significantly higher leaf ratios of Fe:K and Al:K measured in dieback plants in 2000, but not 2001 are also consistent with this scenario. Acute dieback may have occurred mainly in saline marshes because of mineral input from rivers and greater accumulation of trace and heavy metals compared to intermediate and freshwater marshes with more organic substrates (Feijtel *et al*., 1988b). Saline marsh sediments also show greater decreases in pH upon oxidation (Feijtel *et al*., 1988a). Our findings thus suggest that soil acidification as a consequence of drought and low tide levels and release of toxic metals could have contributed to dieback of saline marshes in the MRDP. This hypothesis requires further testing, however, and experiments are currently underway to evaluate the relative tolerance limits of *S. alterniflora* and other salt marsh species to low pH and metals.

Copper did not show any trends associated with the oxidation and redox patterns across changes in hydroperiod.

The patterns of manganese and zinc fit the oxidation hypothesis of soil biogeochemistry under less frequent tidal inundation and no rain. This is the soil that has the greatest water deficit, and thus the highest oxidation potential. This resulted in the lowest pH values in clay, and to a degree in organic soils, as result of decomposition of pyrite as described above. The increased solubility of Mn and Zn in clay under these specific hydroperiod conditions in the greenhouse demonstrate that this could particularly be a mechanism of marsh stress in the field. Sandy soils did not exhibit such a strong shift in pH or metal concentration, yet it had the highest changes in salinity. The rain effect could be reducing the oxidation potential by filling pore space in between the tidal occurrences, thus reducing the negative effects of decrease in tidal frequency.

Conclusions

1) The purpose of this study was to simulate the effects of increased drought, caused by both decreased frequency of tides and lack of rainfall, on biogeochemical properties across different types of salt marsh soils.
2) Strong patterns were observed for some soil characteristics, but they were inconsistent across soil type, tidal frequency, and influence of precipitation.
3) There was a distinct pattern of decreased marsh biomass as tidal frequency and precipitation decreased, indicative of increased stress with drought conditions.
4) Plant biomass in clay and organic soils decreased under drought conditions (no precipitation) as tidal frequency decreased to once per month. Under more frequent tidal inundations, or under presence of precipitation, these plant stress conditions were not observed.
5) The most stressed condition, measured based on the deflection of biomass from reference conditions in daily tidal treatments was in the 30-day tidal treatment with no precipitation in clay soils.
6) The organic soils exhibited lower soil salinity than clay and sandy soils, yet all three types demonstrated that reduced tidal exchange and lack of rain could increase soil salinity. The most pronounced effect was 30 days duration between tides without a rainfall event.
7) The effect of tidal inundation frequency can increase soil salinity as predicted in our conceptual model of drought effects on vegetation; however, these salinities were not in the range sufficient to cause salt marsh mortality.
8) Redox values did increase with decrease in tidal inundation and no rainfall, suggesting that soils oxidation was enhanced with this hydroperiod condition associated with drought.
9) There were examples of soil fertility from decreased tidal frequency and more oxidized environment including elevated nitrates in sandy soil due apparently to nitrification; and the spike of ammonium in soils with less tidal inundation demonstrates the stimulation of ammonification linked to increased oxidation of soils..
10) Patterns for phosphate in soils across the hydroperiod treatments does not support the oxidation of organic matter providing a pulse of nutrients to soils.
11) Calcium and magnesium also had higher concentrations in soils with less frequent tidal inundations, but differed in effects of precipitation. The form may again support the effect of soil oxidation on soil biogeochemistry; the latter may be an effect of dilution as tidal frequency decreases in presence of rainfall.
12) The degree of oxidation in clay and organic soils under less frequent tidal inundations and no precipitation resulted in decreased levels of pyrite and higher concentrations of iron, all supporting the pyrite oxidation hypothesis associated with the drought of 2000.
13) Salinity increased and pH decreased as the tidal frequency was reduced from daily to monthly occurrences along with absence of precipitation. Yet the salinity peak occurred in the sandy soils, whereas the lowest pH values occurred in the clay soils. pH was more sensitive to treatments than salinity; and there was more response in the clay and organic

soils for pH and none in sandy. In contrast, there was little change in salinity across hydroperiod treatments for clay and organic soils, compared to sandy soils.

14) Sulfide has strongest signal in 7-day tidal treatment while the strongest pH signal was in the 30-day tidal treatment. Yet the soil difference is consistent for both pH and hydrogen sulfide, with the strongest signal in the clay soils.
15) These patterns suggest that 30-day tidal frequency has strong influence on increasing salinity in sandy soils and decreasing pH in clay and organic soils, but actually minimizes the effects of sulfide (which are highest in 7-day tidal treatments).
16) The patterns of manganese and zinc fit the oxidation hypothesis that under less frequent tidal inundation and no rain there would be reduced pH and more soluble ions. Lower pH values in clay, and to a degree in organic soils, resulted in increased solubility of Mn and Zn demonstrating that this could particularly be a mechanism of marsh stress in the field.
17) Sandy soils did not exhibit such a strong shift in pH or change in metal concentration with increased soil oxidation; yet it had the highest increase in soil salinity with decreased tidal inundation and rain frequency.
18) The rain effect could be reducing the oxidation potential by filling pore space in between the tidal occurrences, thus reducing the negative effects of decrease in tidal frequency.
19) The greenhouse studies confirm that soil biogeochemistry can be strongly controlled by the degree of water deficits driven by decreased tidal inundation frequency and precipitation inputs, which increases soil oxidation potential.

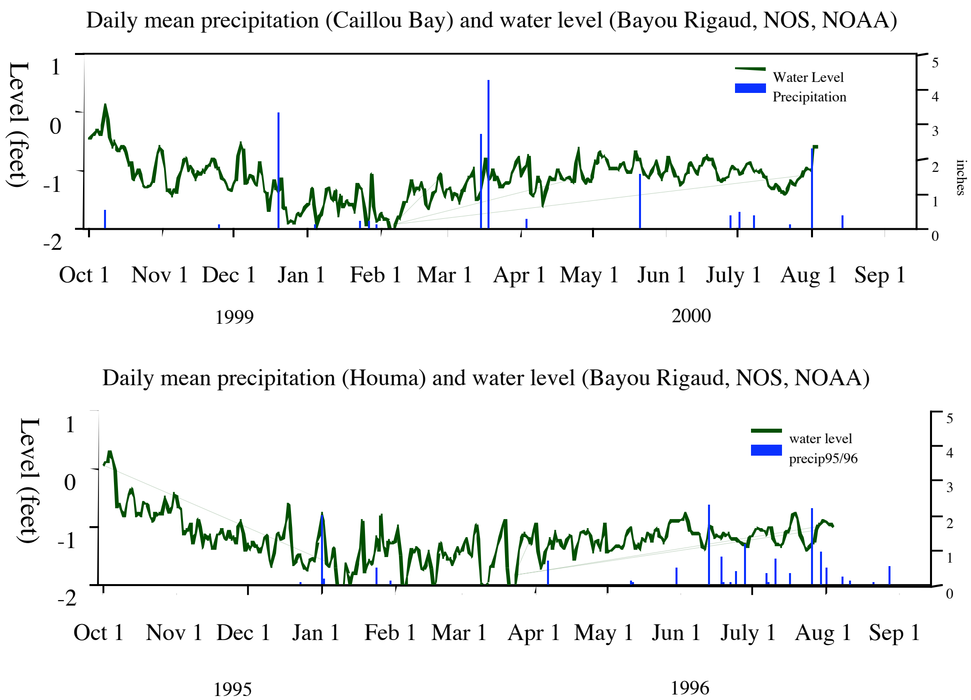

Figure 1. Comparison of daily mean precipitation and daily mean water levels for 1995/96 and 1999/2000.

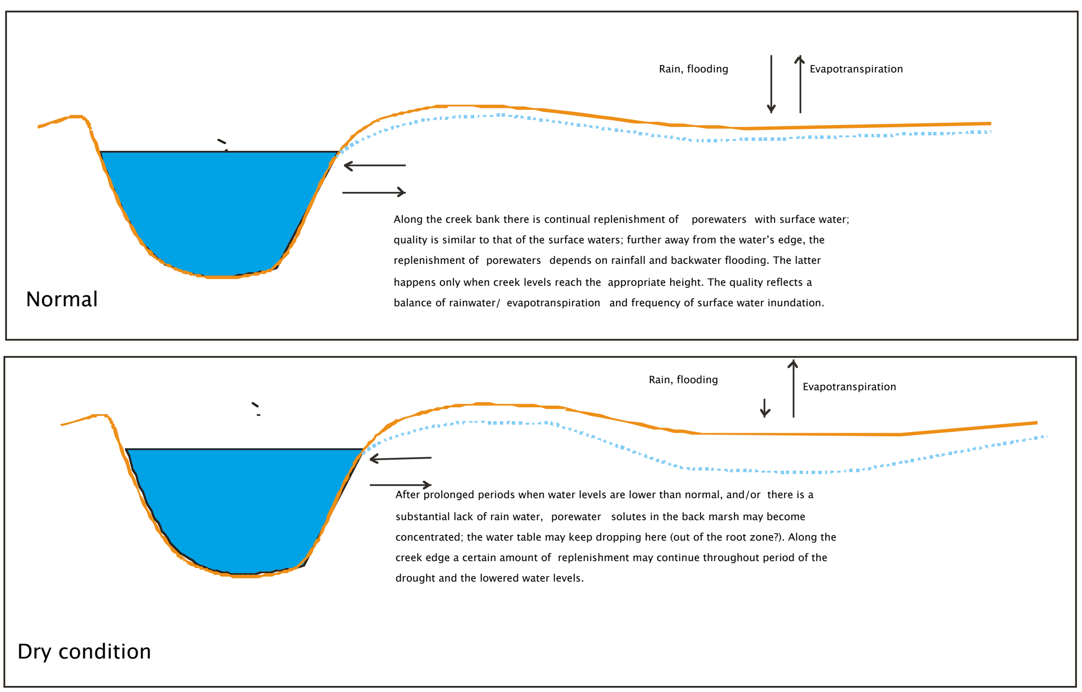

Figure 2. Conceptual model showing how water deficits can occur in the interior of salt marsh ecosystems in response to different hydrologic drivers.

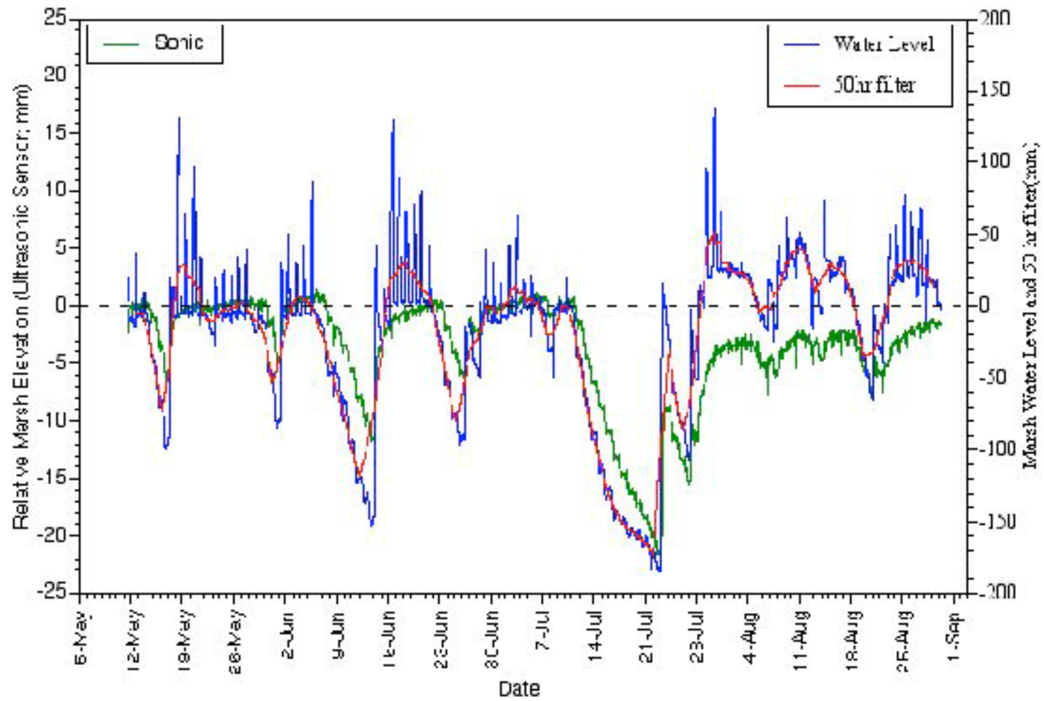

Figure 3. Field measurements of water and surface elevations at Old Oyster Bayou from May to August 2000.

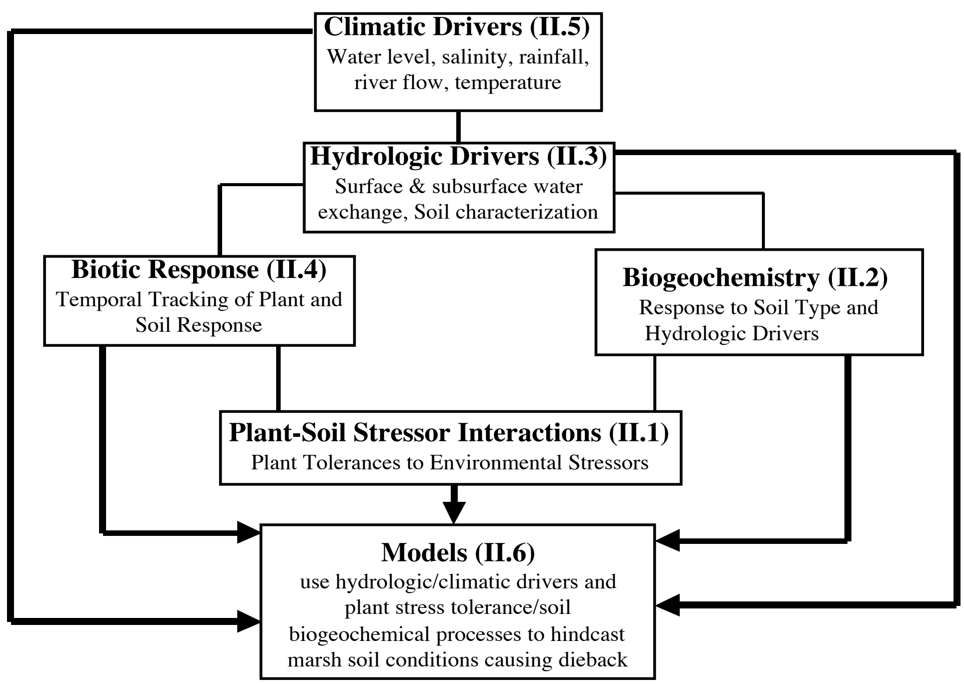

Figure 4. Conceptual diagram of the integrated research program to study the brown marsh phenomemn

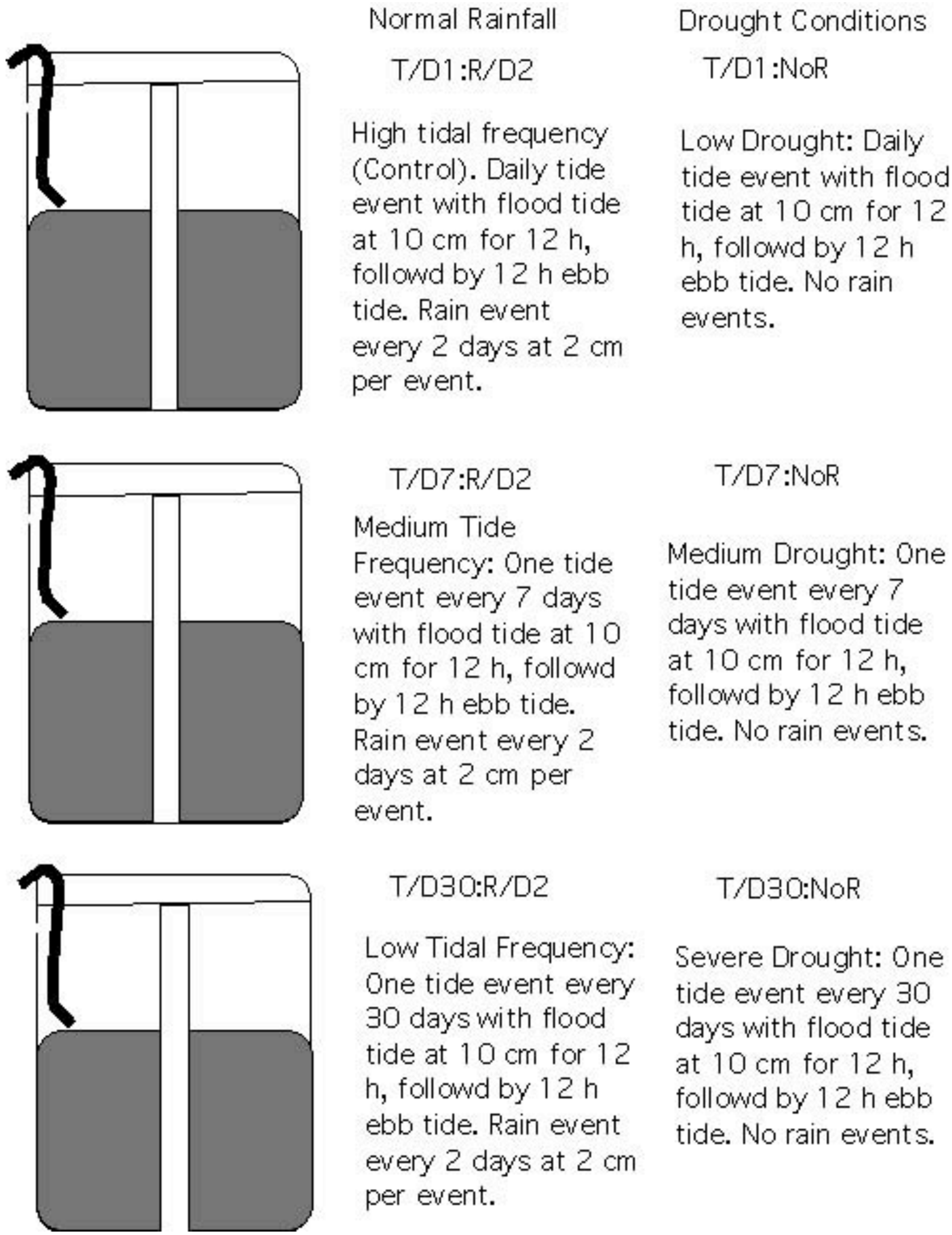

Figure 5. Experimental design of the greenhouse mesocosm study that includes combination of tidal and rainfall treatments to simulate drought effects by varying duration between tidal events (1, 7 and 30 days) with and without augmentation from rainfall. These tidal and rainfall treatments were applied to three soil types under two different salinity treatments.

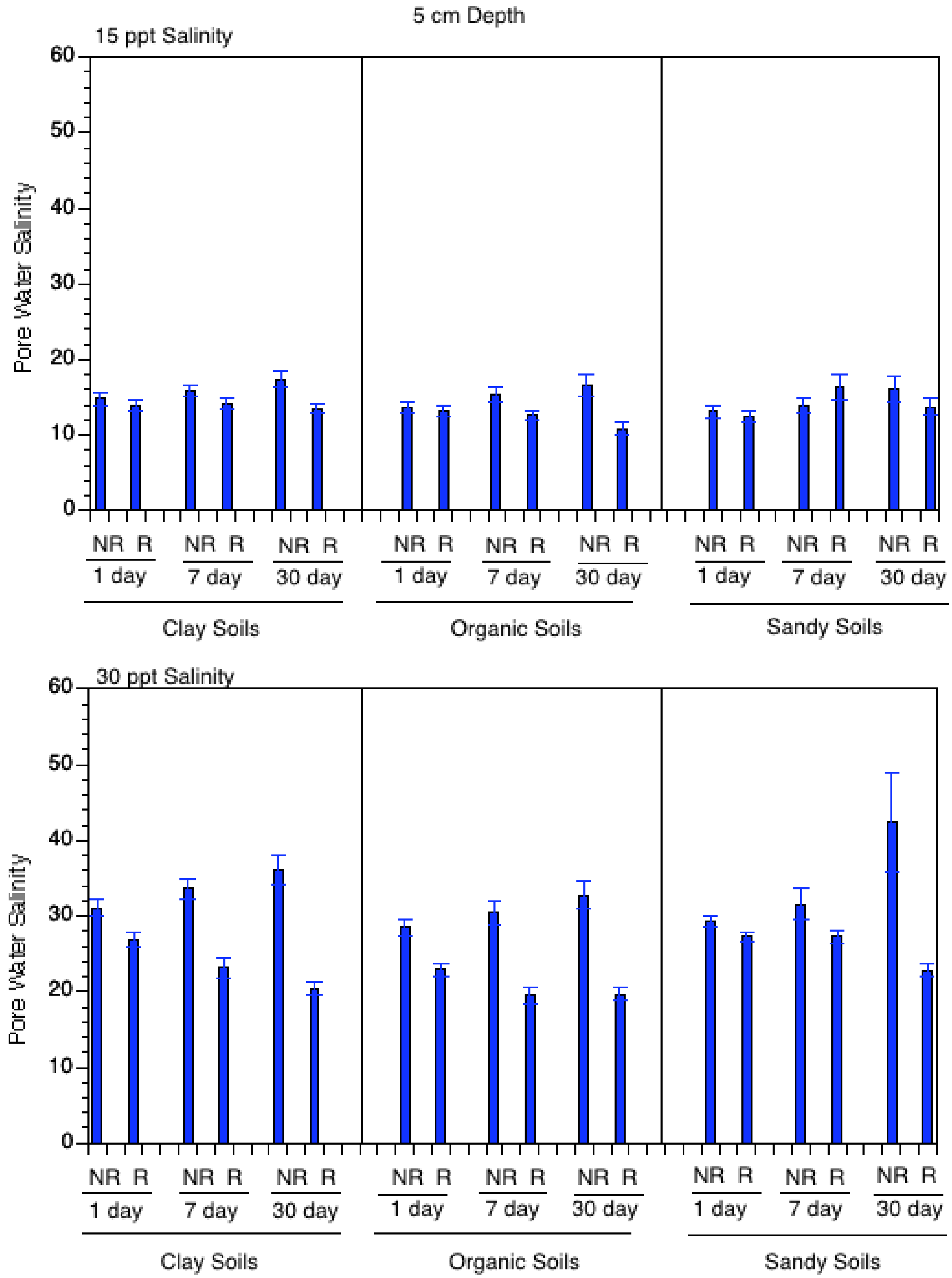

Figure 6. Porewater salinity at 5 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

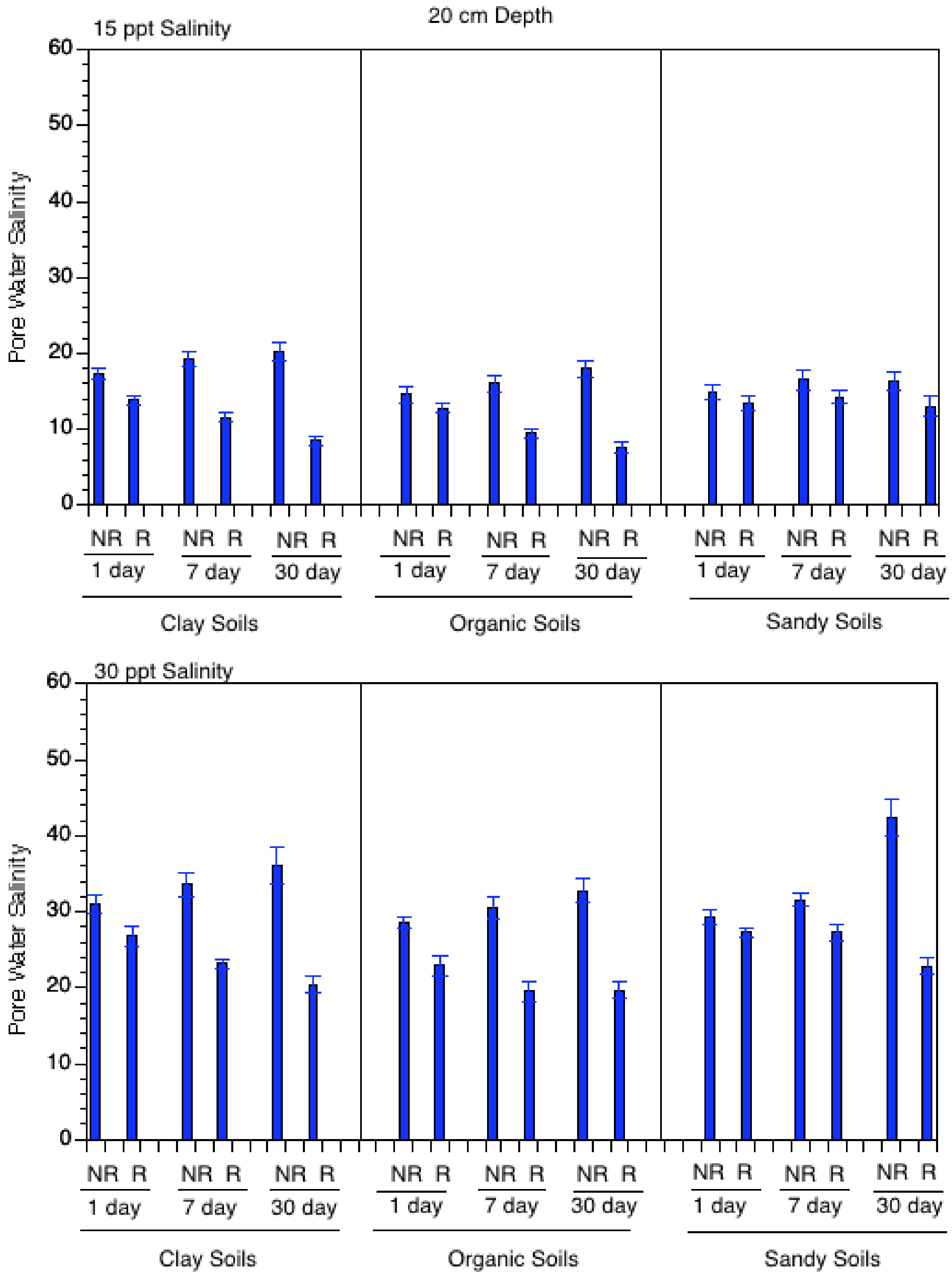

Figure 7. Porewater salinity at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

Table 1. Statistical results of porewater salinity at two depths in experiments run at two different salinities (15 and 30 g/kg) each with treatments of three soil types (clay, organic, sandy) subjected to two tidal regimes (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain.

	Soil Salinity (g/kg)					
	Salinity = 15			Salinity = 30		
Source	DF	F Ratio	Prob > F	DF	F Ratio	Prob > F
				Depth = 0-5 cm		
Soil TRT	2	194.7963	<.0001	2	10.7831	<.0001
Tide TRT	2	4.4444	0.0126	2	0.1114	0.8946
Rain TRT	1	0.149	0.6998	1	1.6933	0.1943
Soil TRT*Tide TRT	4	1.9883	0.0967	4	3.8575	0.0046
Soil TRT*Rain TRT	2	0.5206	0.5948	2	3.7998	0.0236
Tide TRT*Rain TRT	2	1.0523	0.3506	2	0.4027	0.6689
Soil TRT*Tide TRT*Rain TRT	4	0.3103	0.871	4	3.95	0.0039
				Depth = 15-20 cm		
Soil TRT	2	195.3949	<.0001	2	17.4226	<.0001
Tide TRT	2	5.5742	0.0042	2	0.6504	0.5226
Rain TRT	1	6.36	0.0122	1	65.3797	<.0001
Soil TRT*Tide TRT	4	1.7332	0.1428	4	2.3668	0.053
Soil TRT*Rain TRT	2	0.8624	0.4233	2	0.108	0.8976
Tide TRT*Rain TRT	2	1.6071	0.2023	2	5.708	0.0037
Soil TRT*Tide TRT*Rain TRT	4	0.4021	0.8071	4	3.1939	0.0138

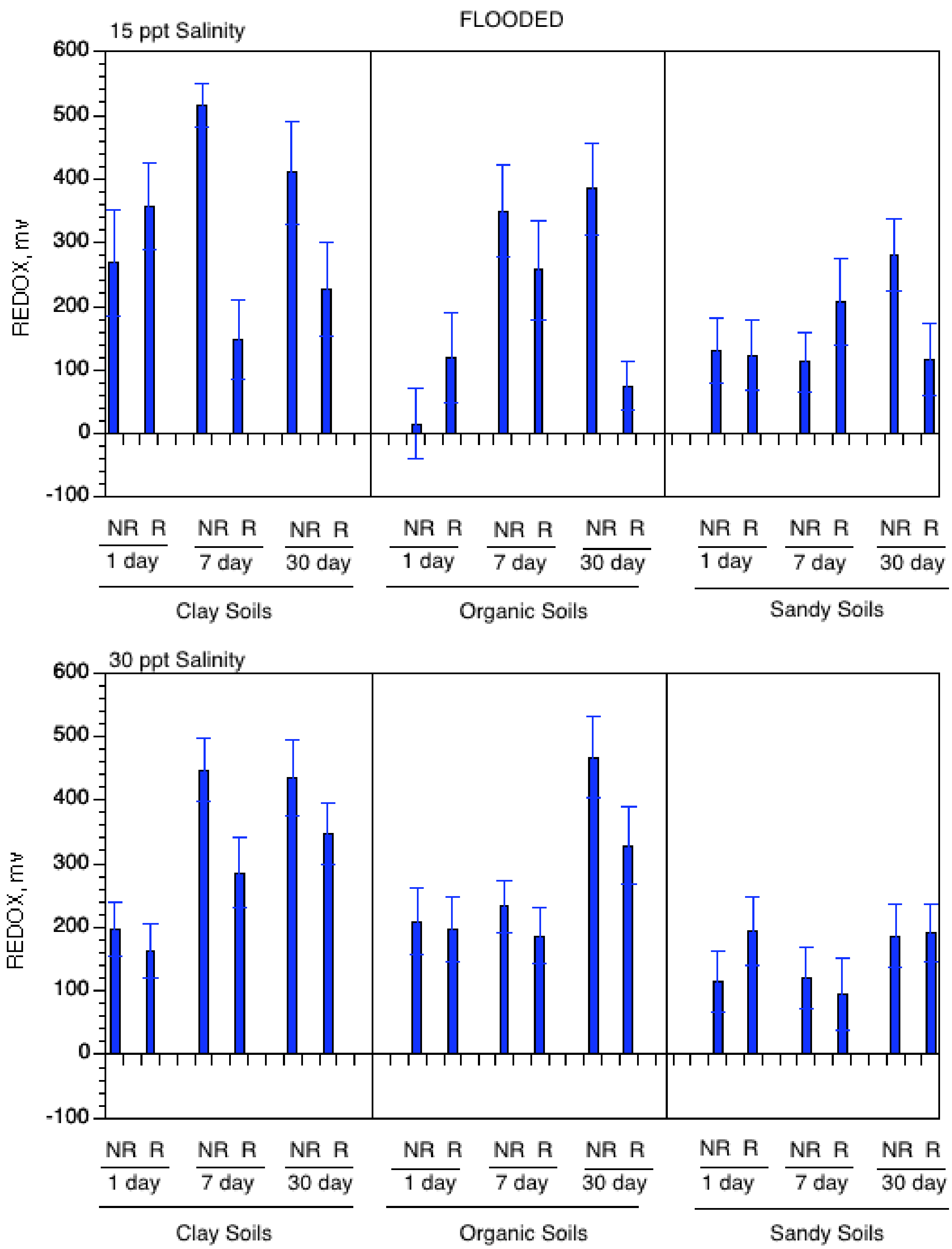

Figure 8. Redox at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

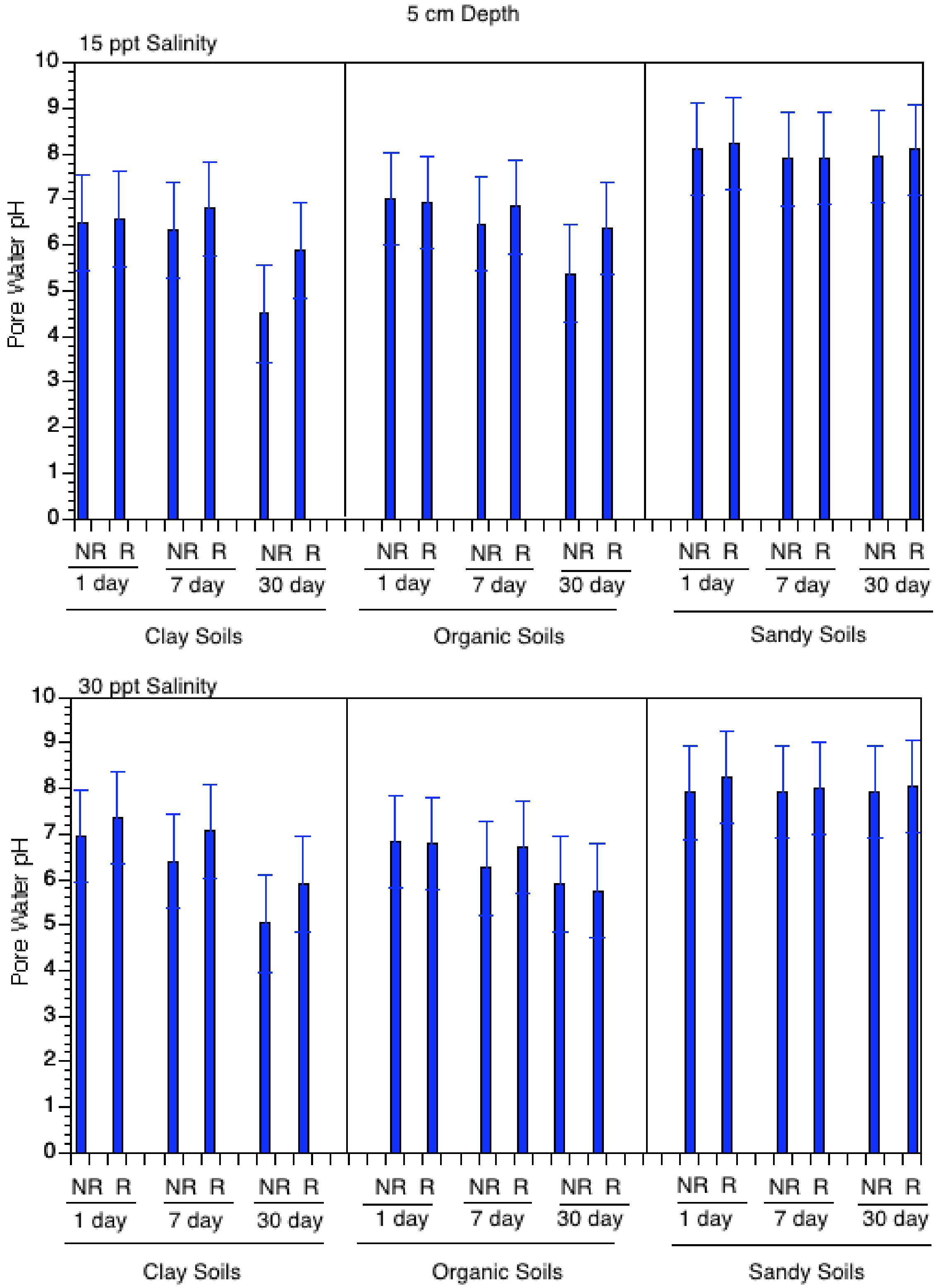

Figure 9. Porewater pH at 5 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain (NR = no rain, R = rain).

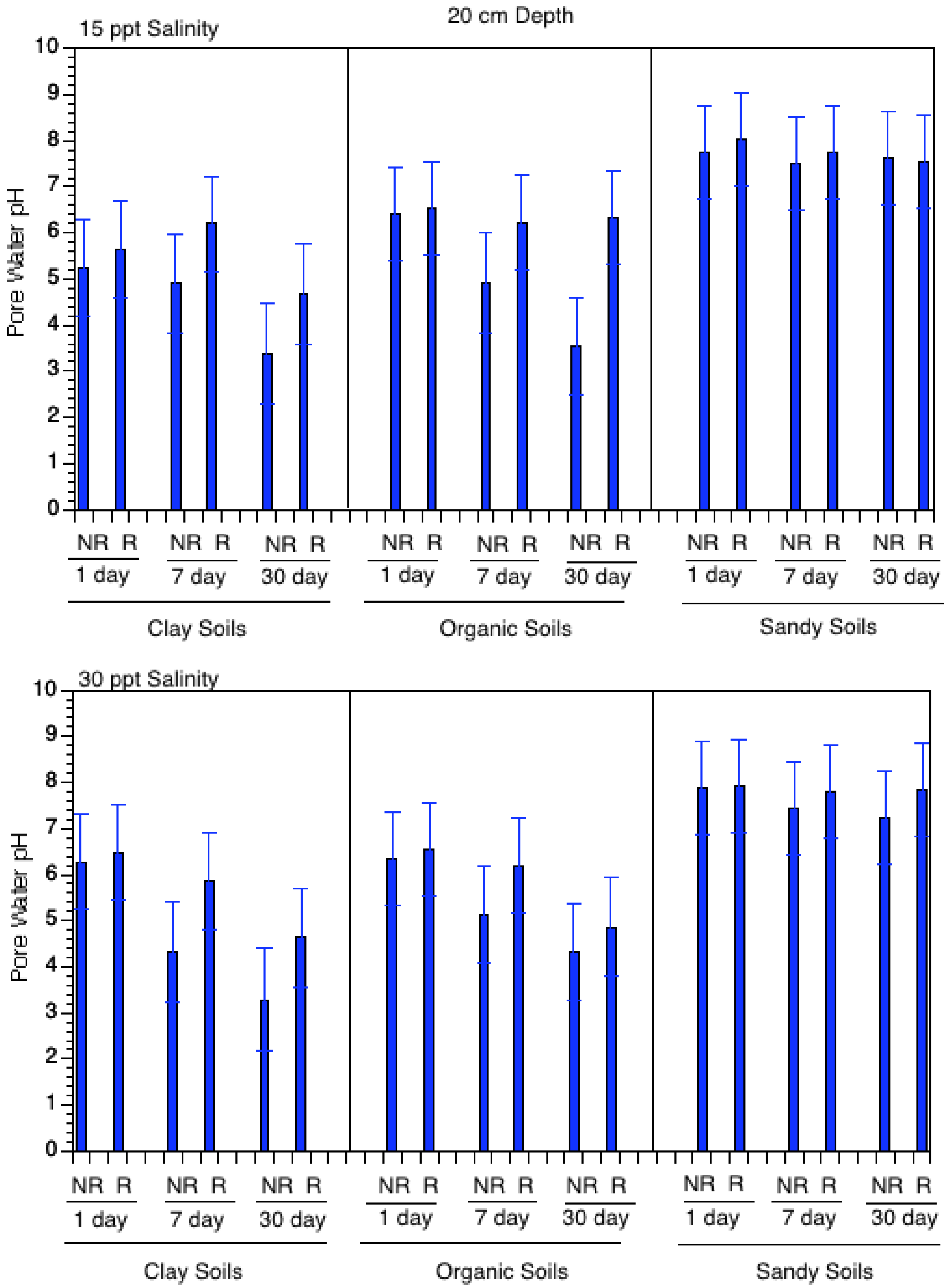

Figure 10. Porewater pH at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

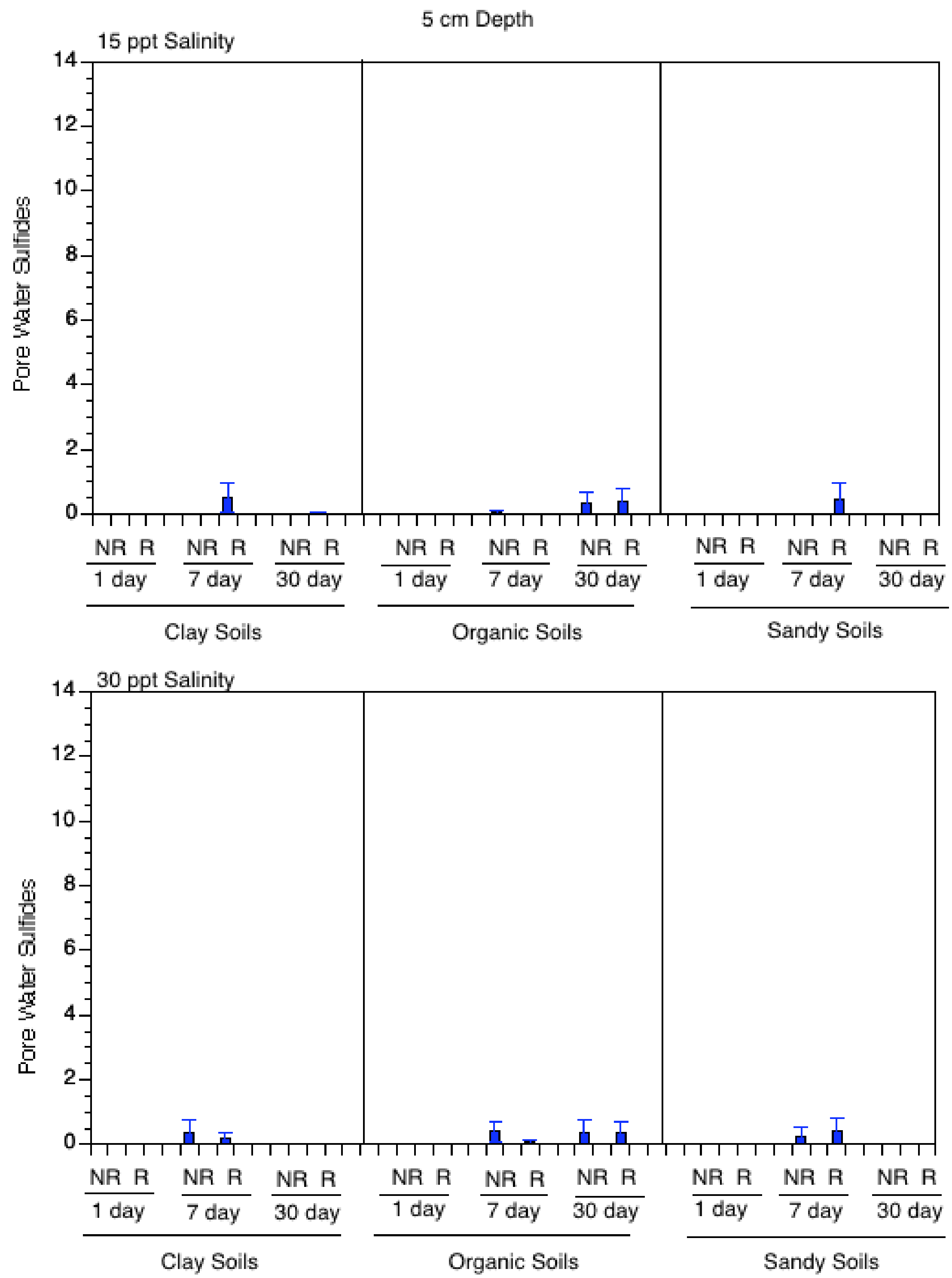

Figure 11. Porewater sulfide at 5 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

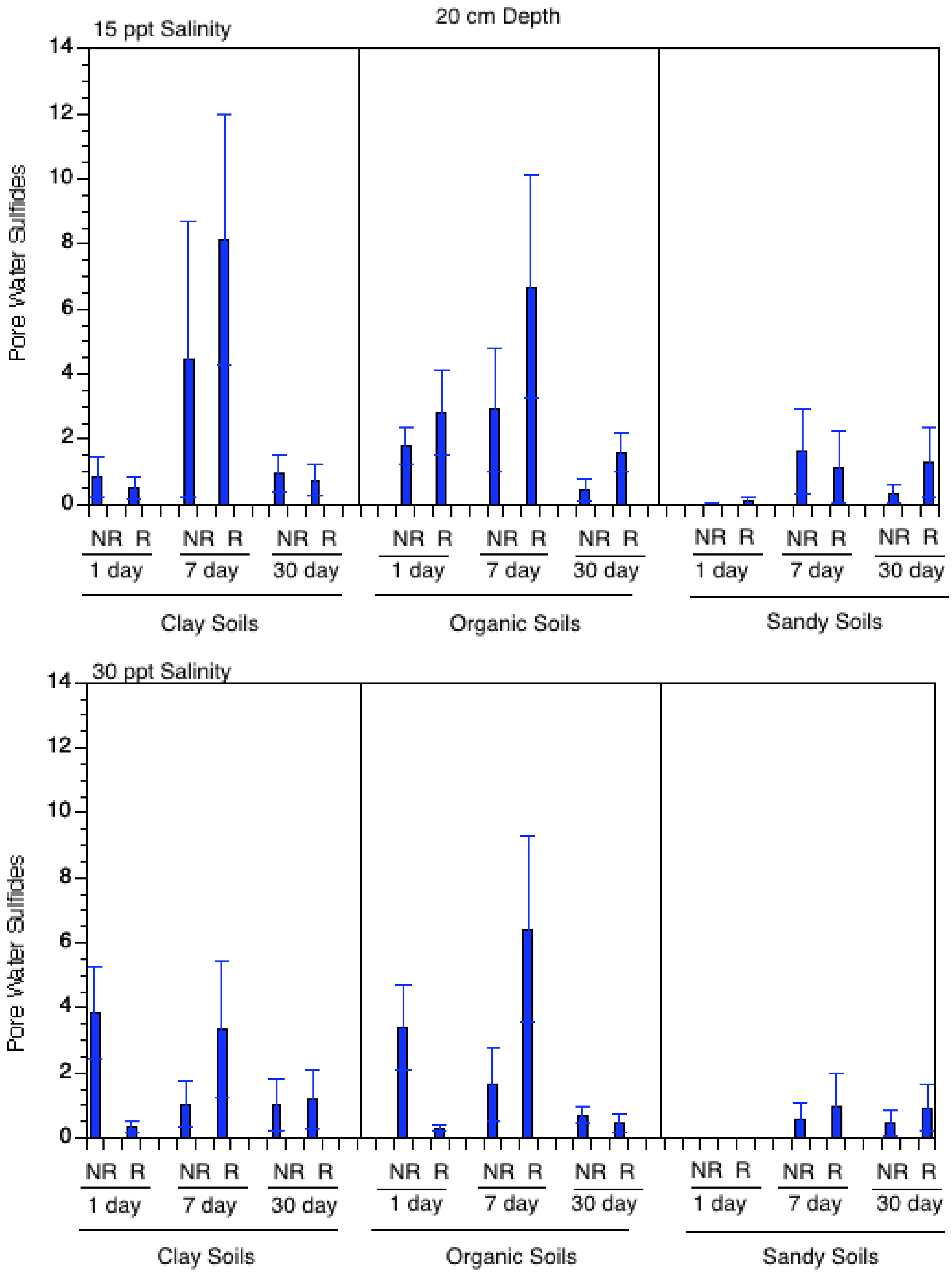

Figure 12. Porewater sulfide at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

Table 2. Statistical results of porewater sulfides at two depths in experiments run at two different salinities (15 and 30 g/kg) each with treatments of three soil types (clay, organic, sandy) subjected to two tidal regimes (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain.

Sulfides (ppm)						
	Salinity = 15			Salinity = 30		
Source	DF	F Ratio	Prob > F	DF	F Ratio	Prob > F
			Depth = 0-5 cm			
Soil TRT	2	4.0281	0.0189	2	0.5084	0.6021
Tide TRT	2	0.0171	0.9831	2	1.2313	0.2936
Rain TRT	1	0.074	0.7858	1	0.1299	0.7189
Soil TRT*Tide TRT	4	2.2675	0.0624	4	0.9909	0.413
Soil TRT*Rain TRT	2	0.4961	0.6095	2	0.3691	0.6917
Tide TRT*Rain TRT	2	0.0312	0.9693	2	0.1294	0.8787
Soil TRT*Tide TRT*Rain TRT	4	0.5879	0.6717	4	0.2698	0.8972
			Depth = 15-20 cm			
Soil TRT	2	8.7459	0.0002	2	4.5144	0.0118
Tide TRT	2	6.1817	0.0024	2	0.4306	0.6506
Rain TRT	1	1.0936	0.2966	1	0.1603	0.6892
Soil TRT*Tide TRT	4	1.5486	0.1883	4	1.3013	0.2697
Soil TRT*Rain TRT	2	0.1972	0.8212	2	0.2774	0.7579
Tide TRT*Rain TRT	2	1.2496	0.2882	2	3.7827	0.0239
Soil TRT*Tide TRT*Rain TRT	4	0.3299	0.8578	4	1.6808	0.1545

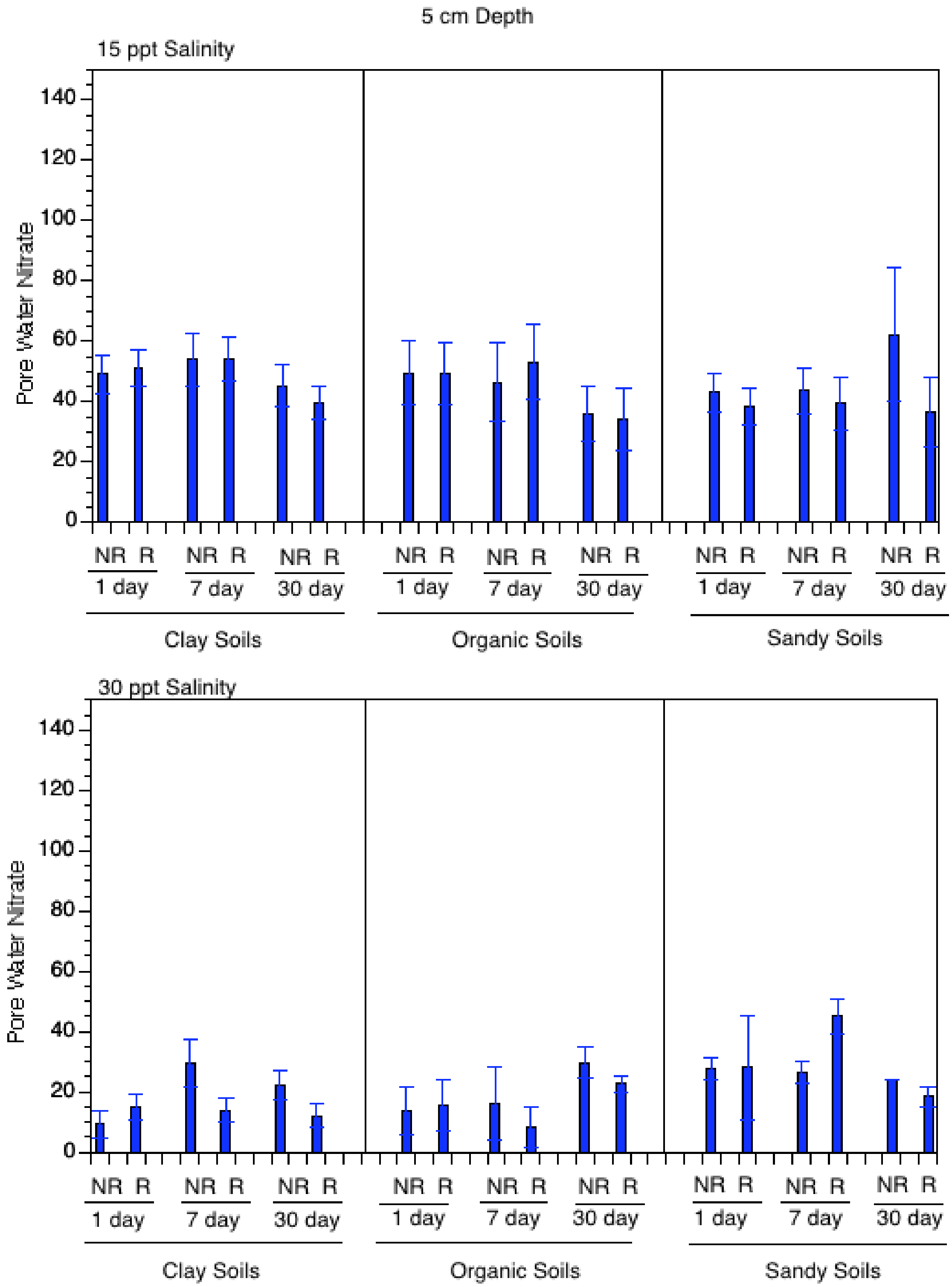

Figure 13. Porewater nitrate (µM) at 5 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

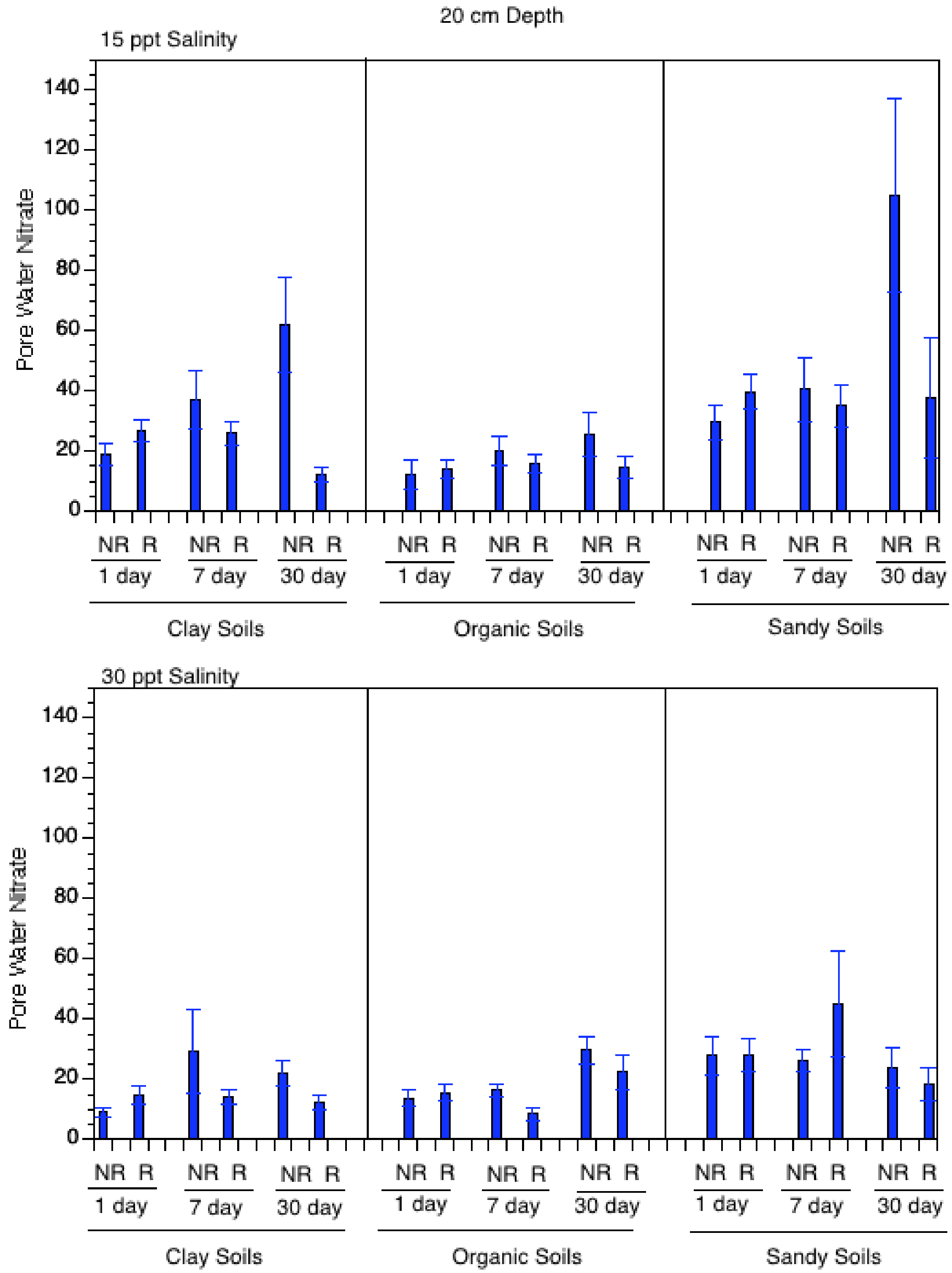

Figure 14. Porewater nitrate (µM) at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

Table 3. Statistical results of porewater nitrite+nitrate at two depths in experiments run at two different salinities (15 and 30 g/kg) each with treatments of three soil types (clay, organic, sandy) subjected to two tidal regimes (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain.

NO3/NO2 (µmol/L)						
	Salinity = 15			Salinity = 30		
Source	DF	F Ratio	Prob > F	DF	F Ratio	Prob > F
				Depth = 0-5 cm		
Soil TRT	2	66.2581	<.0001	2	2.363	0.0961
Tide TRT	2	1.0633	0.3468	2	0.0521	0.9492
Rain TRT	1	0.1282	0.7206	1	0.7172	0.3978
Soil TRT*Tide TRT	4	1.0714	0.3711	4	6.0054	0.0001
Soil TRT*Rain TRT	2	0.8231	0.4402	2	2.7131	0.0682
Tide TRT*Rain TRT	2	0.4854	0.616	2	0.2151	0.8066
Soil TRT*Tide TRT*Rain TRT	4	0.2625	0.9018	4	5.8889	0.0001
				Depth = 15-20 cm		
Soil TRT	2	51.0691	<.0001	2	7.2908	0.0008
Tide TRT	2	0.2839	0.753	2	1.4697	0.2317
Rain TRT	1	1.476	0.2254	1	1.9514	0.1635
Soil TRT*Tide TRT	4	1.7728	0.1344	4	2.6818	0.0319
Soil TRT*Rain TRT	2	0.7458	0.4753	2	1.9345	0.1464
Tide TRT*Rain TRT	2	1.9938	0.1381	2	2.123	0.1216
Soil TRT*Tide TRT*Rain TRT	4	1.438	0.2216	4	2.449	0.0465

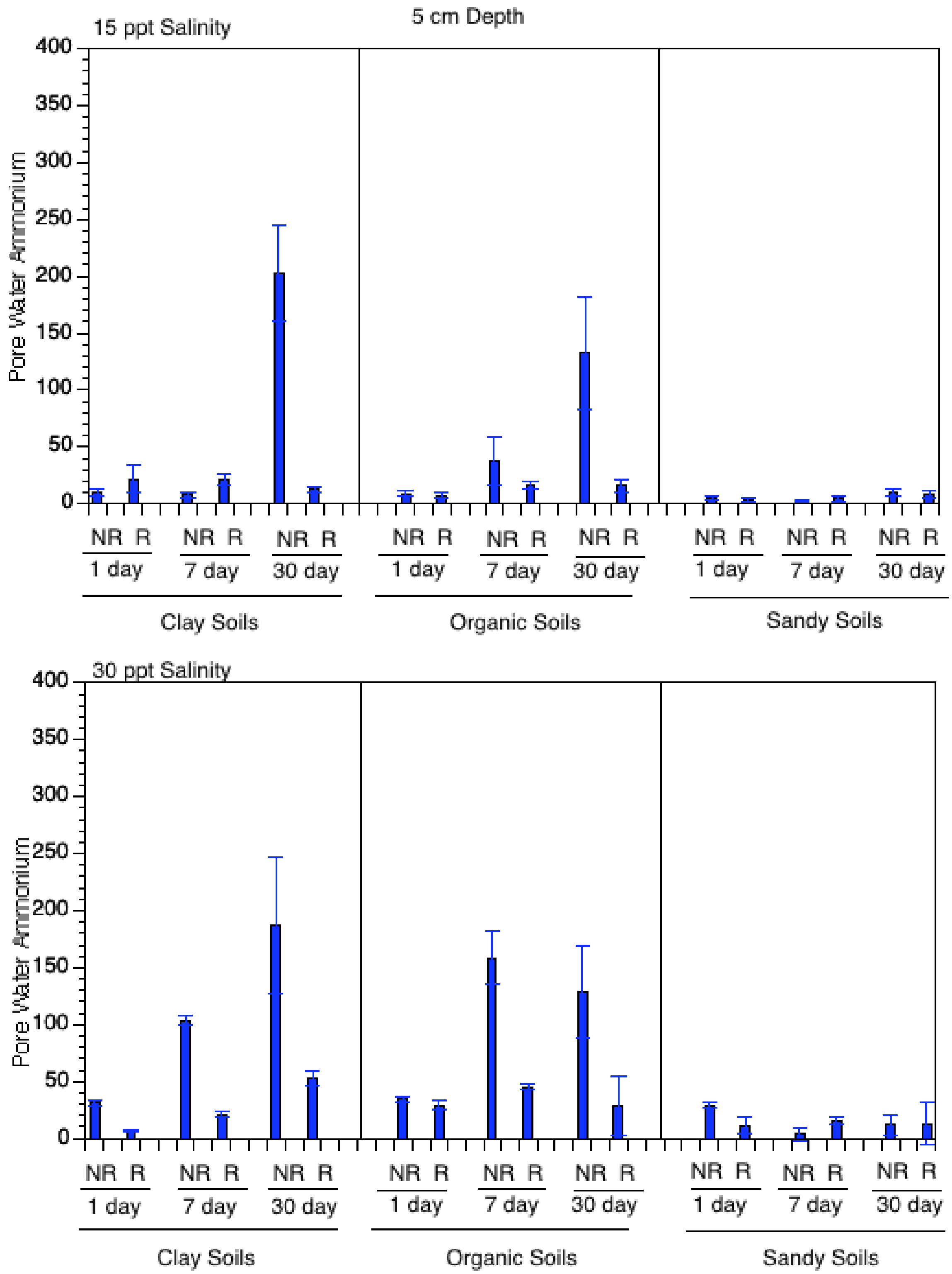

Figure 15. Porewater ammonium (µmol/L) at 5 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

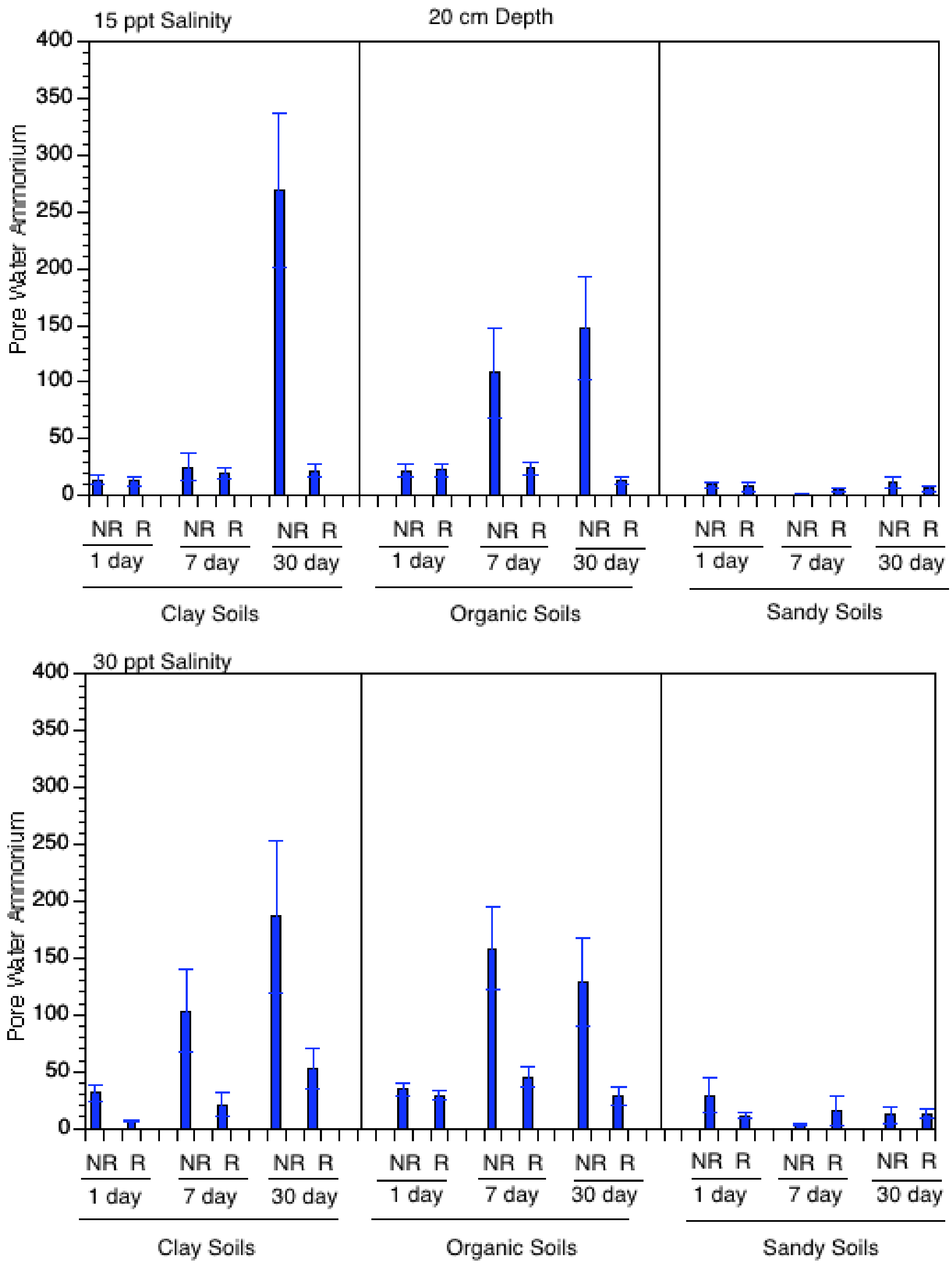

Figure 16. Porewater ammonium (μmol/L) at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

Table 4. Statistical results of porewater ammonium at two depths in experiments run at two different salinities (15 and 30 g/kg) each with treatments of three soil types (clay, organic, sandy) subjected to two tidal regimes (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain.

NH4 (µmol/L)						
	Salinity = 15			Salinity = 30		
Source	DF	F Ratio	Prob > F	DF	F Ratio	Prob > F
				Depth = 0-5 cm		
Soil TRT	2	11.6392	<.0001	2	4.495	0.012
Tide TRT	2	26.9945	<.0001	2	14.2891	<.0001
Rain TRT	1	15.4765	0.0001	1	13.7146	0.0003
Soil TRT*Tide TRT	4	6.9559	<.0001	4	3.0539	0.0175
Soil TRT*Rain TRT	2	4.3667	0.0136	2	3.8282	0.023
Tide TRT*Rain TRT	2	29.97	<.0001	2	9.7328	<.0001
Soil TRT*Tide TRT*Rain TRT	4	7.9857	<.0001	4	2.9172	0.0218
				Depth = 15-20 cm		
Soil TRT	2	18.6312	<.0001	2	10.7994	<.0001
Tide TRT	2	20.5673	<.0001	2	9.8613	<.0001
Rain TRT	1	15.5393	0.0001	1	21.8761	<.0001
Soil TRT*Tide TRT	4	6.28	<.0001	4	3.9243	0.0041
Soil TRT*Rain TRT	2	4.8461	0.0085	2	6.0219	0.0027
Tide TRT*Rain TRT	2	18.3829	<.0001	2	3.2216	0.0414
Soil TRT*Tide TRT*Rain TRT	4	5.1326	0.0005	4	1.8304	0.1231

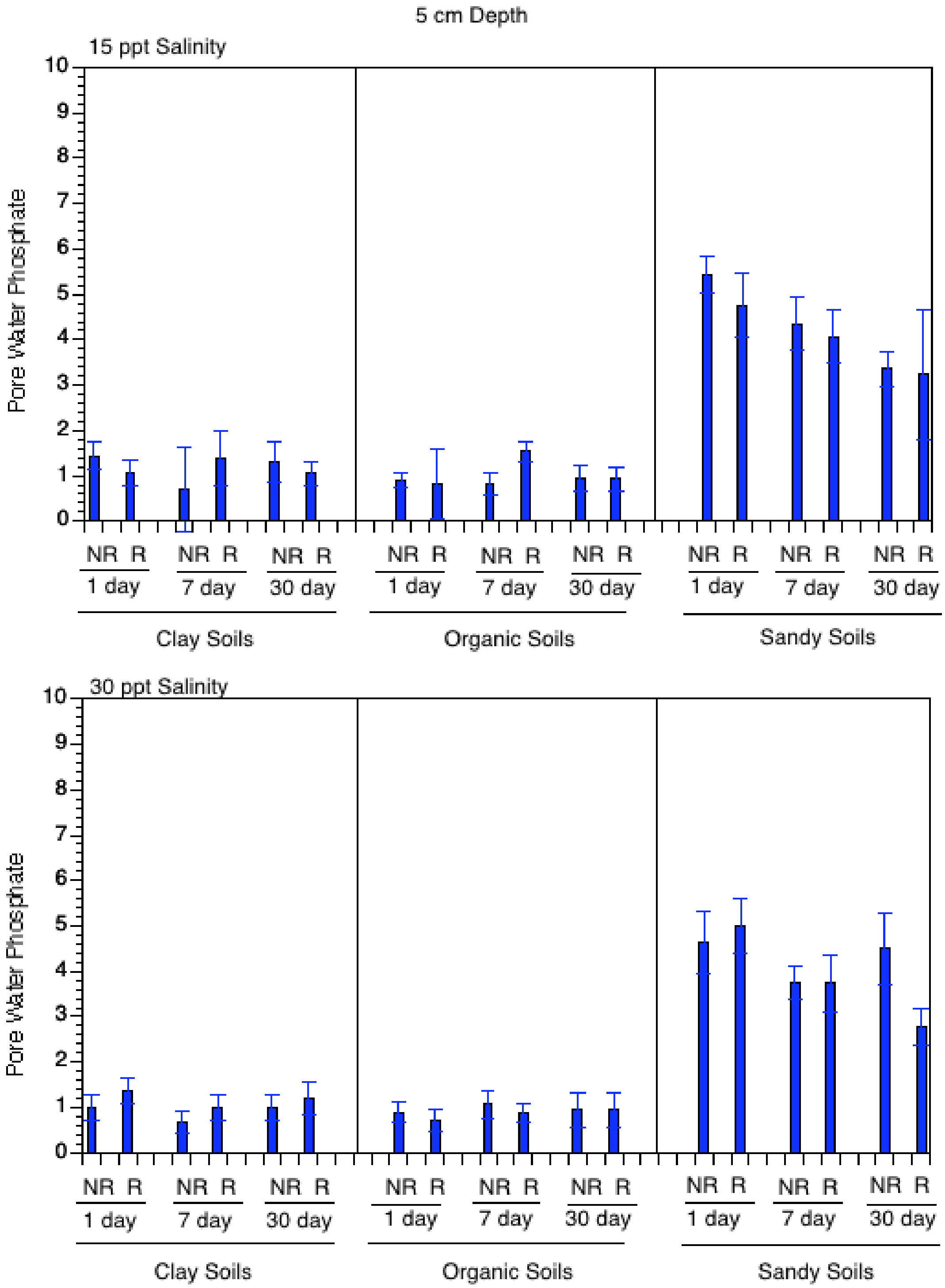

Figure 17. Porewater soluble reactive phosphate (µmol/L) at 5 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

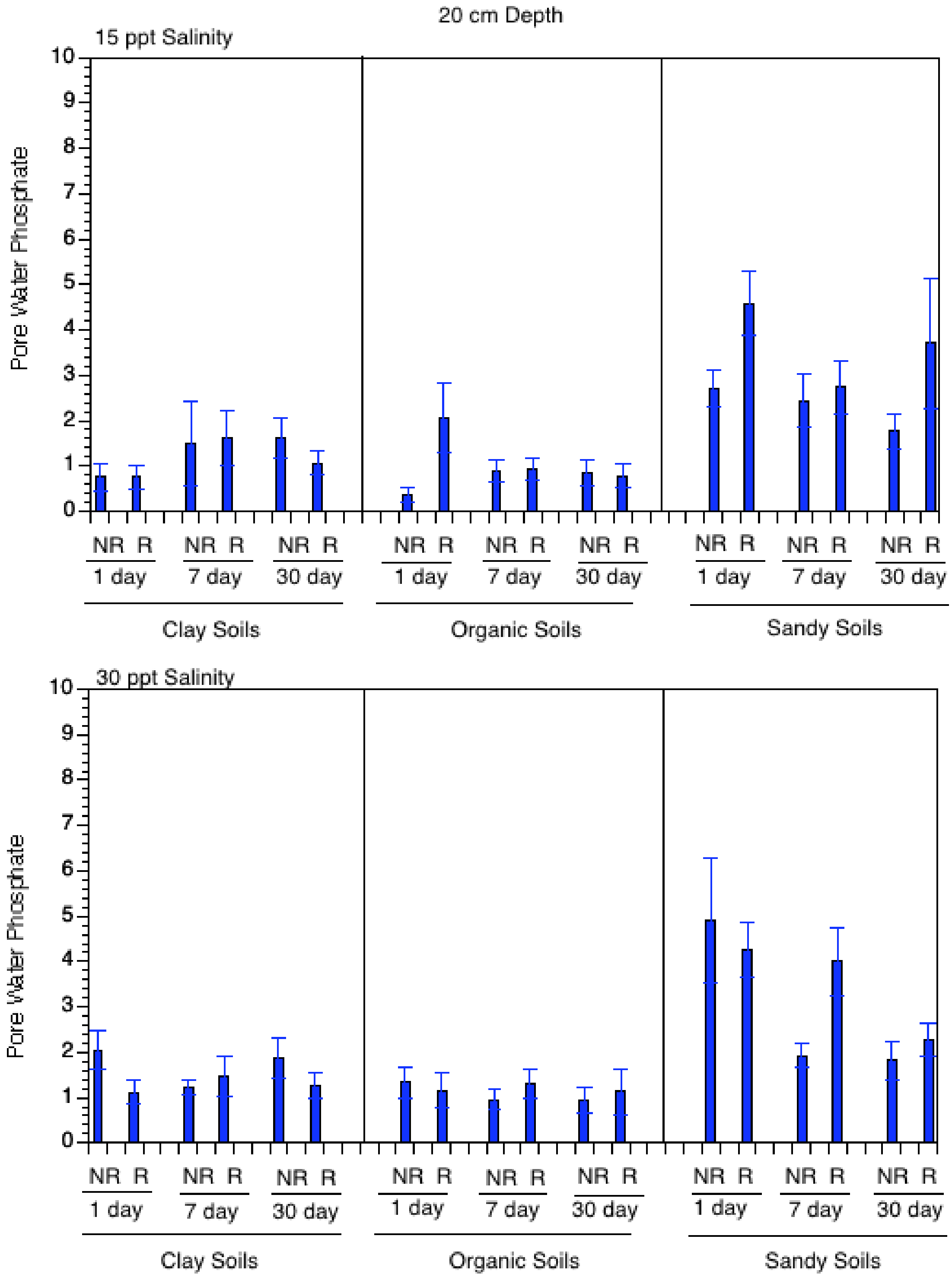

Figure 18. Porewater soluble reactive phosphate (µmol/L) at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

Table 5. Statistical results of porewater soluble reactive phosphorus at two depths in experiments run at two different salinities (15 and 30 g/kg) each with treatments of three soil types (clay, organic, sandy) subjected to two tidal regimes (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain.

	PO_4 (µmol/L)					
	Salinity = 15			Salinity = 30		
Source	DF	F Ratio	Prob > F	DF	F Ratio	Prob > F
				Depth = 0-5 cm		
Soil TRT	2	195.2668	<.0001	2	97.5827	<.0001
Tide TRT	2	0.5865	0.557	2	0.164	0.8488
Rain TRT	1	0.0468	0.8289	1	0.8216	0.3655
Soil TRT*Tide TRT	4	2.7172	0.0303	4	1.8229	0.1247
Soil TRT*Rain TRT	2	0.7667	0.4656	2	1.2569	0.2862
Tide TRT*Rain TRT	2	1.0014	0.3688	2	0.029	0.9714
Soil TRT*Tide TRT*Rain TRT	4	0.2333	0.9195	4	1.1364	0.3397
				Depth = 15-20 cm		
Soil TRT	2	72.2149	<.0001	2	22.465	<.0001
Tide TRT	2	0.6528	0.5214	2	0.0196	0.9806
Rain TRT	1	0.0007	0.9789	1	0.7082	0.4007
Soil TRT*Tide TRT	4	0.9788	0.4194	4	3.2915	0.0117
Soil TRT*Rain TRT	2	1.7216	0.1807	2	1.0386	0.3553
Tide TRT*Rain TRT	2	0.2251	0.7986	2	0.8542	0.4267
Soil TRT*Tide TRT*Rain TRT	4	0.6982	0.5937	4	0.4383	0.7809

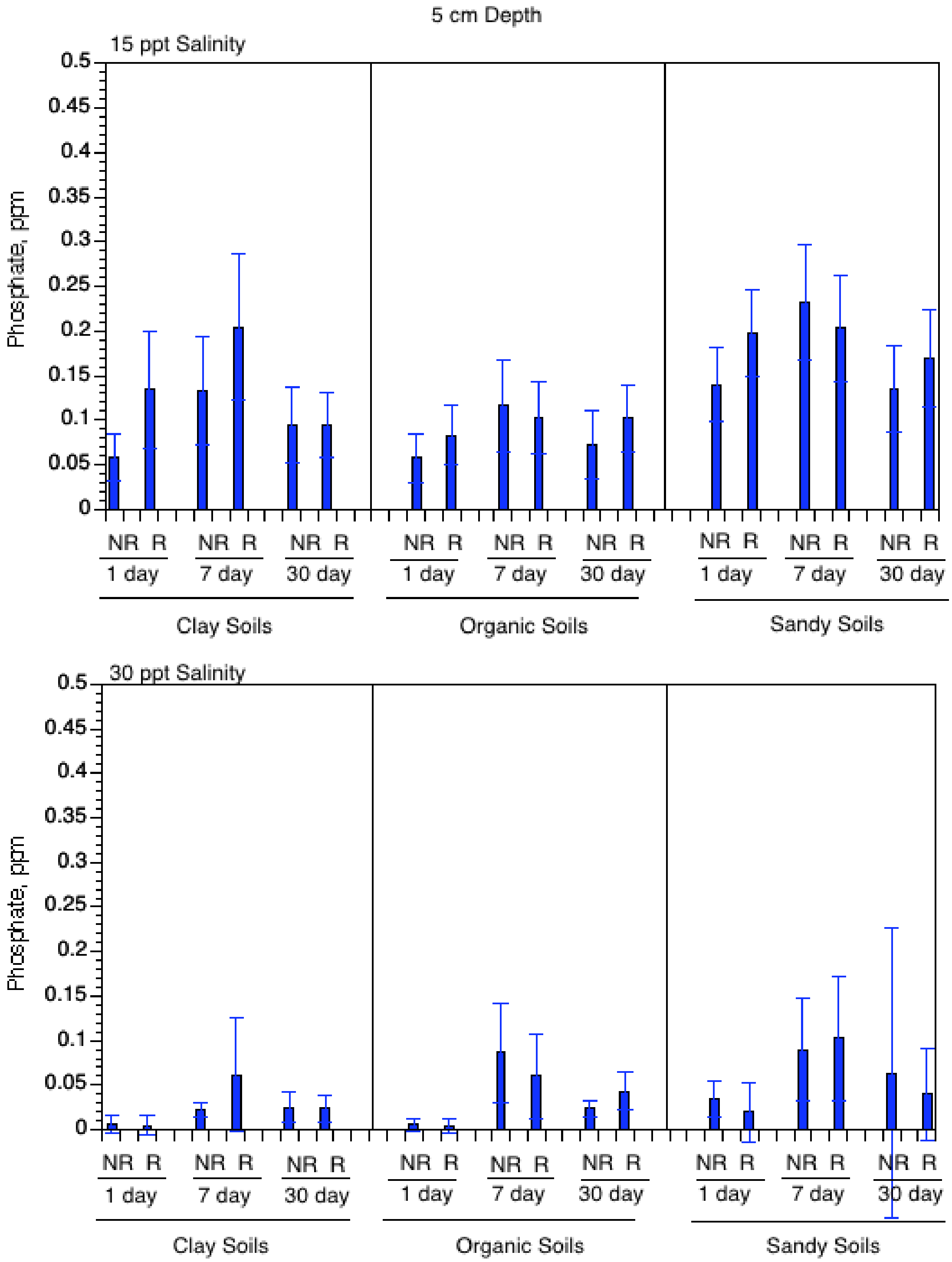

Figure 19. Porewater phosphate (ppm) at 5 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain (NR = no rain, R = rain).

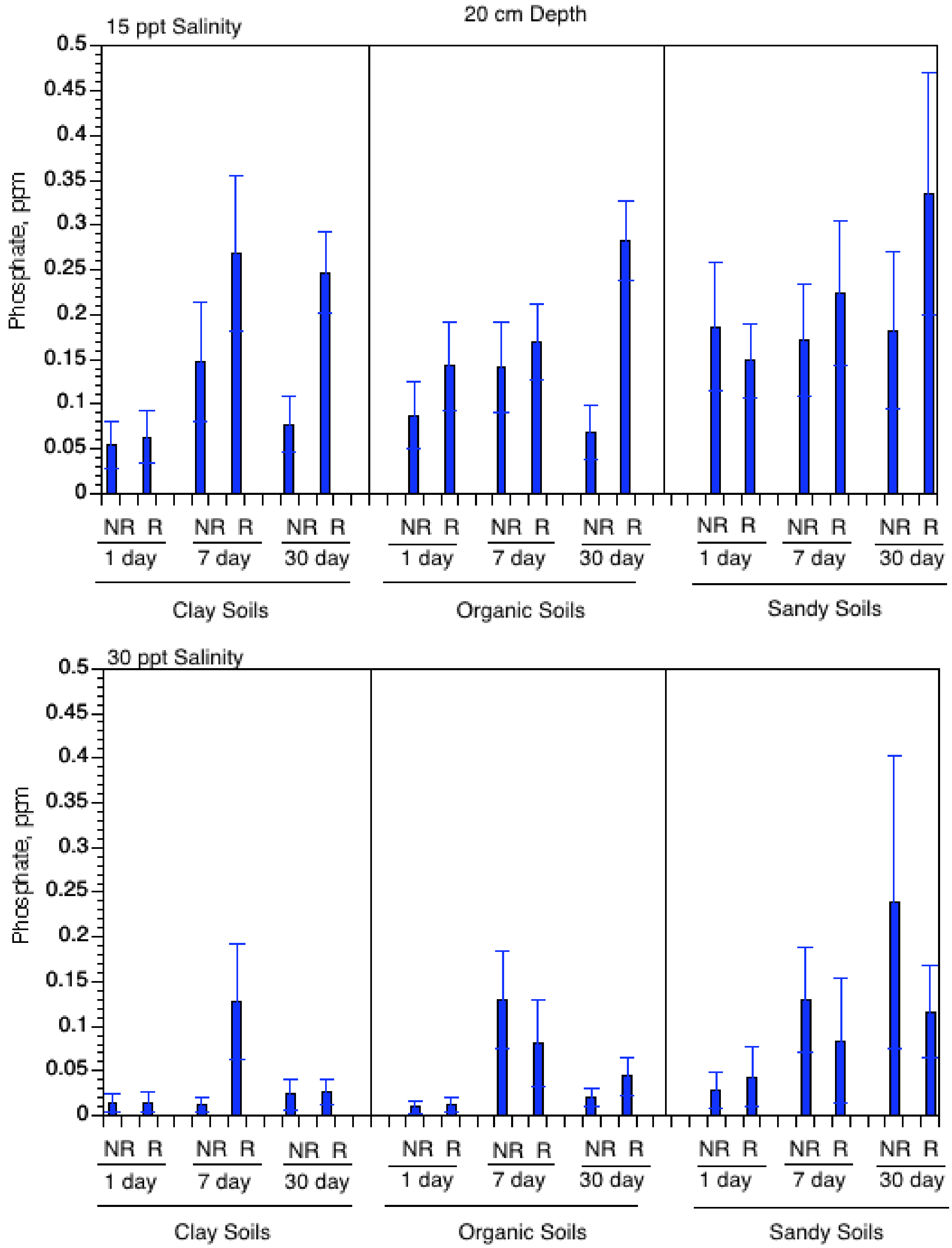

Figure 20. Porewater phosphorus (ppm) at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain (NR = no rain, R = rain).

Table 6. Statistical results of porewater phosphorus at two depths in experiments run at two different salinities (15 and 30 g/kg) each with treatments of three soil types (clay, organic, sandy) subjected to two tidal regimes (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain.

P (ppm)						
	Salinity = 15			Salinity = 30		
Source	DF	F Ratio	Prob > F	DF	F Ratio	Prob > F
				Depth = 0-5 cm		
Soil TRT	2	52.1469	<.0001	2	2.732	0.0669
Tide TRT	2	0.0121	0.9879	2	1.0423	0.3541
Rain TRT	1	1.2167	0.271	1	0.3031	0.5824
Soil TRT*Tide TRT	4	0.4066	0.8038	4	0.416	0.7971
Soil TRT*Rain TRT	2	0.1891	0.8278	2	0.1626	0.85
Tide TRT*Rain TRT	2	0.1851	0.8312	2	0.4186	0.6584
Soil TRT*Tide TRT*Rain TRT	4	0.2046	0.9357	4	0.1501	0.9629
				Depth = 15-20 cm		
Soil TRT	2	48.4066	<.0001	2	1.4981	0.2253
Tide TRT	2	1.2779	0.2802	2	1.3332	0.2653
Rain TRT	1	2.4462	0.1189	1	1.5427	0.2152
Soil TRT*Tide TRT	4	0.0367	0.9974	4	0.2247	0.9245
Soil TRT*Rain TRT	2	0.0147	0.9854	2	1.2598	0.2853
Tide TRT*Rain TRT	2	0.7745	0.4619	2	1.5666	0.2106
Soil TRT*Tide TRT*Rain TRT	4	0.267	0.899	4	0.934	0.4446

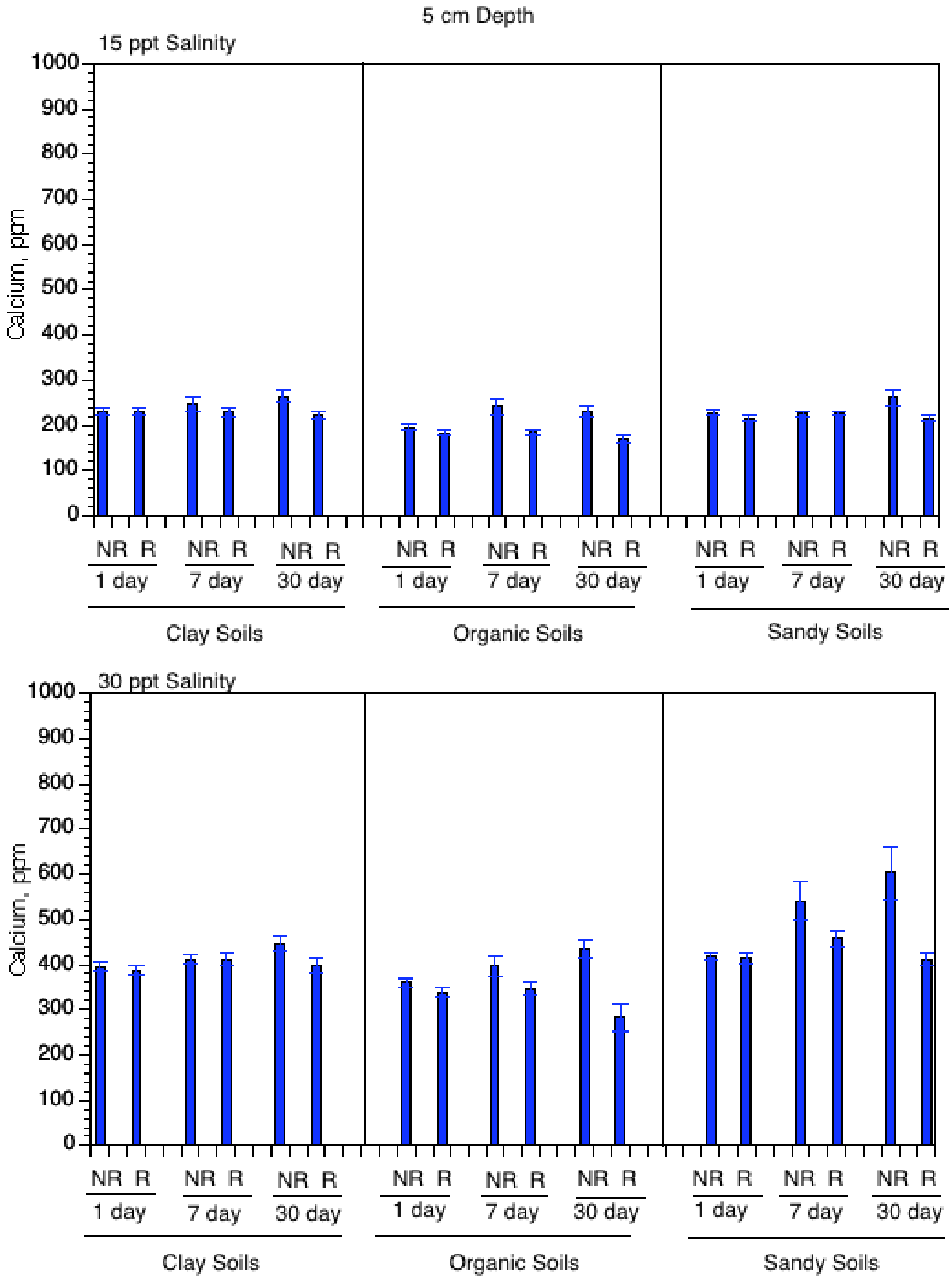

Figure 21. Porewater calcium (ppm) at 5 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain (NR = no rain, R = rain).

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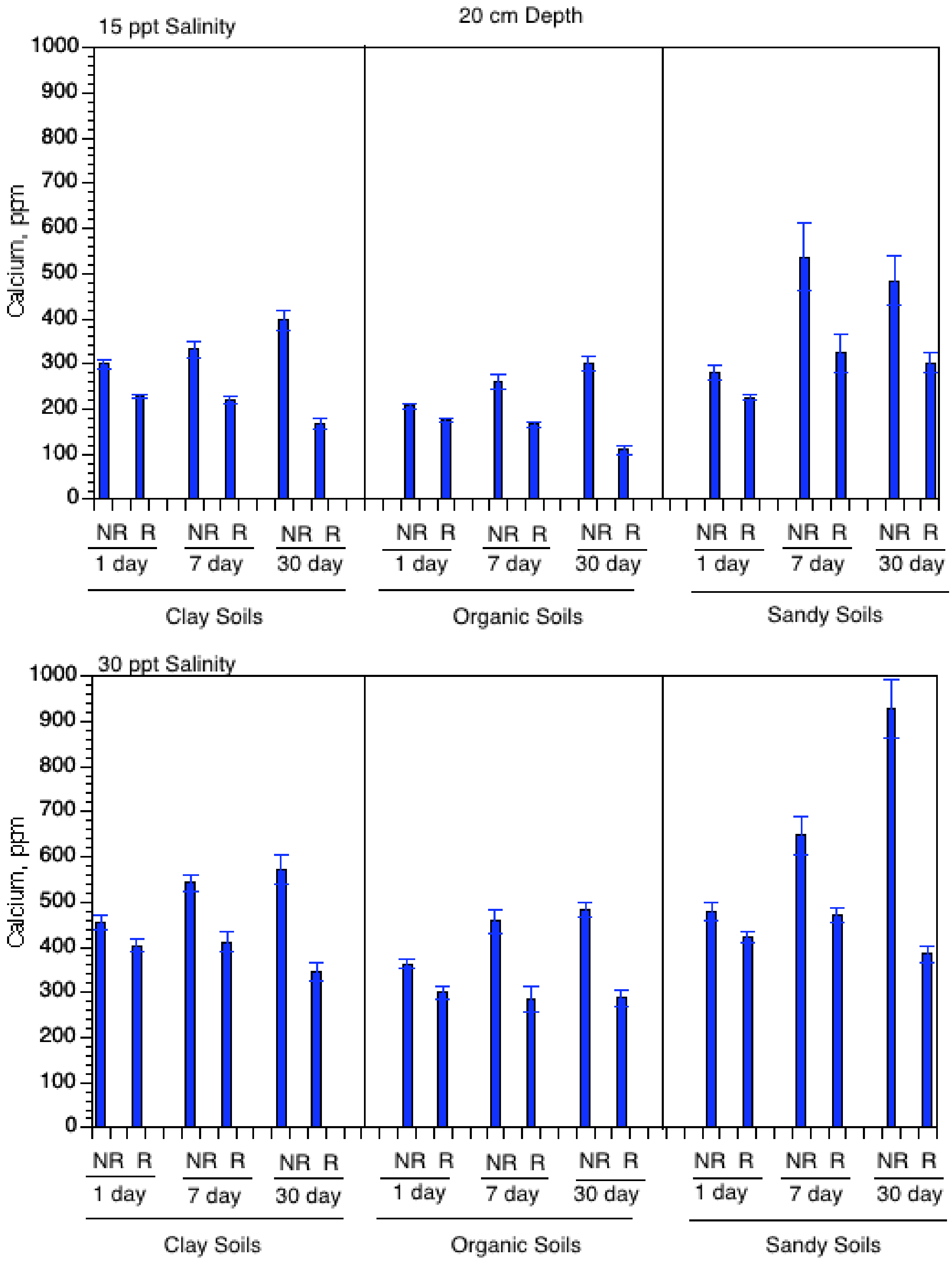

Figure 22. Porewater calcium (ppm) at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain (NR = no rain, R = rain).

Table 7. Statistical results of porewater calcium at two depths in experiments run at two different salinities (15 and 30 g/kg) each with treatments of three soil types (clay, organic, sandy) subjected to two tidal regimes (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain.

Ca (ppm)						
	Salinity = 15			Salinity = 30		
Source	DF	F Ratio	Prob > F	DF	F Ratio	Prob > F
				Depth = 0-5 cm		
Soil TRT	2	206.4329	<.0001	2	33.3523	<.0001
Tide TRT	2	4.4959	0.012	2	0.7137	0.4908
Rain TRT	1	0.0316	0.859	1	0.5327	0.4661
Soil TRT*Tide TRT	4	1.8421	0.1211	4	2.0112	0.0933
Soil TRT*Rain TRT	2	0.6685	0.5133	2	4.1285	0.0172
Tide TRT*Rain TRT	2	0.9271	0.397	2	0.3953	0.6739
Soil TRT*Tide TRT*Rain TRT	4	0.3584	0.8381	4	1.375	0.2429
				Depth = 15-20 cm		
Soil TRT	2	209.5844	<.0001	2	78.2717	<.0001
Tide TRT	2	3.6455	0.0274	2	1.6248	0.1988
Rain TRT	1	5.6301	0.0183	1	31.1694	<.0001
Soil TRT*Tide TRT	4	4.2175	0.0025	4	8.1507	<.0001
Soil TRT*Rain TRT	2	0.4112	0.6632	2	12.9686	<.0001
Tide TRT*Rain TRT	2	2.2337	0.109	2	3.6065	0.0284
Soil TRT*Tide TRT*Rain TRT	4	0.5934	0.6677	4	9.1927	<.0001

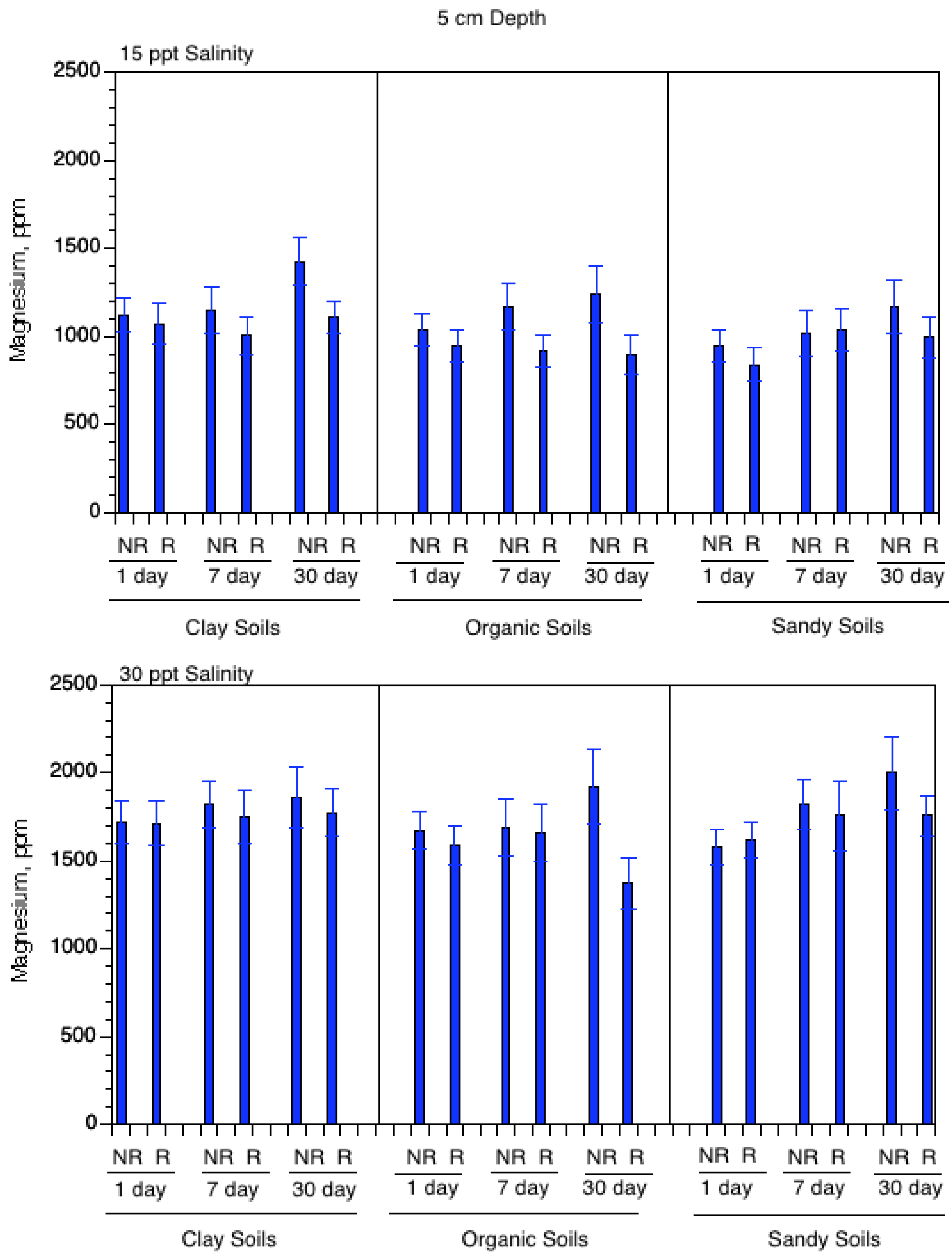

Figure 23. Porewater magnesium (ppm) at 5 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

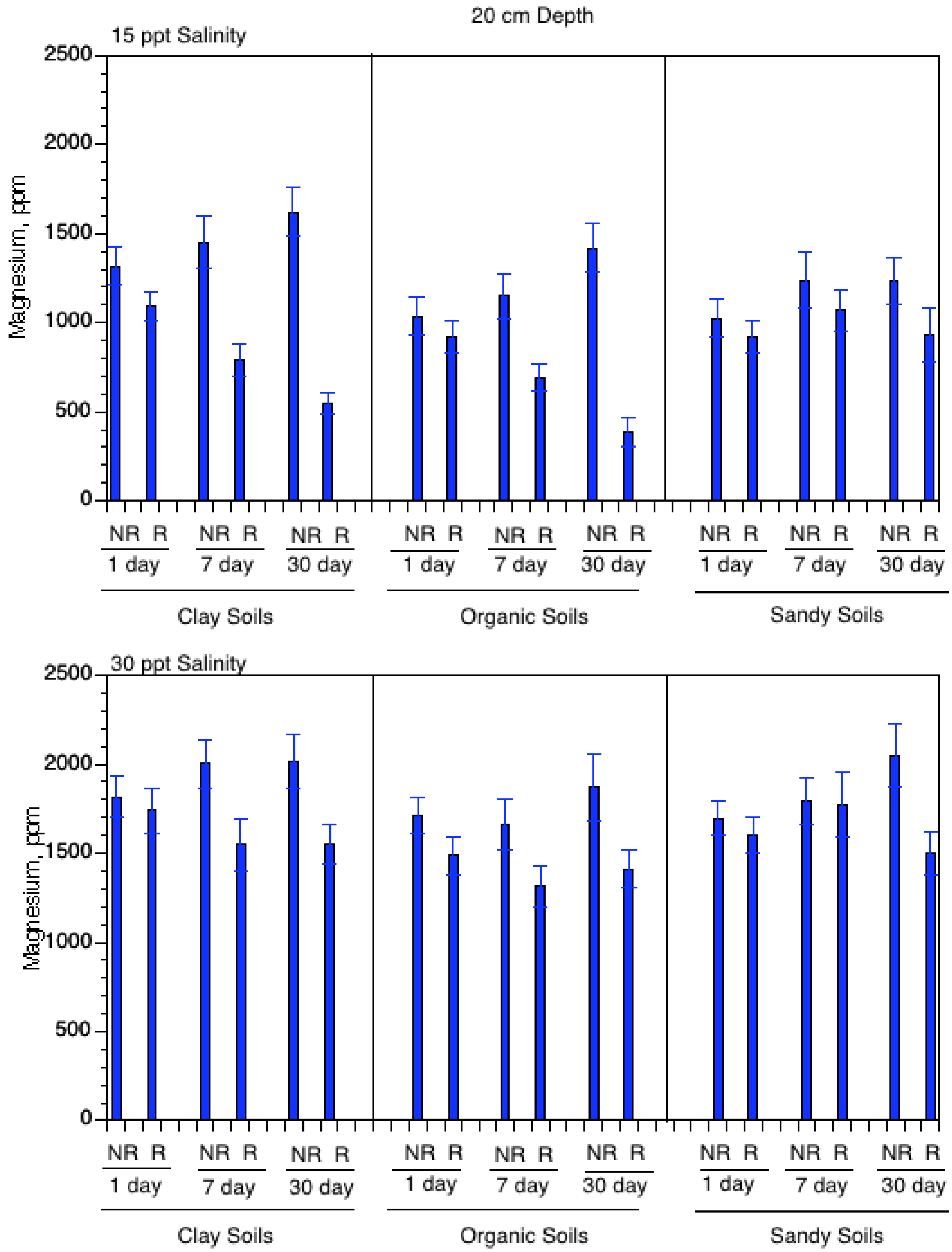

Figure 24. Porewater magnesium (ppm) at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

Table 8. Statistical results of porewater magnesium at two depths in experiments run at two different salinities (15 and 30 g/kg) each with treatments of three soil types (clay, organic, sandy) subjected to two tidal regimes (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain.

Mg (ppm)						
	Salinity = 15			Salinity = 30		
Source	DF	F Ratio	Prob > F	DF	F Ratio	Prob > F
				Depth = 0-5 cm		
Soil TRT	2	135.3417	<.0001	2	33.3523	<.0001
Tide TRT	2	5.3866	0.0051	2	0.7137	0.4908
Rain TRT	1	0.1259	0.723	1	0.5327	0.4661
Soil TRT*Tide TRT	4	1.4518	0.2174	4	2.0112	0.0933
Soil TRT*Rain TRT	2	0.1677	0.8457	2	4.1285	0.0172
Tide TRT*Rain TRT	2	0.8616	0.4237	2	0.3953	0.6739
Soil TRT*Tide TRT*Rain TRT	4	0.2034	0.9364	4	1.375	0.2429
				Depth = 15-20 cm		
Soil TRT	2	140.4987	<.0001	2	3.1173	0.0458
Tide TRT	2	6.4993	0.0017	2	0.6596	0.5178
Rain TRT	1	6.83	0.0094	1	6.2103	0.0133
Soil TRT*Tide TRT	4	2.0733	0.0845	4	0.5976	0.6647
Soil TRT*Rain TRT	2	0.8579	0.4252	2	0.6536	0.521
Tide TRT*Rain TRT	2	2.6315	0.0737	2	0.9763	0.378
Soil TRT*Tide TRT*Rain TRT	4	0.4539	0.7695	4	1.0187	0.398

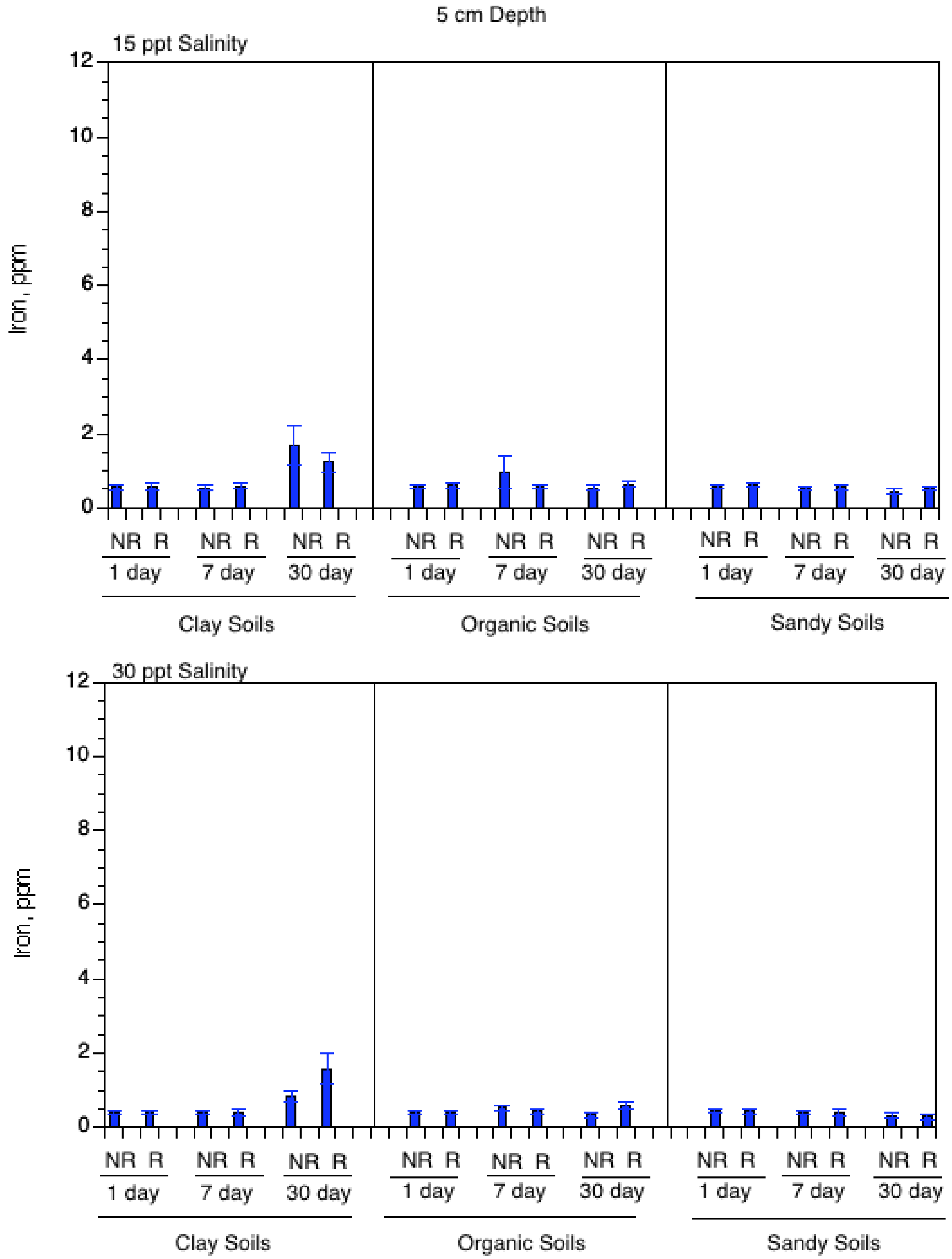

Figure 25. Porewater iron (ppm) at 5 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain (NR = no rain, R = rain).

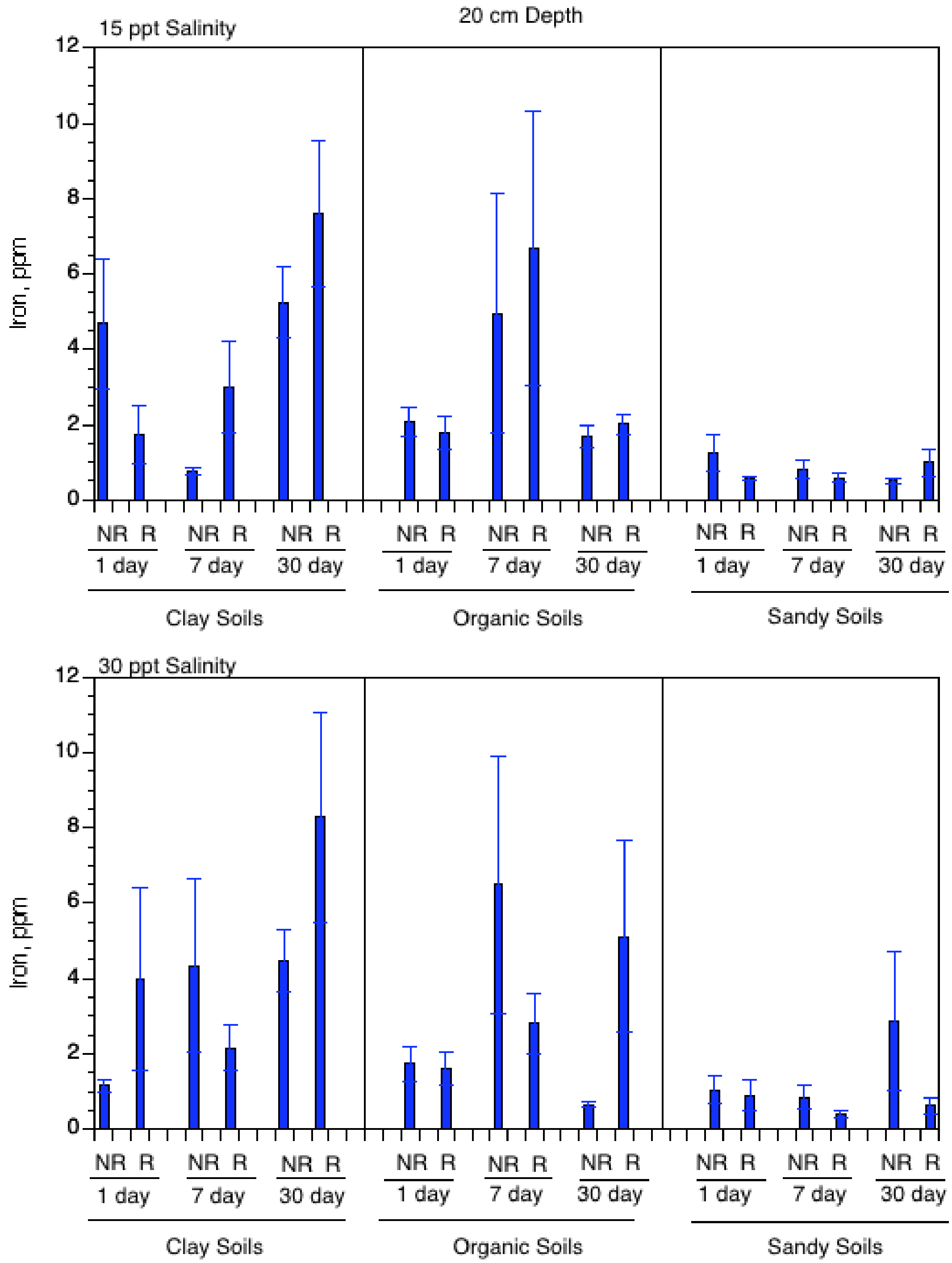

Figure 26. Porewater iron (ppm) at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain (NR = no rain, R = rain).

Table 9. Statistical results of porewater soluble iron at two depths in experiments run at two different salinities (15 and 30 g/kg) each with treatments of three soil types (clay, organic, sandy) subjected to two tidal regimes (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain.

Fe (ppm)						
	Salinity = 15			Salinity = 30		
Source	DF	F Ratio	Prob > F	DF	F Ratio	Prob > F
				Depth = 0-5 cm		
Soil TRT	2	41.294	<.0001	2	6.7097	0.0014
Tide TRT	2	11.9866	<.0001	2	19.4262	<.0001
Rain TRT	1	0.0935	0.76	1	6.2948	0.0127
Soil TRT*Tide TRT	4	5.5127	0.0003	4	8.2261	<.0001
Soil TRT*Rain TRT	2	0.229	0.7955	2	2.0654	0.1288
Tide TRT*Rain TRT	2	1.3025	0.2736	2	6.0974	0.0026
Soil TRT*Tide TRT*Rain TRT	4	1.1032	0.3555	4	1.7181	0.1463
				Depth = 15-20 cm		
Soil TRT	2	12.7445	<.0001	2	5.3673	0.0052
Tide TRT	2	7.538	0.0006	2	2.3474	0.0975
Rain TRT	1	0.8387	0.3606	1	1.0086	0.3161
Soil TRT*Tide TRT	4	4.7555	0.001	4	1.1794	0.32
Soil TRT*Rain TRT	2	0.6356	0.5304	2	0.5092	0.6015
Tide TRT*Rain TRT	2	3.3954	0.0349	2	1.7939	0.1682
Soil TRT*Tide TRT*Rain TRT	4	1.3944	0.236	4	1.0748	0.3692

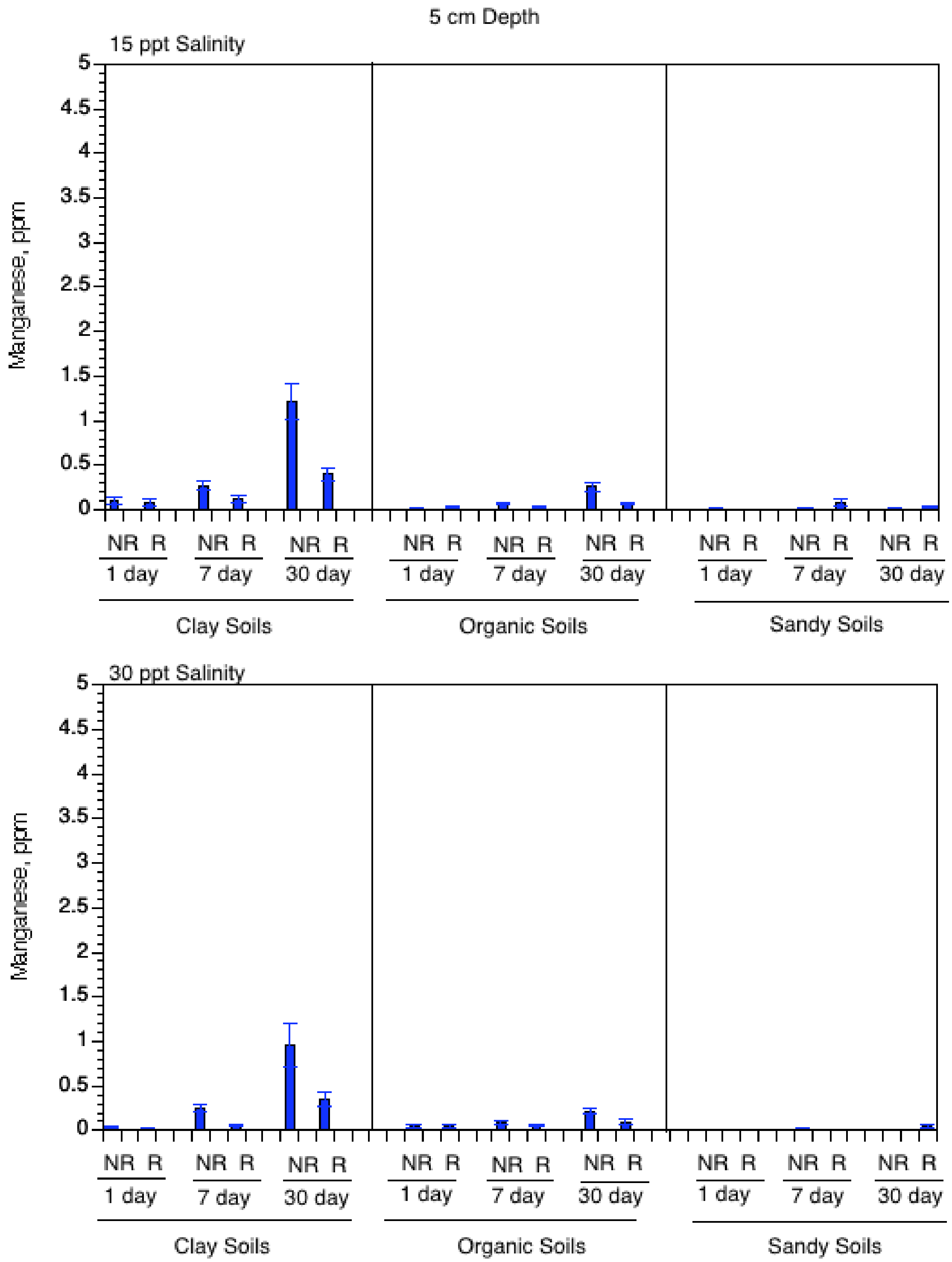

Figure 27. Porewater manganese (ppm) at 5 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

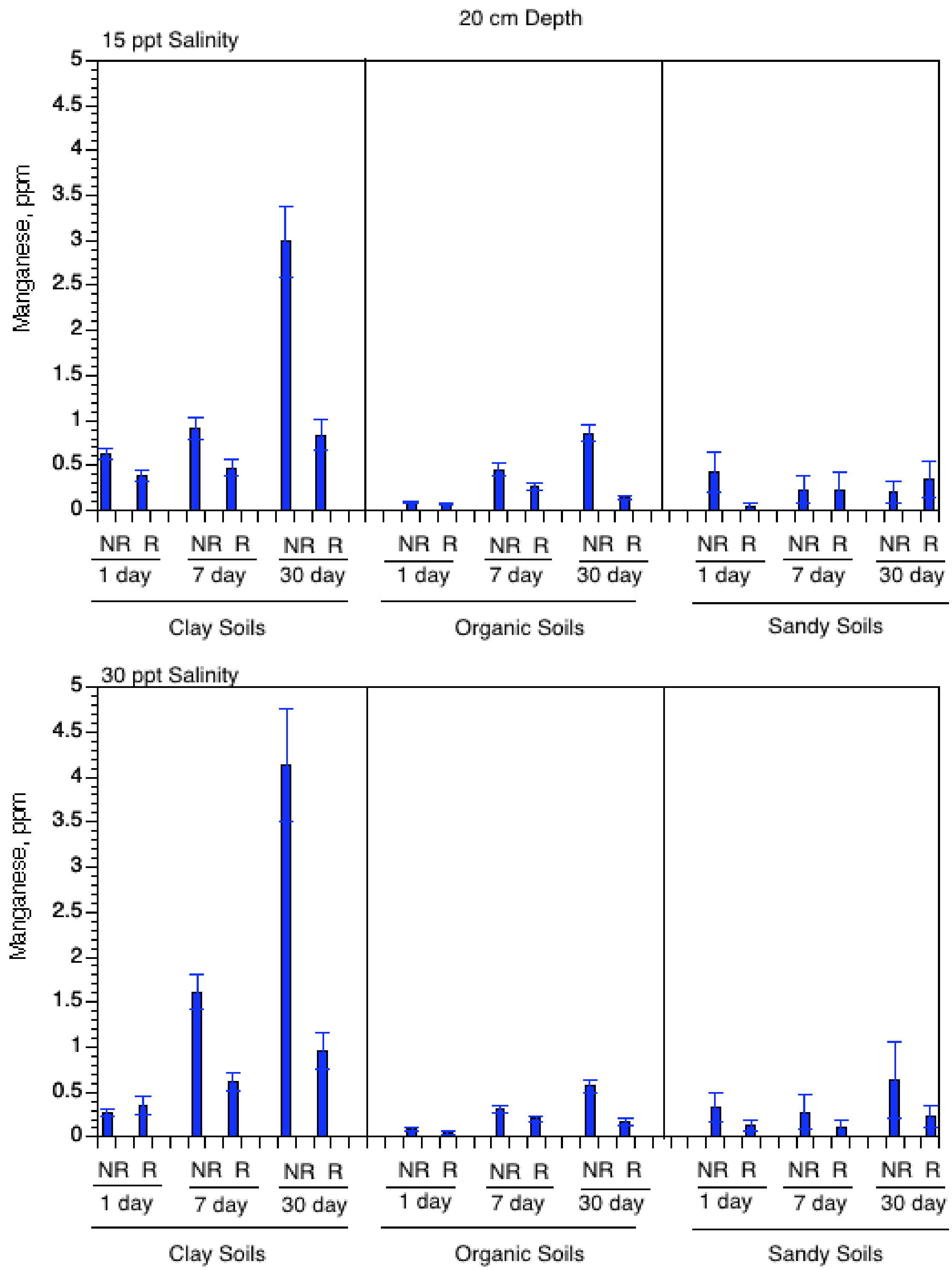

Figure 28. Porewater manganese (ppm) at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

Table 10. Statistical results of porewater manganese at two depths in experiments run at two different salinities (15 and 30 g/kg) each with treatments of three soil types (clay, organic, sandy) subjected to two tidal regimes (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain.

	Mn (ppm)					
	Salinity = 15			Salinity = 30		
Source	DF	F Ratio	Prob > F	DF	F Ratio	Prob > F
				Depth = 0-5 cm		
Soil TRT	2	3.4086	0.0346	2	46.6481	<.0001
Tide TRT	2	51.0283	<.0001	2	82.5932	<.0001
Rain TRT	1	15.9303	<.0001	1	44.2386	<.0001
Soil TRT*Tide TRT	4	14.8902	<.0001	4	22.1706	<.0001
Soil TRT*Rain TRT	2	5.0302	0.0072	2	12.7198	<.0001
Tide TRT*Rain TRT	2	15.0719	<.0001	2	14.6279	<.0001
Soil TRT*Tide TRT*Rain TRT	4	4.2395	0.0024	4	4.5896	0.0013
				Depth = 15-20 cm		
Soil TRT	2	9.3668	0.0001	2	55.9371	<.0001
Tide TRT	2	30.351	<.0001	2	57.6617	<.0001
Rain TRT	1	19.4119	<.0001	1	59.2265	<.0001
Soil TRT*Tide TRT	4	9.0765	<.0001	4	17.4541	<.0001
Soil TRT*Rain TRT	2	4.8966	0.0081	2	14.2564	<.0001
Tide TRT*Rain TRT	2	14.2141	<.0001	2	27.941	<.0001
Soil TRT*Tide TRT*Rain TRT	4	5.6872	0.0002	4	8.6125	<.0001

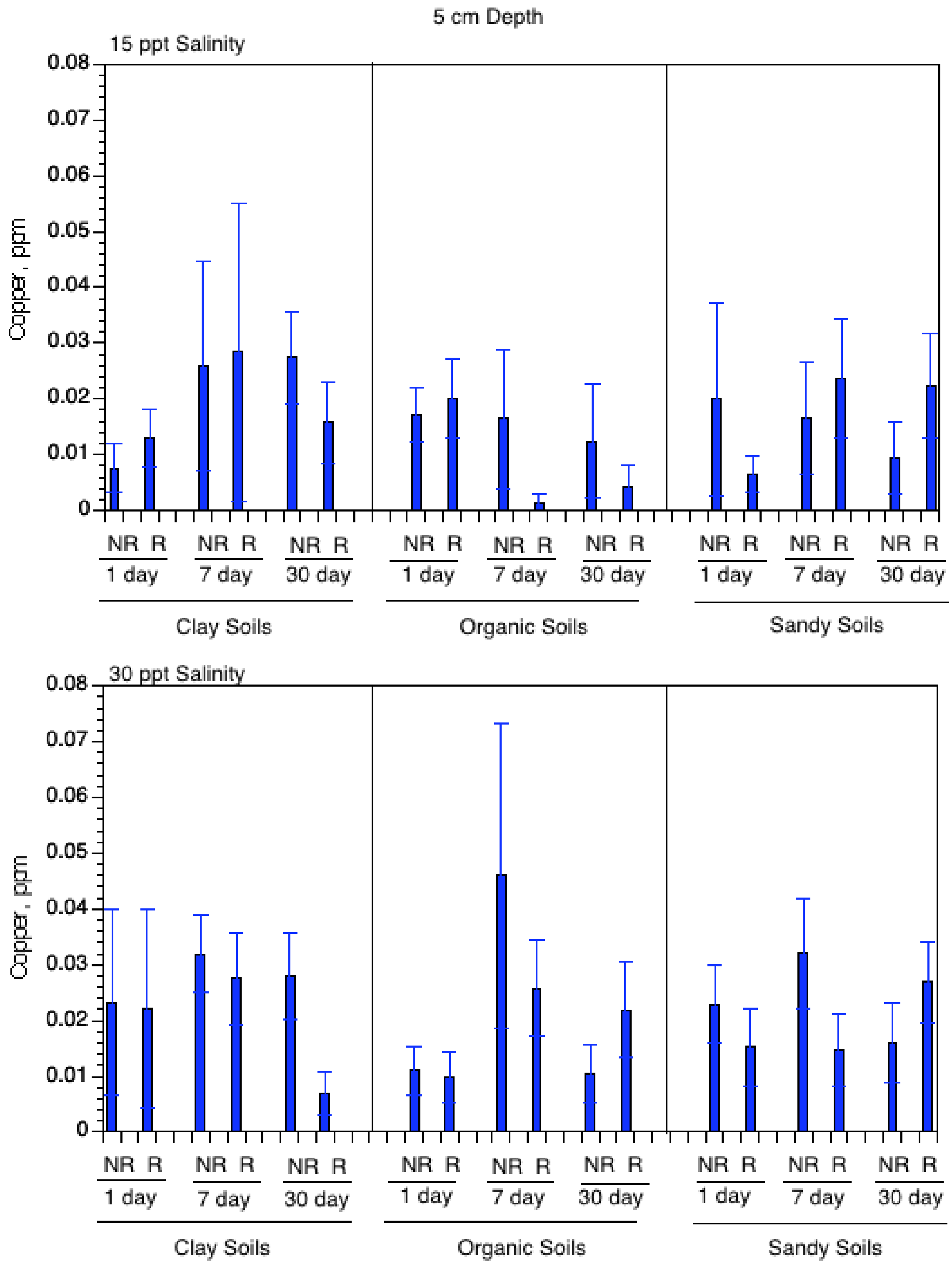

Figure 29. Porewater copper (ppm) at 5 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain (NR = no rain, R = rain).

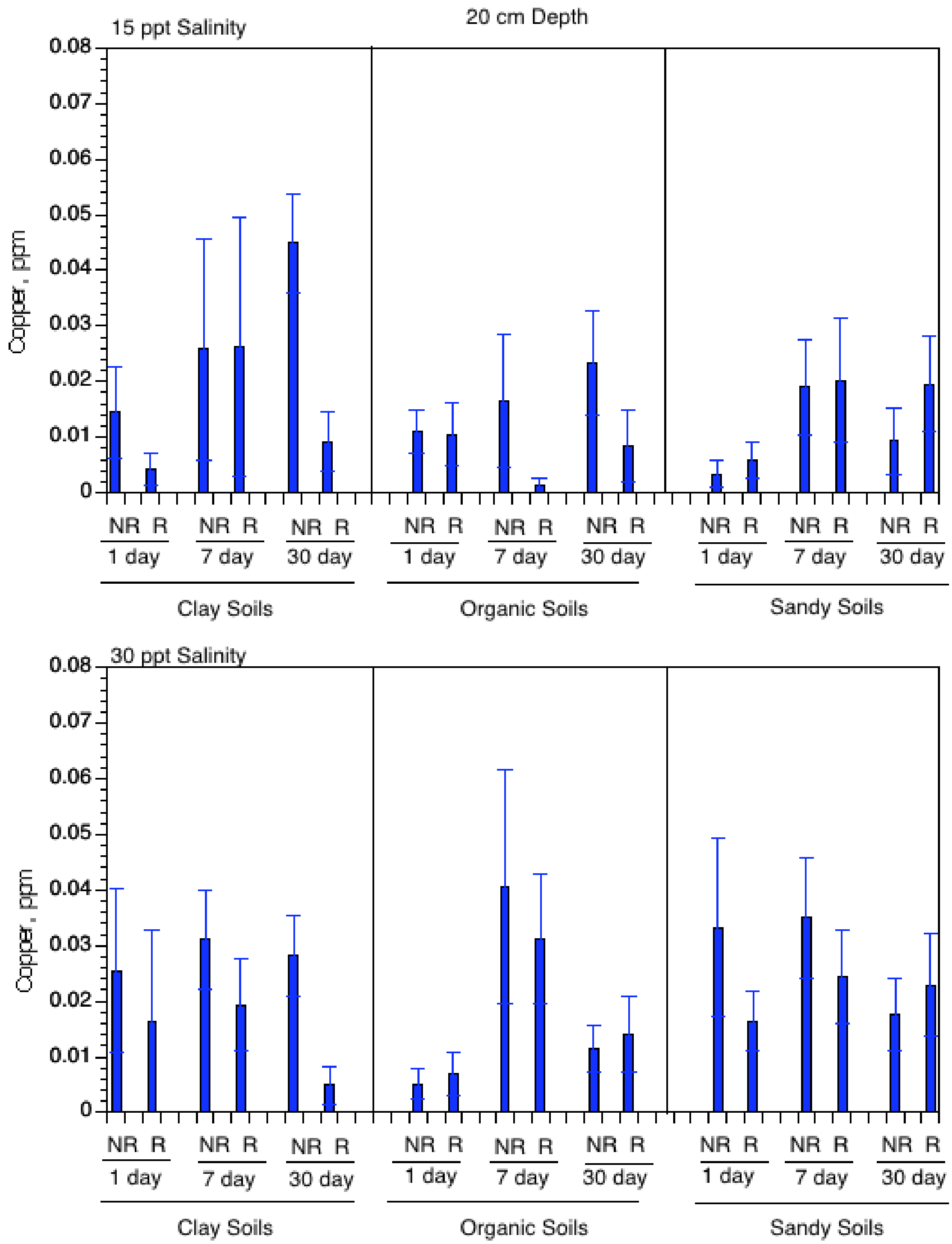

Figure 30. Porewater copper (ppm) at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain (NR = no rain, R = rain).

Table 11. Statistical results of porewater copper at two depths in experiments run at two different salinities (15 and 30 g/kg) each with treatments of three soil types (clay, organic, sandy) subjected to two tidal regimes (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain.

	Cu (ppm)					
	Salinity = 15			Salinity = 30		
Source	DF	F Ratio	Prob > F	DF	F Ratio	Prob > F
				Depth = 0-5 cm		
Soil TRT	2	16.4295	<.0001	2	1.487	0.2279
Tide TRT	2	3.0735	0.0479	2	0.6583	0.5186
Rain TRT	1	0.1278	0.7211	1	0.9709	0.3254
Soil TRT*Tide TRT	4	2.3922	0.0511	4	0.1979	0.9393
Soil TRT*Rain TRT	2	0.2995	0.7414	2	0.7398	0.4782
Tide TRT*Rain TRT	2	0.6009	0.5491	2	0.3456	0.7081
Soil TRT*Tide TRT*Rain TRT	4	1.4837	0.2075	4	0.6768	0.6086
				Depth = 15-20 cm		
Soil TRT	2	16.4452	<.0001	2	2.084	0.1263
Tide TRT	2	4.6471	0.0103	2	0.3126	0.7318
Rain TRT	1	2.5487	0.1115	1	4.0228	0.0458
Soil TRT*Tide TRT	4	2.8866	0.0229	4	0.1645	0.9562
Soil TRT*Rain TRT	2	1.2534	0.2871	2	1.0368	0.3559
Tide TRT*Rain TRT	2	2.0802	0.1268	2	0.4062	0.6665
Soil TRT*Tide TRT*Rain TRT	4	1.2932	0.2729	4	0.3177	0.866

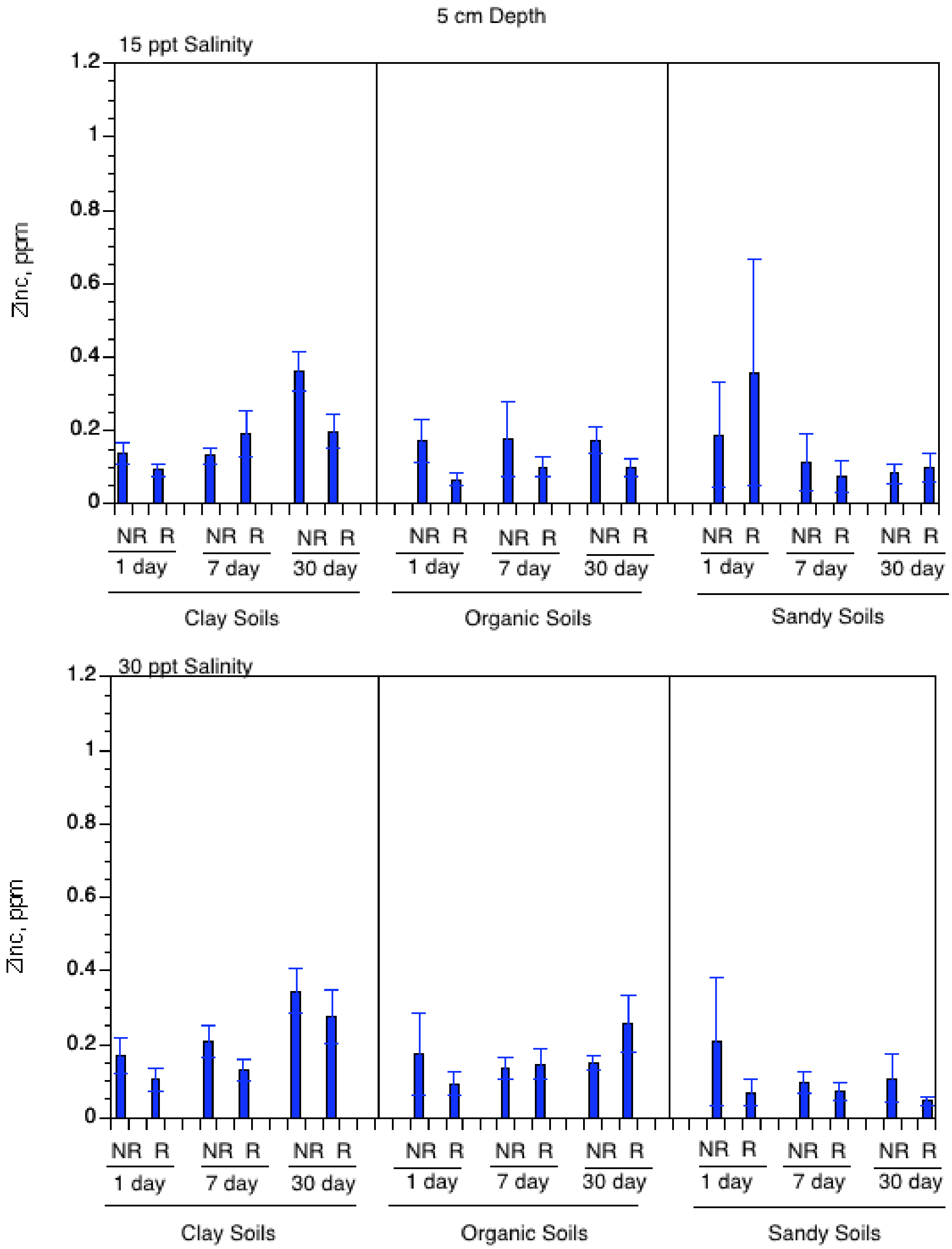

Figure 31. Porewater zinc (ppm) at 5 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

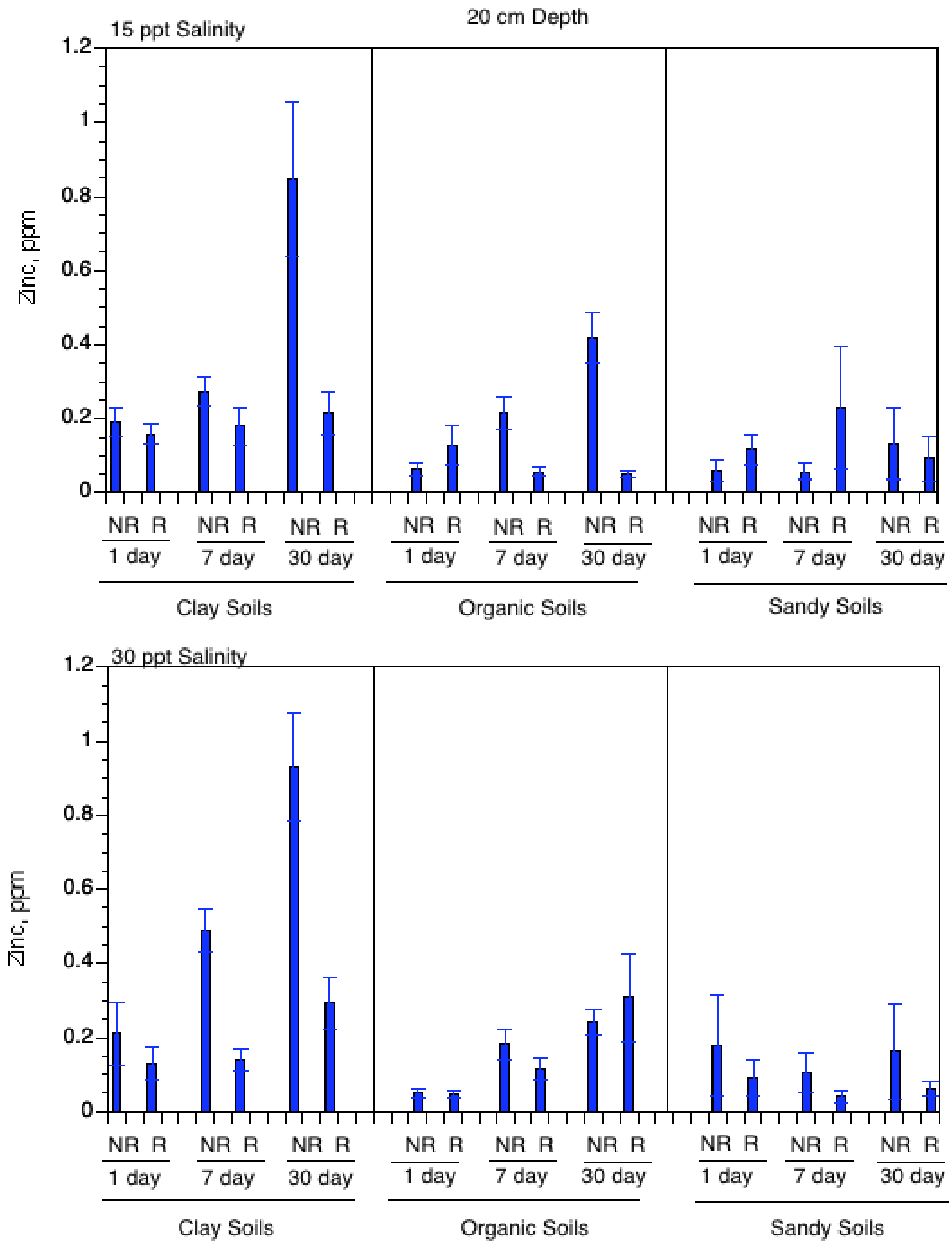

Figure 32. Porewater zinc (ppm) at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain (NR = no rain, R = rain).

Table 12. Statistical results of porewater zinc at two depths in experiments run at two different salinities (15 and 30 g/kg) each with treatments of three soil types (clay, organic, sandy) subjected to two tidal regimes (water exchanged) at 1, 7 and 30 day intervals with or without augmentation of rain.

Zn (ppm)						
	Salinity = 15			Salinity = 30		
Source	DF	F Ratio	Prob > F	DF	F Ratio	Prob > F
				Depth = 0-5 cm		
Soil TRT	2	9.1222	0.0001	2	3.1092	0.0463
Tide TRT	2	1.7267	0.1799	2	3.0927	0.047
Rain TRT	1	0.0347	0.8524	1	1.2271	0.269
Soil TRT*Tide TRT	4	1.3714	0.2442	4	1.2766	0.2795
Soil TRT*Rain TRT	2	0.5922	0.5539	2	0.5923	0.5538
Tide TRT*Rain TRT	2	0.7102	0.4925	2	0.0953	0.9091
Soil TRT*Tide TRT*Rain TRT	4	0.4792	0.751	4	0.4044	0.8054
				Depth = 15-20 cm		
Soil TRT	2	12.5361	<.0001	2	15.9759	<.0001
Tide TRT	2	13.2116	<.0001	2	12.7306	<.0001
Rain TRT	1	7.907	0.0053	1	24.3307	<.0001
Soil TRT*Tide TRT	4	3.7059	0.0059	4	3.4227	0.0094
Soil TRT*Rain TRT	2	3.9403	0.0205	2	7.2223	0.0009
Tide TRT*Rain TRT	2	7.6761	0.0006	2	4.0246	0.0189
Soil TRT*Tide TRT*Rain TRT	4	1.3932	0.2364	4	1.8204	0.125

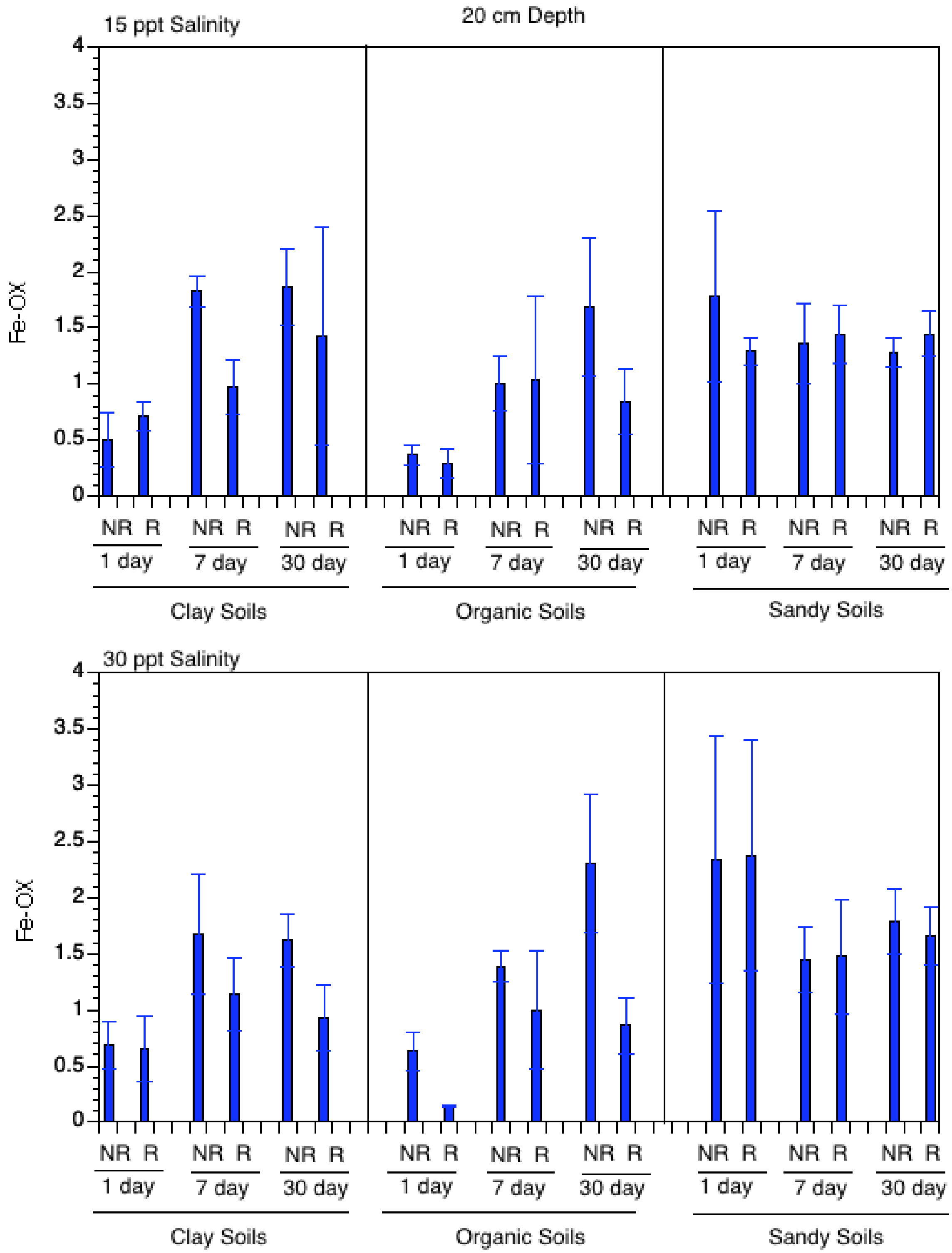

Figure 33. Oxalate-extractable iron (FE-OX, mg/g) at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

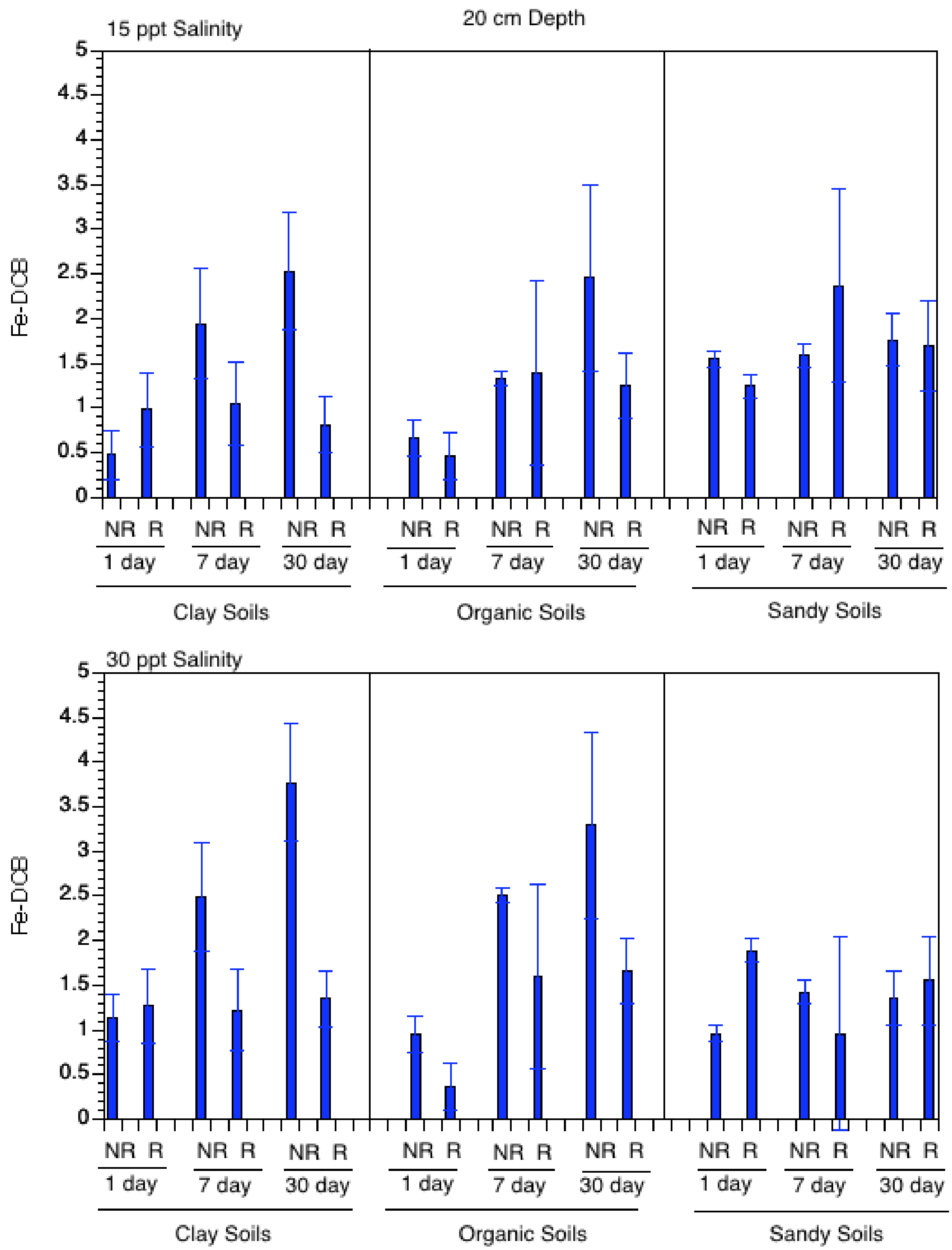

Figure 34. Citrate-dithionite extractable iron (FE-DCB, mg/g) at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

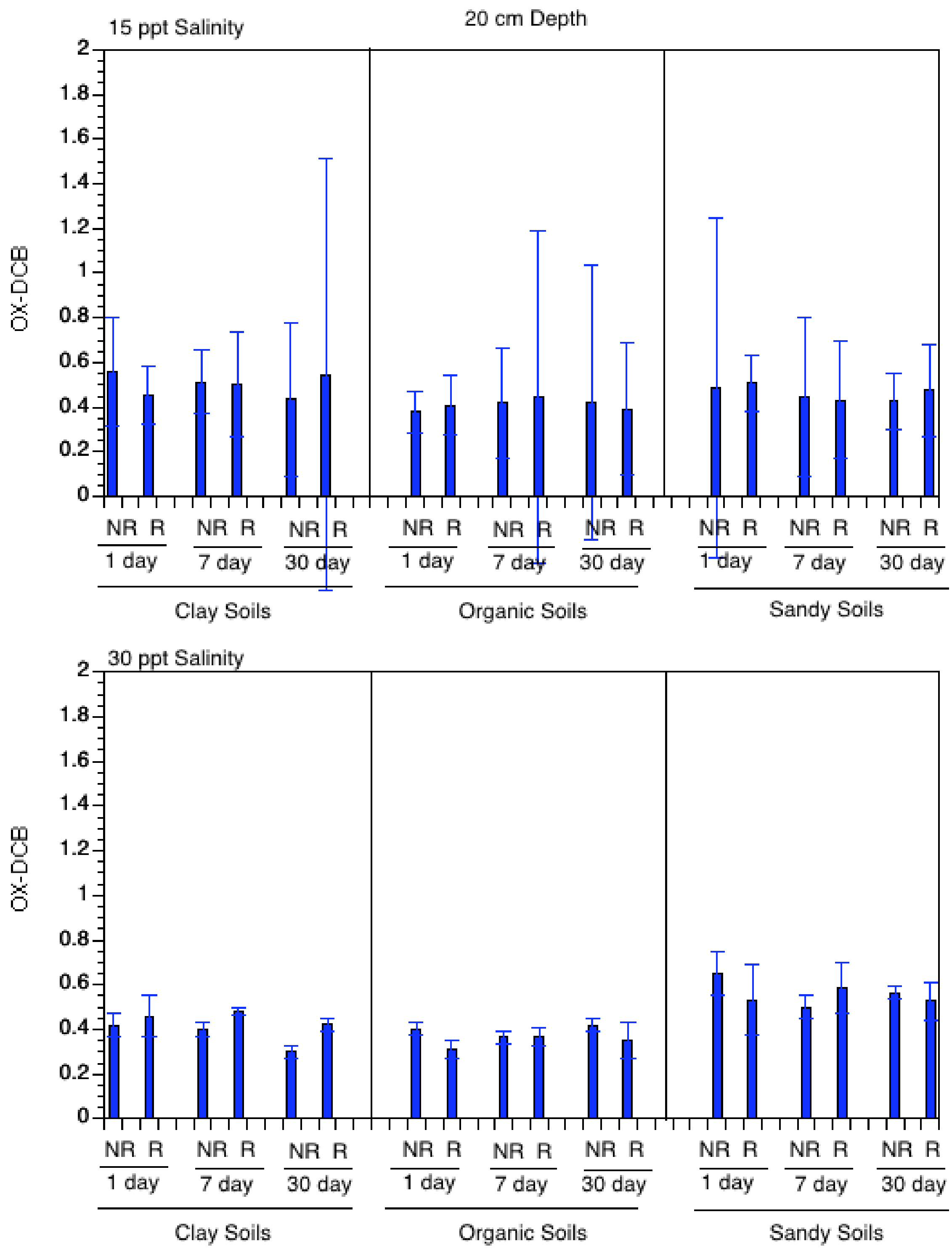

Figure 35.Oxalate-Dithionite Ratio (OX-DCB) at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

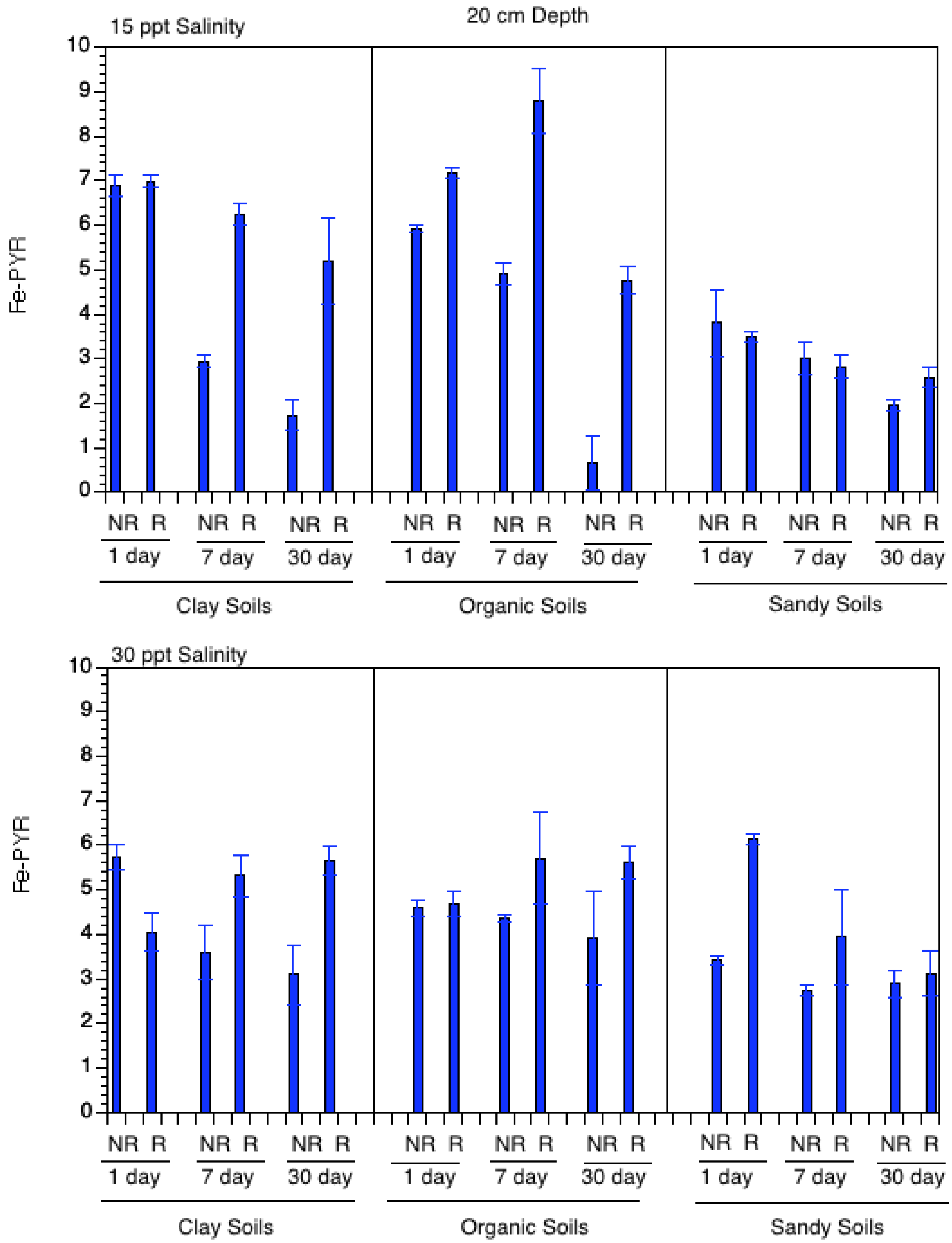

Figure 36. Pyrite (FE-PYR, mg/g) at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

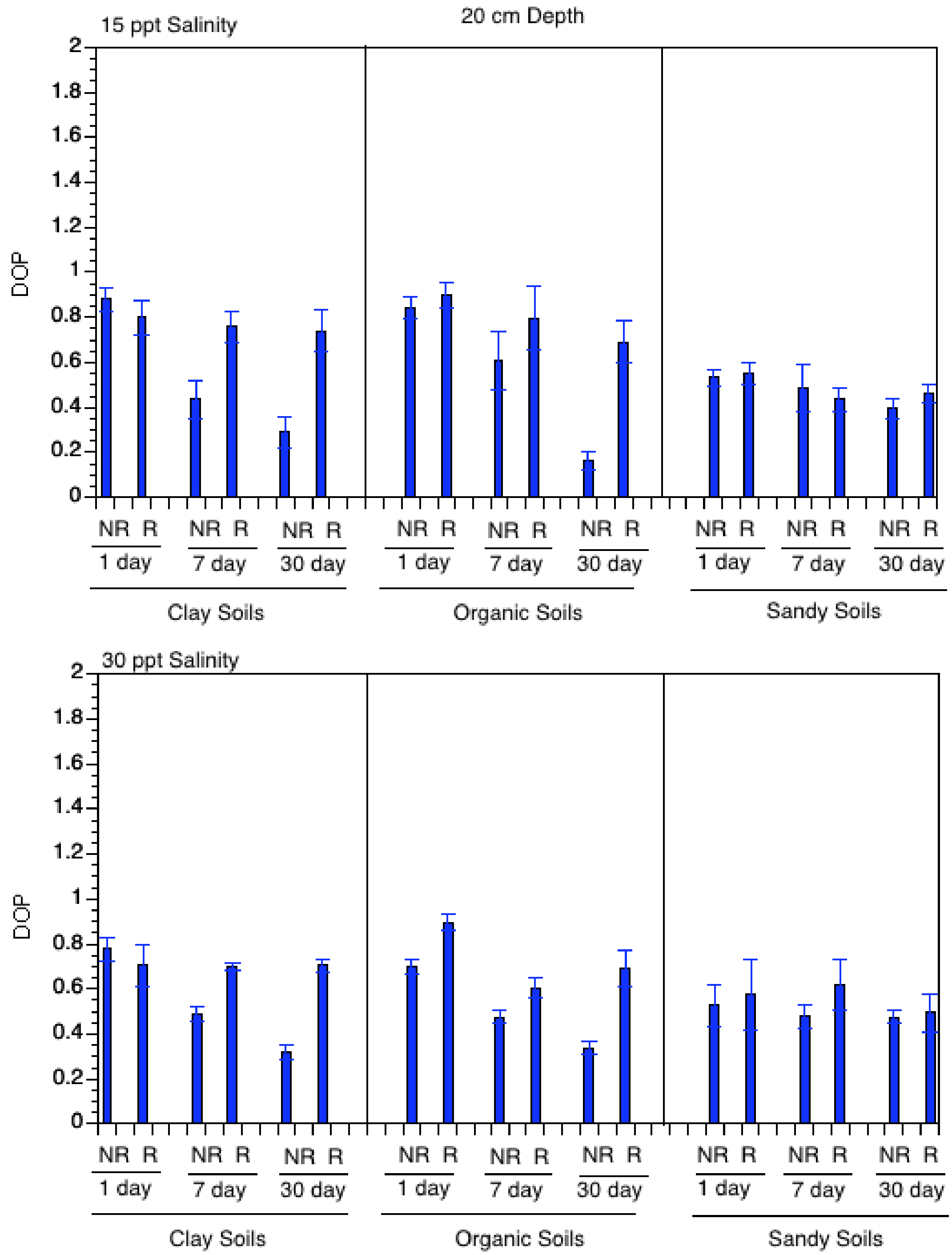

Figure 37. Degree of Pyritization (DOP) at 20 cm depth among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

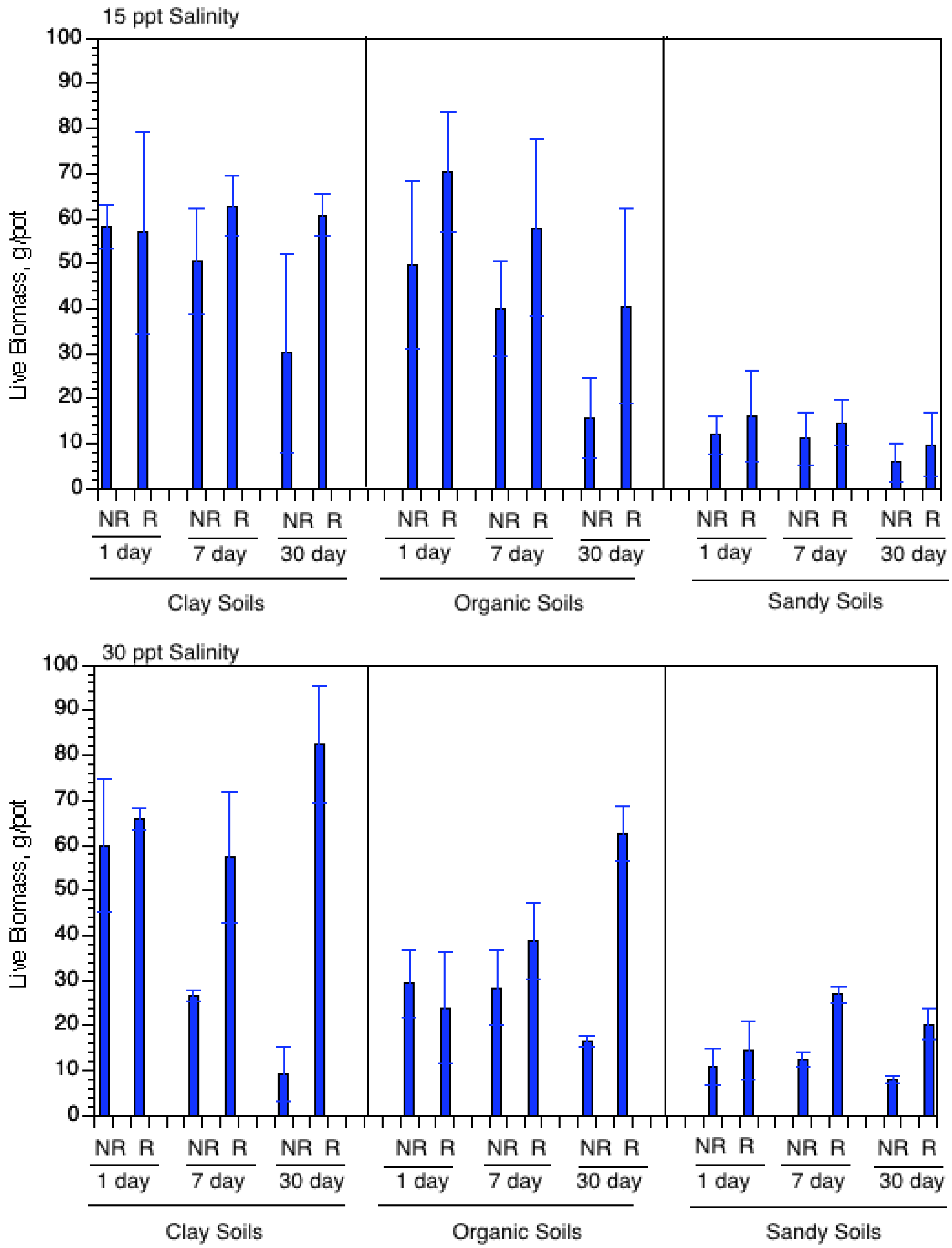

Figure 38 Biomass among three soil types (clay, organic, sandy) subjected to two salinity treatments (15 and 30 g/kg) that have tides (water exchanged) at 1, 7 and 30 day intervals with or without rain (NR = no rain, R = rain).

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