Applied Geochemistry 90 (2018) 87–100

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Soil quality changes due to flood irrigation in agricultural fields along the Rio Grande in western Texas

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ARTICLE INFO

Handling Editor: Prof. M. Kersten

Keywords:
Salt buildup
Pedogenic carbonate
Salinity and sodicity

ABSTRACT

Growing populations demand more food, putting more pressure on soil productivity and sustainability around the world. In western Texas along the Rio Grande Valley, the low natural rainfall requires frequent irrigations for sustaining agriculture. To investigate the impacts of irrigation on soil quality, we collected and modelled geochemical data (major elements and nutrients) on irrigation water, soil pore water, drainage water, and soil samples, and monitored soil moisture, temperature, and electrical conductivity with sensors from two pecan, one cotton, and one alfalfa fields in western Texas.

This study showed that flood irrigation with both surface (Rio Grande river) and ground waters significantly increased the root-zone salinity, soil sodicity, and nutrient leaching from soils to the underlying aquifers and Rio Grande river from agricultural fields of the arid southwest. The water used for irrigation was high in total dissolved solids (>500 ppm generally), dominated by Na^+, Cl^-, Ca^{2+} and SO_4^{2-}. After flood irrigation, infiltrating water dissolved salts such as gypsum that have accumulated in the soils due to previous irrigations, or/and mixed existing concentrated soil waters, and approached saturation with respect to these evaporite minerals. Soil water was supersaturated with respect to carbonates as pedogenic calcite precipitated out and reached concentrations of ~ 10 wt% of total soil mass. This suggested that pedogenic carbonate is an important carbon reservoir and precipitation kinetics and controls of such secondary calcite need further investigation for the irrigated agricultural fields in arid regions of the world.

Chemistry of agricultural return flow samples collected from drainage ditches was similar to that of irrigation water, suggesting that most of the irrigation water had taken a shallow and short flowpath through the fields to drains. Between irrigation events, soil water became more concentrated as water was lost through evapotranspiration that led to precipitation of evaporite salts. As a result, sodicity and salinity of soils, especially clayey soils, frequently exceeded the tolerance levels of major crops grown in the region. Here in these fine-textured soils, combination of high evapotranspiration rates, intensive irrigation with water of elevated salinity, and limited infiltration stunted crop growth, decreased soil porosity and permeability, led to poor aeration, and accelerated salt buildup via a positive feedback mechanism.

During initial irrigation where soils were saturated, soil water also percolated and recharged to underlying aquifers, and thus salts, nutrients, and trace metals from agricultural practices (i.e., application of fertilizers, irrigation, soil amendments, and pesticide) could be mobilized to shallow groundwaters. This implied that chemistry of Rio Grande river, groundwater, and soil was closely linked. Thus the sustainability of agriculture depended on appropriate water, soil and crop management practices.

1. Introduction

Arid and semiarid lands cover approximately 40% of the terrestrial land surface and support more than two billion people (Grace et al., 2006; Wang et al., 2012). As population continues to grow worldwide, the demand on food, fiber, and forage will only increase, putting additional pressure on fragile lands of arid and semiarid ecosystems. However, such ecosystems are already impacted heavily by climate and

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https://doi.org/10.1016/j.apgeochem.2017.12.019
Received 19 October 2017; Received in revised form 13 December 2017; Accepted 18 December 2017

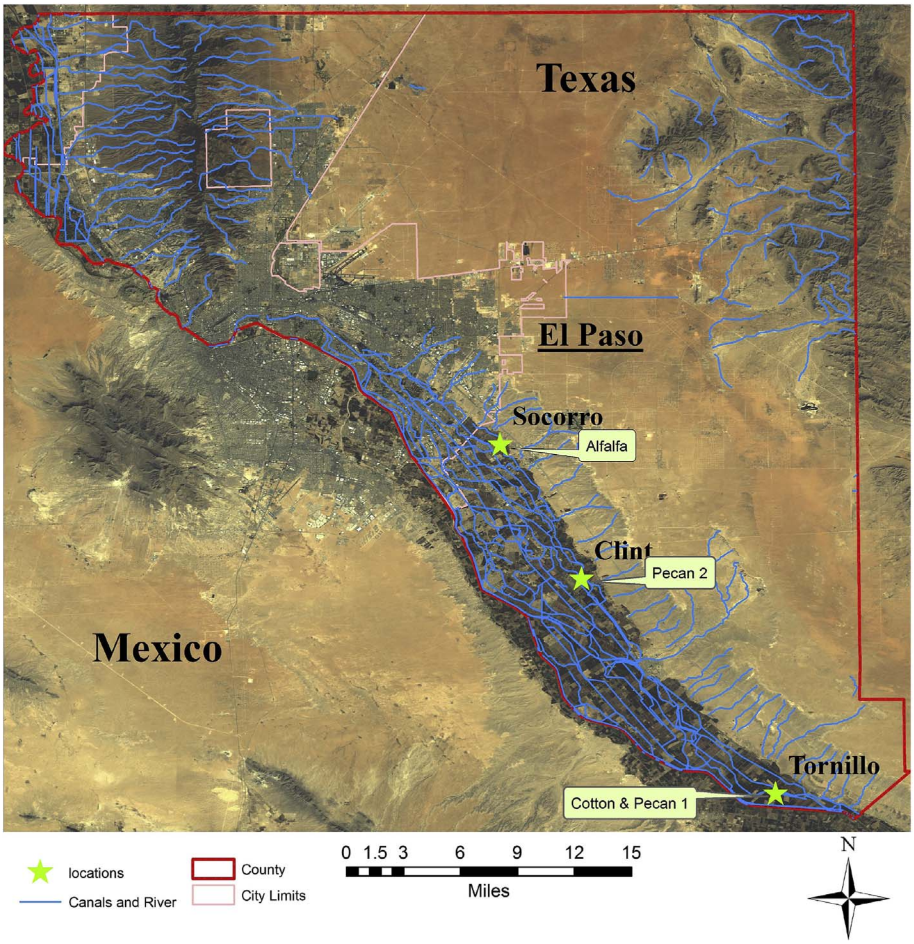

Fig. 1. Location maps of study sites (Alfalfa, Pecan 1, Pecan 2, and Cotton) for the El Paso County in western Texas. Extensive network of irrigation and drainage canals are shown in blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

human induced changes, leading to deteriorating hydrological conditions and soil properties, and losses in ecosystems and their productivities (D'Odorico et al., 2012). Crop growth under limited precipitation conditions are typically intensively irrigated, leading to waterlogging, oxygen deficiency, and salt buildup (Miyamoto and Storey, 1995; Graham and O'Geen, 2010; Szynkiewicz et al., 2014). Indeed, secondary salinization is commonly observed, in agricultural fields of arid and semi-arid regions due to intensive irrigation, fertilizers application and high evapotranspiration rates (e.g., Sheta et al., 2000; Schoups et al., 2005; Jafari et al., 2012). Worldwide, it is estimated that more than 830 million hectares of arable land are impacted by soil salinization (Rath and Rousk, 2015). Salt buildup in soils can lead to water stress in trees and crops by increasing soil water osmotic potential (Miyamoto, 2010). High soil salinity also affects crop growth by limiting nutrient availability (e.g. P, Fe, Cu, Zn, Mo) and through specific ion toxicity (e.g. Na, Cl). Soils with high salinity also have high soil sodicity, which decreases the soil permeability due to clay dispersion.

In the Rio Grande Project area, that includes southern New Mexico and El Paso County in Texas, about 178,000 acres of farmlands are irrigated with Rio Grande river water (Fig. 1). The river is dammed 150 km upstream of El Paso at Elephant Butte, New Mexico, to control seasonal discharge mainly for irrigation usage. River water becomes progressively saline as it moves away from headwaters in San Juan Mountains in south-central Colorado, due to the combined influences of evapotranspiration, salt addition from geologic and anthropogenic sources including saline groundwater upwelling, return flows from agricultural fields, and contribution from waste-water treatment plants (Phillips et al., 2003; Hutchison, 2006; Hogan et al., 2007; Szynkiewicz et al., 2011, 2015; Borrok and Engle, 2015). Near El Paso, Rio Grande river water salinity (expressed as electrical conductivity, EC) averages at 1.2 dS/m, and thus often exceeds 0.75 dS/m, a threshold value for irrigation water salinity (Miyamoto et al., 1995; Ganjegunte et al., 2011). Other water sources available for irrigation include groundwater, agricultural return flow, and treated wastewater. These waters are more saline than river water and add to cost of crop production.

The cropping pattern in the Rio Grande Project area is dominated by pima cotton (*Gossypium hirsutum* L.), pecan (*Carya illinoinensis* (Wang) K. Koch), and alfalfa (*Medicago sativa* L.). The climate of this region is arid, with the annual precipitation around 16 cm and potential evapotranspiration around 194 cm (Arguez et al., 2012; Ganjegunte et al., 2017). Since evapotranspiration exceeds annual precipitation by many folds, agriculture in the region is totally dependent on irrigation. On average, growers in the region apply about 83 cm (pima cotton) to 153 cm (pecans) of irrigation water in a growing season/year (Ganjegunte et al., 2017). Both alfalfa and pecan are water intensive crops that require application at a high frequency, typically ranging from 10 to 12 irrigations per season from April to October (Sammis et al., 2004; Ganjegunte and Clark, 2017). These crops are also salt sensitive with alfalfa, and pecan having salinity threshold values of 2.0, and 2.6 dS m^{-1}, respectively (Maas and Grattan, 1999; Picchioni et al., 2000). Ghassemi et al. (1995) suggested that 73% of the irrigated area in the Rio Grande Basin is affected by salinity and sodicity, leading to poor soil conditions, reduced crop yields, and declining farm profitability. Salt accumulation in soil was estimated to be ~20–50 tons/acre (or equivalent of 5000 to 12,000 g/m^2) in a 10-year period if there were no drainage (Miyamoto, 2010).

Irrigation affects the environments beyond shallow soils near the root zone by leaching salts down and altering their distribution (Rengasamy, 2006; Bossio et al., 2007). For example, the introduction of flood irrigation adds ions to the soils, which will further be redistributed with depth, even to the underlying aquifer system. Indeed, leaching of the salts has been locally shown to increase recharge of salt-rich groundwater under agricultural fields, resulting in degradation of groundwater quality (Rodriguez and Lougheed, 2010; Szynkiewicz et al., 2011, 2015; Sheng, 2013). Thus soil salinity and surface water quality are inextricably linked in the Rio Grande valley. It is important to understand the interactions among soil, irrigation water, shallow groundwater, and crop performance for ensuring long-term agricultural productivity, managing soil salinity and maintaining environmental quality.

The objective of this study was to evaluate impacts of irrigation and other agricultural practices on soil salinity and sustainability, focusing on three major crops (cotton -*Gossypium hirsutum* L., pecan- *Carya illinoinensis*, and alfalfa- *Medicago sativa*.) in far west Texas, United States. The specific goals are (1) to evaluate the current soil salinity and investigate its correlation to soil texture and original deposition environments; (2) to study irrigation water and soil water characteristics in a context of salt and nutrient loading to soils, and (3) to determine the historical effects of farming and irrigation on soil sustainability.

2. Methodology

2.1. Study sites

Four study sites representing the three major crops (alfalfa, pecan, and cotton) were selected to conduct field experiments during 2011–2012. These consisted of two pecan fields: Pecan 1 (Tornillo, Texas) and Pecan 2 (Clint, TX); one cotton field (Cotton) in Tornillo, Texas and one alfalfa field (Alfalfa) in Socorro, Texas (Fig. 1). Soil texture and mineral composition differ with locations and are mainly controlled by the types and history of ancient river-bed sediments (Supplementary material, Table 1S). Briefly, the dominant soil map units in the study sites were Harkey silty clay loam (Coarse-silty, mixed (calcareous), thermic Typic Torrifluvents) in sites Alfalfa and Pecan 2; Saneli silty clay (Clayey over sandy or sandy-skeletal, montmorillonitic (calcareous), thermic Vertic Torrifluvents) in site Cotton, andTigua silty clay (Very-fine, montmorillonitic (calcareous), thermic Vertic Torrifluvents) in site Pecan 1 (USDA-NRCS, 2010). In addition to irrigation and fertilizers, other soil amendments to lower soil sodicity and improve crop yields were typically applied to these soils. To be specific, about 500 lbs of elemental S (92%) was added per acre per year ($56\,g\,m^{-1}\,yr^{-1}$).

2.2. Soil sample collection and characterization

Baseline soil samples were collected from each of the study sites in April of 2011 at 10 cm intervals down to a total depth of 60 cm to cover the effective root zone of three major crops of the region. After collection, soils were dried at room temperature.

Processed soil samples were analyzed for saturated paste extract (SPE) and its electrical conductivity - EC_e (Rhoades, 1996), pH (Thomas, 1996), and concentrations of major cations Na^+, Ca^{2+}, and Mg^{2+} using inductively coupled plasma spectrometry (Helmke and Sparks, 1996; Suarez, 1996). Sodium adsorption ratio (SAR) of the soil samples were estimated using the following equation (Essington, 2003):

$$SAR = \frac{[Na^{+}]}{\sqrt{[Ca^{2+}] + [Mg^{2+}]}} \tag{1}$$

where $[Ca^{2+}]$, $[Mg^{2+}]$, and $[Na^+]$ represent concentrations of the respective cations in SPE (in the unit of mmol/L).

Cation exchange capacity (CEC) and concentrations of exchangeable cations were measured according to Sumner and Miller (1996). The CEC of soil samples was determined by a two-stage sequential extraction process that is necessary for soils of high salt contents: 1 M sodium acetate (NaOAC) extraction at pH 8.2, followed by 1M ammonium acetate (NH_4OAC) at pH 7. After adding each reagent, the slurry was shaken and then centrifuged for 10 min at 2000 rpm. Between the two extractions, ethanol was used to ensure all the reagents were completely removed. The extracts from the 1M NaOAC extraction were discarded and those from 1M NH_4OAC were analyzed for Na^+ (to determine total CEC) using a Perkin Elmer 5300DV inductively coupled plasma optical emission spectrometry (ICP-OES) in the Department of Geological Sciences at the University of Texas at El Paso (UTEP).

Concentrations of exchangeable cations in bulk soils, such as Ca^{2+}, Mg^{2+}, and Na^+, were determined separately based on standard methods with 1M NH_4OAC solution (Sparks, 1996). Standards for the ICP-OES analyses were prepared in the same 1M NH_4OAC matrix. As existing Ca-bearing minerals continued to release Ca from structural form into NH_4OAC, exchangeable Ca was quantified from the difference between CEC and sum of other major cations (Na^+, K^+ and Mg^{2+}). Data collected from this procedure was then used to estimate the exchangeable sodium percentage (ESP), the sodium to CEC ratio expressed in percentage unit (Essington, 2003).

A representative portion of each soil sample was ground using a Micronizing mill to pass a sieve (#200 mesh, or 75 μm). For total carbon analysis (TC), ~0.2–0.5 g of a ground soil sample were weighed, placed in ceramic boats that were previously washed and combusted in an oven at 500 °C for 2 h, and introduced to the solid module of the Lachat IL 550 TOC-TN analyzer in the Department of Biological Sciences at UTEP. Six standards of pure calcite powder with weights between 0.005 and 0.05 g were used for calibration. For total organic carbon (TOC) analysis, ~0.2–0.5 g of a ground soil sample were weighed, and acidified with 10% HCl to remove all inorganic carbonate, dried completely at 105 °C, and then measured in Lachat TOC-TN analyzer. The difference between TC and TOC for each soil sample is attributed to total inorganic carbon (TIC; i.e., carbonate carbon). Additionally, the carbonate carbon content was quantified for soil samples from the cotton field using pressure-calcimeter method (Sherrod et al., 2002), where TIC was determined by measuring the pressure of CO_2 after acidification of soil samples in a sealed glass bottle. Mixtures of calcite and quartz (inert) powders of different weight ratios were used as standards.

2.3. Water sample collection and characterization

Each agricultural field was irrigated by flooding. Three types of waters were collected in order to gain a better understanding of soil and water interaction along the flow path that connects soils with the Rio Grande water and shallow groundwater aquifer: (1) irrigation water (IRW), (2) soil water, and (3) drainage water (DRW). IRW was sampled from irrigation canals at each site before the onset of irrigation to the fields. For the Cotton and Alfalfa sites, only Rio Grande surface water was used for irrigation. Compared to cotton and alfalfa, pecan trees are more water demanding, needing about 1–2 m of water each year in the study area. For the Pecan 1 and Pecan 2 sites, groundwater from local wells was also used for irrigation when the water supply from the Rio Grande was limited, especially during droughts. DRW was sampled from the drainage canals approximately four days after the onset of irrigation. This four-day period allowed water on the field to infiltrate the soil profile and some of it to reach the drainage canal. Soil water was collected using 1900-series tension lysimeters (SoilMoisture Ltc, Barbara, CA). Lysimeters were cleaned by 10% hydrochloric acid, followed by a thorough rinse with de-ionized water. At each study site, a nest of three lysimeters was installed at 15 cm, 30 cm and 60 cm respectively. A hole was augered to the desired depth, then back filling around the lysimeters using the same soil in original order to preserve the soil layer. A vacuum of 50 centibar was applied to each lysimeter one day before every irrigation event. Disposable plastic tubing was lowered to the lysimeter cup and soil water samples were collected using a syringe, attached to the tubing.

If the sample volume allowed, separate aliquots of water samples

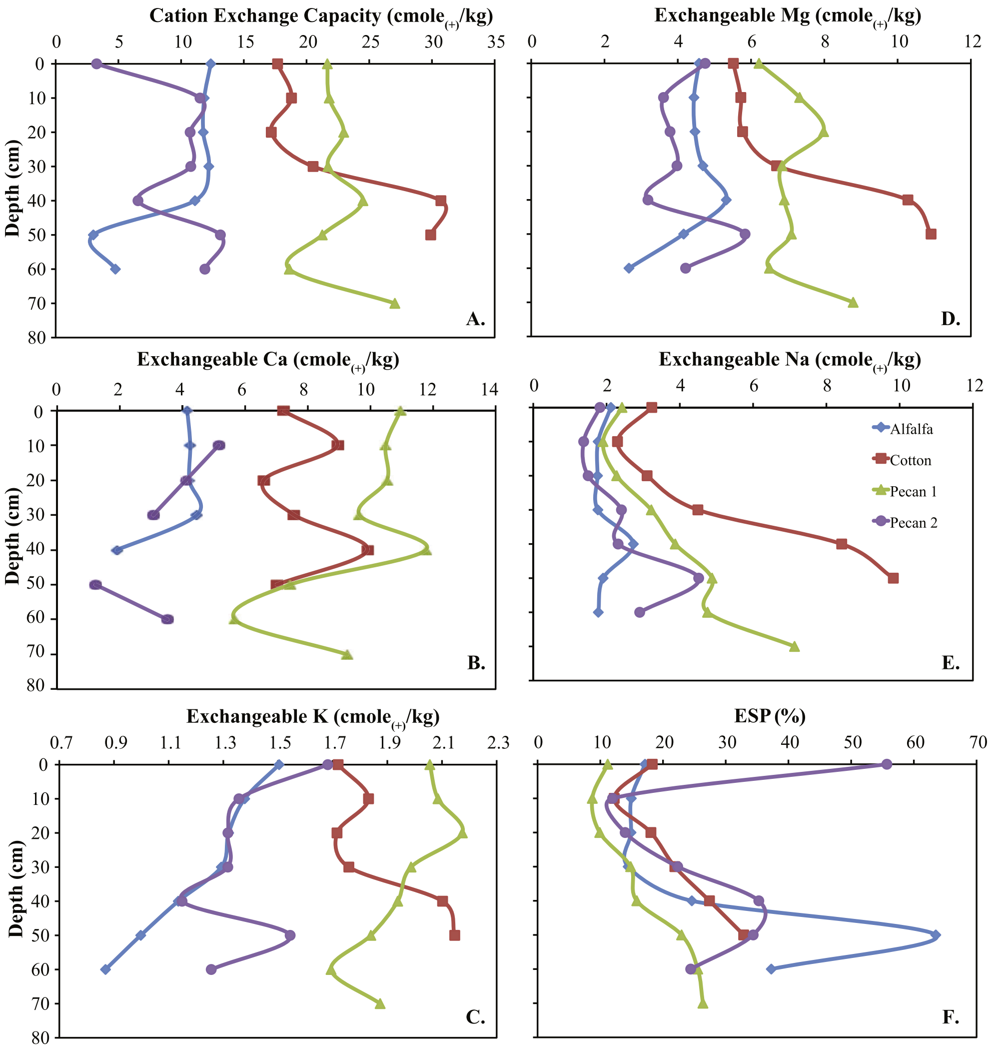

Fig. 2. Soil cation exchangeable capacity (CEC; A), exchangeable Ca^{2+} (B), K^+ (C), Mg^{2+} (D), Na^+ (E), and exchangeable sodium percentage (ESP; F) as a function of depth at each study site.

were collected for the analyses of alkalinity, major cations, major anions, dissolved organic carbon (DOC) and total nitrogen (TN). Samples were filtered in the field with a nylon syringe filter (0.45 µm pore size; 25 mm diameter), and refrigerated until analysis. Cation samples were acidified with several drops of ultrapure nitric acid in the field during collection, while anion and alkalinity samples were left untreated in 30-ml plastic bottles. The alkalinity samples were filled completely to avoid degassing. DOC and TN samples were acidified with several drops of 10% HCl in 30-ml and pre-combusted glass bottles, and kept frozen until analysis.

A total of 57 water samples were collected from the four field locations during the 2011 irrigation season. The pH and EC values of each water sample were measured in the field using a Symphony pH meter and a Orion 012005MD conductivity meter. Meters were calibrated before each analysis using two standards, respectively. Water samples were diluted by 1:10 using deionized water before elemental analysis. Concentrations of major cations (Ca^{2+}, K^+, Na^+, Mg^{2+}, and Sr^{2+}) and silica in water samples were measured on ICP-OES. Two reference water samples were used as external checks of accuracy, USGS M-210 and NIST 1640a. Anion concentrations (Cl^-, SO_4^{2-}, NO_3^-, Br^-, PO_4^{3-}, and F^-) were measured on a Dionex 2100 ion chromatograph (IC) at UTEP. An Anion Mix A solution from Alltech was used as an external check for quality control. Alkalinity was titrated by diluted HCl acid on a Mettler Toledo DL15 Titrator and calculated using a Gran plot (Drever, 1997). A sodium bicarbonate solution prepared in deionized water was used as a standard for alkalinity titration. The DOC and TN were measured using the Lachat IL 550 TOC-TN analyzer in a liquid module. Potassium hydrogen phthalate dissolved in deionized water was used as a standard at concentrations ranging from 0.5 to 50 mg/L. All reagents used for this study were trace-metal grade and thus contributed negligible to the background or procedure blanks.

For geochemical modeling calculations, the elemental chemistry of the water and pH were used as inputs for the geochemical program SOLMINEQ.88 and the saturation indexes of seven evaporite minerals were reported: calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), disordered dolomite, gypsum ($CaSO_4·2H_2O$), halite (NaCl), nacholite ($NaHCO_3$), and thenardite (Na_2SO_4). Water temperature was assumed to be 22 °C for all three depths, which was close to air temperature during the irrigation period. For the SOLMINEQ program, the Pitzer model was used to calculate activity coefficients.

2.4. Sensor installation and data collection

Three ECH$_2$O-5 TE (Decagon Devices Inc., Pullman, WA) sensors were installed at each site to measure soil moisture, temperature, and bulk soil EC at the depths of 15 cm, 30 cm, and 60 cm, as they effectively cover the rooting depths of crops grown in these fields. These were the same depths as soil waters sampled through the lysimeters. Data from sensors were collected at a 5-min interval and stored in a datalogger and collected every three months. Sensors for the pecan fields were placed halfway between a pecan tree base and its canopy to provide an accurate representation of soil conditions influenced by pecan trees. Sensors for the cotton field were located beneath a row of cotton and in the same vicinity as the lysimeters. No special placement was needed in the alfalfa fields.

3. Results

3.1. Soil texture and chemistry

Select soil properties, including particle size and bulk density, were available at each location from WebSoil Survey (retrieved from websoilsurvey.com on April 17, 2012) and summarized in Supplementary material, Table 1S. According to the field survey, soils in all our study sites were fine-textured. Soils from the Alfalfa and Pecan 2 sites contained 60% silt and 33% clay for the top 30 cm, and with 72% silt and 14% clay below 30 cm. The Cotton site had 55% silt and 37% clay. Pecan 1 site had 50% clay and 45% silt for the top 25 cm soils, and 25% silt and 65% clay in 25–120 cm, and 40% silt and 20% clay below 120 cm.

The soil chemistry data including CEC, concentrations of individual exchangeable cations, concentrations of water-soluble cations, organic and inorganic carbon contents, soil pH, and soil EC, as well as calculated SAR and ESP were reported in Supplementary material, Table 2S. The CEC of soils from the Alfalfa and Pecan 2 sites ranged from 3 to 15 $\text{cmol}_{(+)}\ \text{kg}^{-1}$. At the Pecan 1 and Cotton sites, soil CEC was higher, between 15 and 35 $\text{cmol}_{(+)}\ \text{kg}^{-1}$ (Fig. 2A). For all sites, divalent Ca^{2+} and Mg^{2+} were dominant in the exchangeable sites, followed by Na^+ and K^+ (Supplementary material, Table 2S; Fig. 2B, 2C, 2D, and 2E). Concentrations of exchangeable Ca^{2+} and Mg^{2+} in the Alfalfa and Pecan 2 soils remained relatively constant around 4 $\text{cmol}_{(+)}\ \text{kg}^{-1}$, which were lower than those in the soils of the Pecan 1 and Cotton sites (6–10 $\text{cmol}_{(+)}\ \text{kg}^{-1}$) (Fig. 2B and 2D). Exchangeable Na^+ showed increases in concentrations with depth in soils of the Pecan 1 and Cotton sites, while its concentration remained relatively constant throughout the soil profiles of the Alfalfa and Pecan 2 sites (Fig. 2E). Exchangeable sodium percentage (ESP) increased with depth in Cotton and Pecan 1 sites, while large fluctuations were observed in Alfalfa and Pecan 2 sites (Fig. 2F).

Soils in all four locations were neutral in pH, with average value at 8.1 (Fig. 3A). Small decreases in pH were observed with increasing depth in Alfalfa, Pecan 1 and Pecan 2 sites. Cotton site showed the most variability in soil pH values; the pH was as low as 7.2 at 50 cm deep below surface. Soil EC, measured from the saturation paste, ranged from 1.0 to 8.8 dS/m and typically increased with depth at the Cotton, Pecan 1, and Pecan 2 sites (Fig. 3B). In contrast, soil EC in Alfalfa, the lowest among all study sites, was relatively constant. Two out of four sites had soils at depth where SAR was greater than 13, Cotton, and Pecan 1; of the four sites, Cotton soils show the highest SAR (Fig. 3C). At each site, the SAR values were higher in deeper soil samples, than shallower ones.

In all four locations, Na^+ was the dominant cation in the water-soluble fraction, ranging from 0.5 to 8 meq/100g. Concentrations of water-soluble Na^+ increased with depth in Pecan and Cotton soils but remained relatively constant in Alfalfa (Fig. 3D). Cotton soils exhibited the largest increase in concentrations of water-soluble Na^+ at 20 cm depth and below. Water-soluble Mg^{2+} and Ca^{2+} behaved similarly as Na^+, but their concentrations were much lower (Fig. 3E and 3F). Indeed, water-soluble Mg^{2+} and Ca^{2+} showed increases in concentrations with depth except for Alfalfa, where they decreased slightly towards deeper soils. Water-soluble K^+ was much lower in concentrations than other cations, from 0.02 to 0.16 meq/100g (Fig. 3G).

Total carbon (TC) contents were the highest at the surface in both Pecan 1 and Pecan 2 sites (~2.8 wt%) and decreased sharply at 10 cm to ~ 1.2 wt% or less (Fig. 4A). Total organic carbon (TOC) contents in the soil ranged from 0.4 to 1.2 wt % and generally decreased with depth (Fig. 4B). Thus, TOC accounted for about 1/3 of TC. Total inorganic carbon (TIC) was present in the soils as pedogenic carbonate, and its contents were converted to soil carbonate contents assuming $CaCO_3$ stoichiometry. The carbonate wt% changed little among different sites and with depth at each site (Fig. 4C). Additionally, TIC of Cotton soils was measured by a pressure-calcimeter method (Sherrod et al., 2002) and the data was in agreement with that calculated from difference between TC and TOC, within uncertainty of two methods (Fig. 4D). The $CaCO_3$ contents slightly decreased with depth, between 6.7 and 10 wt% in the Cotton site.

3.2. Water chemistry

The elemental chemistry of the water samples and the calculated saturation indexes were reported in Supplementary material, Tables 3S and 4S, respectively. Charge balances were evaluated by calculating the major cation contributions from Ca^{2+}, K^+, Mg^{2+}, and Na^+, and major anion contributions from Cl^-, NO_3^-, SO_4^{2-} and alkalinity. All points either lied on or were very close to the 1:1 line, suggesting that all dominant ions that contributed to charges were analyzed and elemental concentrations were measured with high quality (Supplementary material, Fig. 1A). Generally, water samples from the Alfalfa site had lower EC values than those from Pecan and Cotton sites (Supplementary material, Fig. 1B).

For plotting purposes, irrigation water (IRW) samples were arbitrarily placed at the depth of 0 cm, and drainage water (DRW) samples at 100 cm on all depth profiles. IRW showed a large variation in pH and EC values (Fig. 5A and 5B), probably reflective of different types of water used for irrigation (Rio Grande versus local groundwaters) and natural seasonal variability of Rio Grande chemistry (Borrok and Engle, 2015). Generally, the pH of soil waters at all four locations varied little with depth, similar to pH values of drainage water. The EC, as well as major ion concentrations (Na^+, Ca^{2+}, K^+, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}, and alkalinity) generally increased with depth at each site from irrigation water to soil water. The highest values were observed in soil waters at 60 cm depth at all sites (Fig. 5C–H). DRW were similar to IRW in their elemental chemistry. As the dominant cation, Na^+ concentrations in soil waters ranged from 4 to ~ < 120 mM (Fig. 5C). IRW and DRW water samples contained lower Na^+ concentrations, ranging from 5 to 21 mM and 6–33 mM, respectively. As the dominant anions, Cl^- and SO_4^{2-} concentrations of soil waters were up to 60 and 45 mM, respectively (Fig. 5E and 5G). IRW and DRW showed lower but more variable levels of Cl^- and SO_4^{2-}. Alkalinity ranged between 2.4 and 5.6 meq/L in IRW, and reached 8.8 meq/L in soil waters collected from 60 cm at Pecan 2 (Fig. 5H).

Other measured dissolved ions (Br^-, F^-, PO_4^{3-}, and Sr^{2+}) were present in water samples at trace levels (Supplementary material, Table 3S). The concentrations of PO_4^{3-} were high in some samples, probably due to application of P-rich fertilizers. Interestingly, IRW, soil water, and DRW samples containing < 10 mM of SO_4^{2-} and Ca^{2+} concentrations exhibited values that fell along a 1:1 line (Supplementary material, Fig. 2A). At higher concentrations, SO_4^{2-} to Ca^{2+} ratios became greater than 1. Similarly, Na^+ and Cl^- concentrations in lower concentration samples plotted close to a 1:1 line (Supplementary material, Fig. 2B). However, as Na^+ and Cl^- concentrations increased, data deviated further from the 1:1 line, towards higher Na^+/Cl^- ratios. Divalent cations Ca^{2+} and Sr^{2+} were correlated linearly in their concentrations, with Sr/Ca molar ratios around 7:1 (μM/mM) (Supplementary material, Fig. 2C).

Saturation index (SI) values of water samples increased with depth for all minerals examined, consistent with increased major elemental concentrations (Supplementary material, Table 4S). Soil waters, IRW, and DRW remained unsaturated with respect to gypsum (SI = −1.6 to −0.1) and halite (SI = −8.0 to −4.3) (Fig. 6C and 6D). However, modeling results indicated that carbonate phases were oversaturated for soil waters, with SI ranging from +0.2 to +0.9 for calcite and +1.0 to +2.6 for dolomite (Fig. 6A and 6B). The IRW waters were mostly oversaturated with a few expectations (SI = −1.4 to +1.7 for calcite and −2.0 to +4.1 for dolomite). The DRW waters were all oversaturated with respect to carbonate phases, with SI values around +0.7

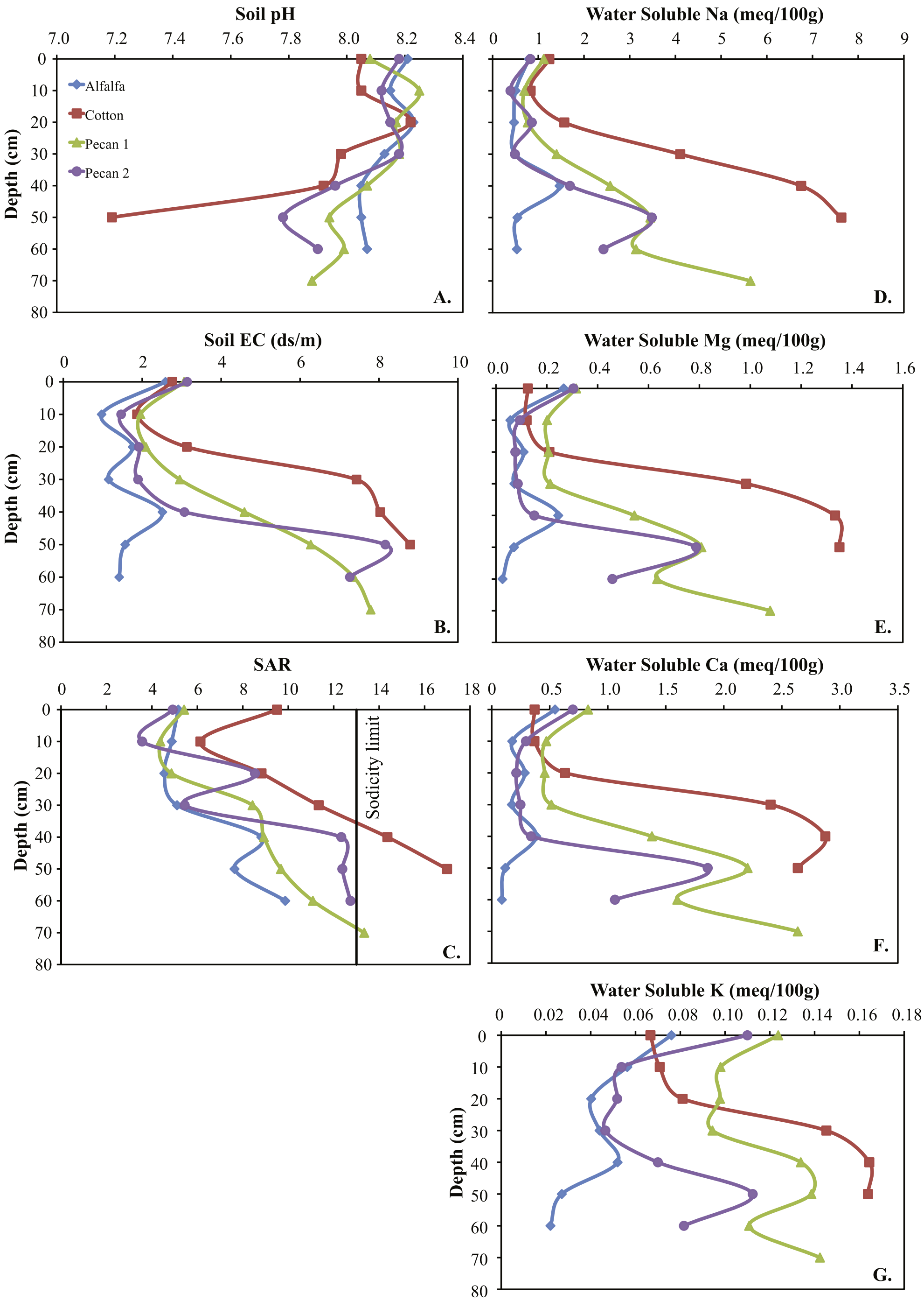

Fig. 3. Soil pH (A), electrical conductivity (EC; B), sodium adsorption ratio (SAR; C), water-soluble Na^+ (D), Mg^{2+} (E), Ca^{2+} (F) and K^+ (G) in soil paste.

for calcite and +2.0 for dolomite. Modeling results indicated that thenardite and nahcolite were both undersaturated in IRW, DRW and soil waters. SI ranged from roughly −10 to −4 for thenardite and −6 to −3 for nahcolite (Fig. 6E and 6F).

Dissolved organic carbon (DOC) concentrations in IRW and DRW samples ranged from 0.2 to 1.3 mM, while that of soil water samples ranged from 1.2 to 3.3 mM with the highest concentrations observed in samples from 30 to 60 cm below the surface (Supplementary material, Fig. 3A). Dissolved inorganic carbon (DIC) concentrations in IRW and DRW samples ranged from roughly 2–4 mM, and in soil water samples ranged from 3.6 to 9.0 mM, with highest concentrations also observed in those collected at depths of 30 and 60 cm (Supplementary material, Fig. 3B). Given the pH of these waters, the dominant DIC species was bicarbonate so we assumed that carbonate alkalinity was equal to DIC on molar basis. Indeed, Supplementary material, Fig. 3C showed that most data points were close to 1:1 line in DIC versus alkalinity diagram. The deviation from the correlation probably suggested that other acid neutralizing agents such as sulfide or organic anions might have contributed to the negative charge.

3.3. Sensor data

Soil moisture content and bulk-soil EC values were elevated at the onset of every irrigation cycle at all three depths for each site, and only Pecan 1 data were plotted for illustration (Fig. 7A and 7B). With continuous loss of water through infiltration, uptake by plants and evaporation, soil moisture content decreased with time until the next irrigation. When there were prolonged gaps between irrigation events,

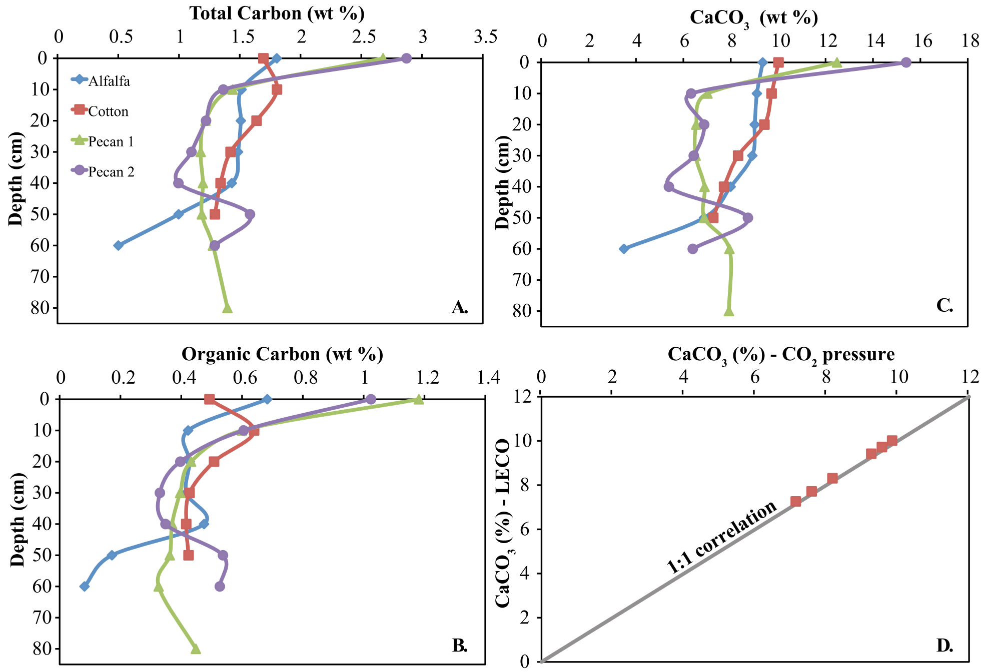

Fig. 4. Total carbon (A), organic carbon (B), and inorganic carbon (C, as in calcite) concentrations as a function of depth for all soils. For Cotton soils (D), inorganic carbon was measured through pressure of calcite-derived CO_2 and LECO C analyzer, yielding similar calcite abundances.

the soil moisture content fell below the calibration range and sensors stopped responding accurately (Hilhorst, 2000). This occurred only in the Alfalfa site, as Pecan and Cotton sites were more intensively irrigated. If saturation was assumed at each depth during the initial flood irrigation, then the maximum soil moisture content was approximate to the effective soil porosity. Based on the maximum soil moisture content, the effective porosity at all our study sites should be around 50–60%. Bulk soil EC showed similar temporal trends as moisture within each irrigation cycle. Bulk EC values were also significantly higher at 60 cm than other depths and also decreased with time after irrigation.

Soil temperature decreased with the onset of irrigation because water temperature was typically lower than soil temperature during growing seasons from April to October (Fig. 7C). After the initial decrease, soil temperature began to rise as soils lost moisture and became equilibrated with ambient conditions through solar radiation. Overall, soil temperature ranged from 17 to 29 °C. This observation justified the use of average temperature 22 °C as water temperature in SI calculations. Moving into summer, the soil temperature fluctuation during and between irrigations was smaller.

The temporal variation in fluid EC values shed lights on the processes that controlled water chemistry such as dissolution and precipitation of evaporite salts, and evapotranspiration. Thus real-time bulk soil EC data from sensors were converted to pore water EC according to the following equation (Hilhorst, 2000):

$$\sigma_p = \frac{\varepsilon'_p \times \sigma_b}{\varepsilon'_b - \varepsilon'_{b=0}}$$

Here, ε'_p is the dielectric permittivity of substrate pore water (unitless), σ_b is the bulk electrical conductivity (ds/m) and measured directly by the Decagon 5 TE sensor, ε'_b is the real portion of the bulk dielectric permittivity (unitless), and $\varepsilon'\sigma_{b=0}$ is the real portion of bulk dielectric permittivity when bulk electrical conductivity σ_b is 0. $\varepsilon'\sigma_{b=0}$ is an offset value (4.1 was used as recommended by Hilhorst (2000)). ε'_p is calculated from soil temperature measured by the sensor as: $\varepsilon'_p = 80.3–0.37 * (T_{soil}\ (^oC) - 20)$.

The fluid EC calculated for soils were in general good agreement with the EC data measured directly on the soil water samples at depths of 15 cm and 30 cm, but higher than those measured for 60 cm. This discrepancy could be caused by mismatch of the empirical values with field conditions. This exercise suggested that fluid EC was lowest at the onset of irrigation at depth of 30 cm (Fig. 7D), and increased continuously with time until the next irrigation event. Furthermore, fluid EC at 15 cm and 60 cm increased after initial irrigation, and then either remained unchanged or decreased slightly.

4. Discussion

4.1. Soil alkalinity, sodicity, and salinity

Soil properties such as alkalinity, salinity and sodicity greatly impact water infiltration, water availability, and nutrient release to crops (Miyamoto and Storey, 1995; Rengasamy et al., 2003; Lambers, 2003; Rengasamy, 2006). This study provides a basis for understanding impacts of agriculture on soil conditions after ~90 years of cultivation along the Rio Grande Valley (Miyamoto et al., 1995). Soils in our study sites were neutral to slightly alkaline, with pH ranging from 7.2 to 8.2 (Fig. 3A). At the high pH conditions, some macro and micronutrients availability to crops becomes limited (Doran et al., 1996; Larson and Pierce, 1994; Seybold et al., 1998). High alkalinity also has implications for the solubility of calcite and its precipitation as discussed below.

EC coupled with saturation paste method is a measure of soil salinity. Soils with EC values > 4 dS/m are considered saline (Brady and Weil, 2002; Strawn et al., 2015). Crops have different salinity tolerance levels: alfalfa, pecan and cotton are negatively affected by soil salinities with EC > 2.0, 2.6, and 7.7 dS/m, respectively (Maas and Grattan, 1999; Picchioni et al., 2000). Using this metric, all sites in this study had saline soils (Fig. 3B), except for Alfalfa site where soil EC values were less than 4 dS/m and also lower than the tolerance level of alfalfa. Soils of high salinity might also have high sodicity in systems dominated by sodium salts (Hanson et al., 2006). The soils with SAR values greater than 13 are considered sodic and often associated with poor aeration and water infiltration (Crescimanno et al., 1995; Barzegar et al., 1996). Elevated Na^+ in soils increases sodicity and replaces Ca^{2+} and Mg^{2+} in the exchangeable sites in the soil, resulting in dispersion of clays, surface sealing and reduced hydraulic conductivity due to breakdown of the soil aggregates (Brady and Weil, 2002). Thus, high sodicity leads to reduced infiltration, poor aeration to roots and lack of water availability to plants. This is especially true for sites such as

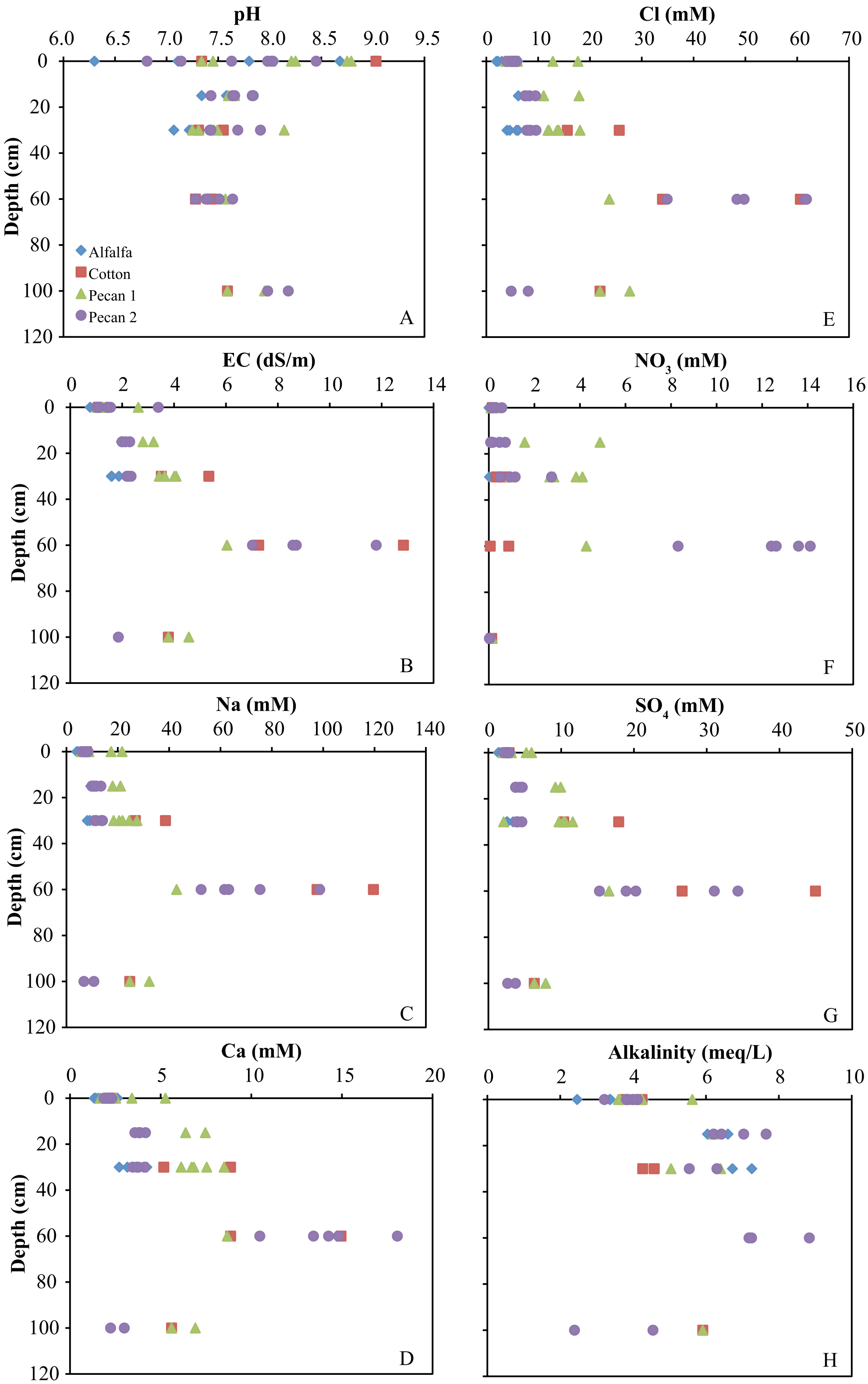

Fig. 5. Major elemental chemistry of soil water (at 15, 30 and 60 cm), irrigation water (placed at 0 cm) and drainage water (placed at 100 cm): pH (A), electric conductivity (B), Na^+ (C), Ca^{2+} (D), Cl^- (E), NO_3^- (F), SO_4^{2-} (G) and total alkalinity (H).

Pecan 1 of the current study, which had higher clay content. In sodium affected soils having high clay content, irrigation water may not effectively infiltrate to leach salts out or carry them into the deeper soil profile. Instead, water may pond and lead to salt accumulation in the soil. Soils were sodic in three out of four sites (Fig. 3). Soils from the Alfalfa site were the only non-saline and non-sodic soil among the four sites, probably because (1) only Rio Grande surface water is used for irrigation at the Alfalfa site, with water quality (i.e., TDS) better than local groundwater that is often used at the Pecan and Cotton sites; and (2) alfalfa fields are left fallow when water is not available for irrigation. Our results support the finding from Ghassemi et al. (1995) which suggested that 73% of the irrigated areas in the Rio Grande Basin were affected by high salinity and sodicity, leading to poor soil conditions, reduced crop yields, and declining farm profitability.

Measures to remediate undesirable soil alkalinity, salinity and sodicity include irrigation in the winter to flush the salts, and addition of

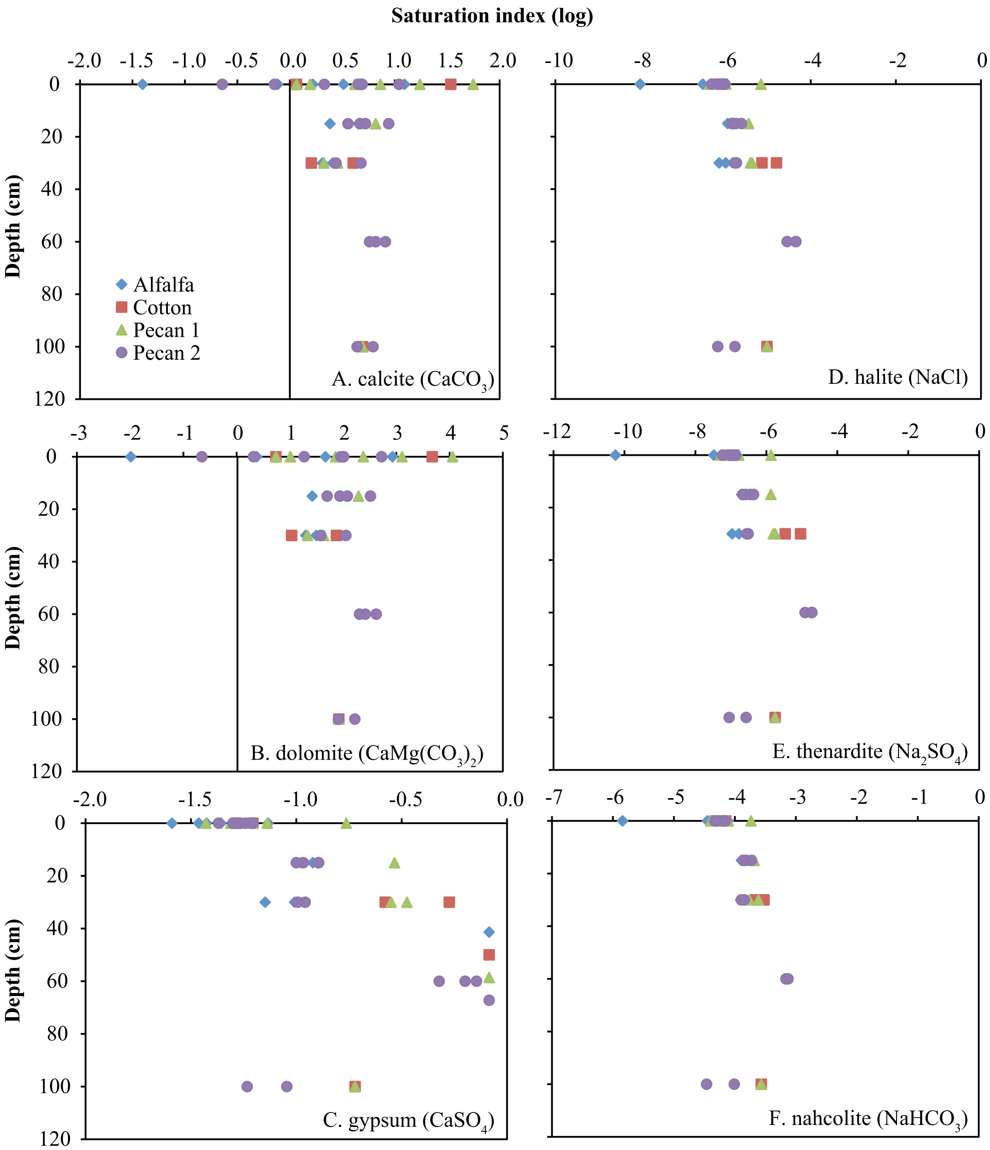

Fig. 6. Saturation indexes of natural waters with respect to carbonate minerals (calcite, A; dolomite, B) and evaporite minerals (gypsum, C; halite, D; thenardite, E; and nahcolite, F).

acids, liming materials, and gypsum (Ilyas et al., 1993). In the El Paso region, common soil amendments include annual addition of gypsum and other sulfur and sulfate granules as well as liquid sulfuric acid to increase soil performance. The inputs of gypsum by farmers release Ca^{2+} and SO_4^{2-} to irrigation water and help to remediate problems caused by sodicity in soils (Reaction (1)). Elemental S applied to the field is slowly oxidized to sulfuric acid (Reaction (2)). Sulfuric acid can dissolve pedogenic calcite according to Reaction (3), thus increasing soil porosity and water infiltration, and releasing Ca^{2+}.

$$CaSO_4{\cdot}2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O \qquad \text{Rxn (1)}$$

$$2S + 2H_2O + 3O_2 = 2SO_4^{2-} + 4H^{+} \qquad \text{Rxn (2)}$$

$$2H^{+} + CaCO_3 = Ca^{2+} + CO_2 + H_2O \qquad \text{Rxn (3)}$$

The Ca^{2+}, produced from these reactions, adsorbs to clays and replaces Na^{+}, making soils less sodic. Indeed, SAR values were lower at the shallow soils during non-irrigation seasons (Fig. 3C), consistent with the application of such soil amendments. However, in the next crop year, irrigation brings Na-rich water and increases soil sodicity again, making soil amendment application a necessary practice every year. It is also suggested that such chemical processes mobilize soil Na^{+} to drainage canal and are responsible for shifting the Rio Grande rivers from Ca-type to Na-type water as the agricultural return flows are enriched in Na^{+} (Borrok and Engle, 2015; Szynkiewicz et al., 2015). Soil amendments however also loaded additional salts to the field and increased soil salinity, on top of the salt loading from irrigation.

We used a simple mass balance calculation below to quantify the potential salt loading rates through irrigation. Annual elemental loading to the field through irrigation was estimated from irrigation water chemistry and amounts of water used (Table 1). Amounts of water used for irrigation varied based on crop type. According to the farmers' record, pecan orchards used ~1.1 m water, cotton fields used 0.9 m, and alfalfa fields used 1.4 m for 2011. Roughly, 1.0 ton Na^{+}/acre was added for pecan trees (0.22 kg/m^2), 0.7 ton Na^{+}/acre for cotton (0.15 kg/m^2), and 0.9 ton Na^{+}/acre for alfalfa (0.20 kg/m^2). The annual irrigation loading for other ions for all the three crops were also calculated: 0.7–1.1 ton/acre for Cl^{-} (0.15–0.24 kg/m^2), 1.1–1.3 ton/acre for SO_4^{2-} (0.24–0.29 kg/m^2), 0.4–0.5 ton/acre for Ca^{2+} (0.09–0.11 kg/m^2), ~0.1 ton/acre for Mg^{2+} (0.02 kg/m^2), and 0.9–1.2 ton/acre for bicarbonate (0.20–0.26 kg/m^2). Miyamoto (2010) studied other agricultural fields in the El Paso region and suggested average salt input from irrigation of 20–50 tons/acre over a 10-year period or 2–5 tons/acre/year (or equivalent to 0.4–1.1 kg/m^2/year). This is in the same order of magnitude as our estimates.

The major ions (Na^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, Ca^{2+} and Mg^{2+}) that were loaded to agricultural soils through flood irrigation could

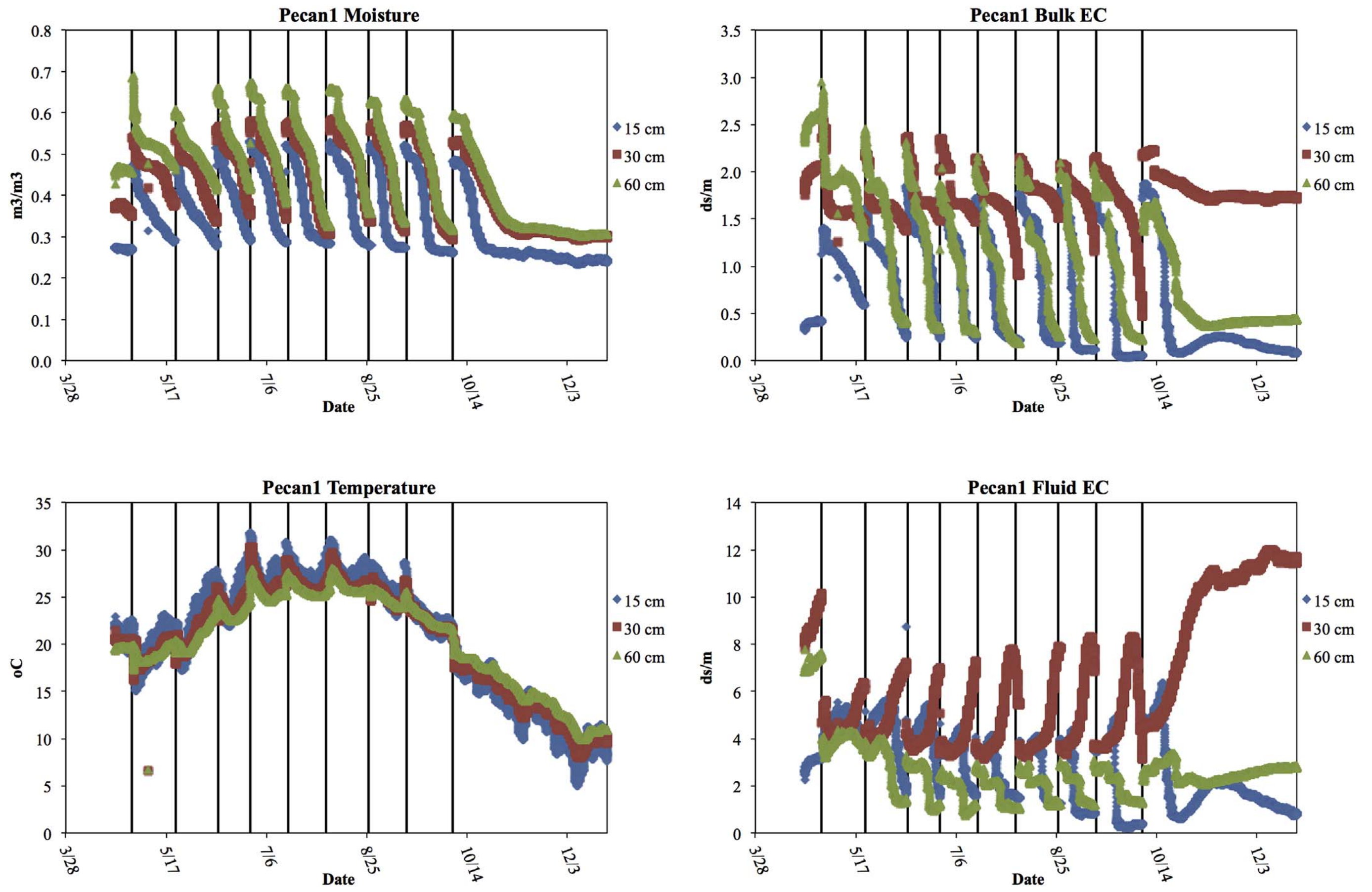

Fig. 7. Variation of volumetric moisture content (A), bulk-soil EC (B), soil temperature (C), and fluid EC (D) as a function of irrigation events for 2011, at Pecan 1 site. Vertical solid lines represent onset of irrigation events.

Table 1
Irrigation leads to salt loading and changes in porosity.

Location Site	Water added feet	Cl^- tons/acre/year	SO_4^{2-} tons/acre/year	Ca^{2+} tons/acre/year	Mg^{2+} tons/acre/year	Na^+ tons/acre/year	HCO_3^- tons/acre/year
Alfalfa	4.5	0.8	1.3	0.4	0.1	0.9	1.2
Cotton	3.0	0.7	1.1	0.4	0.1	0.7	0.9
Pecan	3.7	1.1	1.4	0.5	0.1	1.0	1.2

Loading of mineral phases as salts

Location Site	NaCl mole/m^2/year	$CaSO_4$ mole/m^2/year	$MgSO_4$ mole/m^2/year	$CaCO_3$ mole/m^2/year	Na_2SO_4 mole/m^2/year
Alfalfa	5.6	0.2	1.1	2.5	2.1
Cotton	5.1	0.3	0.8	1.9	1.2
Pecan	8.0	0.5	1.1	2.5	1.6

Assuming salts are loaded evenly to a 0.6-m thick soil
Porosity decreased due to salt loading after 100 years

						Total%
Alfalfa	2.5%	0.2%	0.9%	1.5%	1.8%	7.0%
Cotton	2.3%	0.3%	0.6%	1.2%	1.1%	5.5%
Pecan	3.6%	0.5%	0.8%	1.5%	1.4%	7.9%

precipitate as calcite ($CaCO_3$), gypsum ($CaSO_4{\cdot}2H_2O$), halite (NaCl), $MgSO_4$ and Na_2SO_4 based on the following reactions and stoichiometry:

$$2HCO_3^- + Ca^{2+} = CaCO_3 + CO_2 + H_2O \qquad \text{Rxn (4)}$$

$$Ca^{2+} + SO_4^{2-} + 2H_2O = CaSO_4{\cdot}2H_2O \qquad \text{Rxn (5)}$$

$$Na^+ + Cl^- = NaCl \qquad \text{Rxn (6)}$$

$$Mg^{2+} + SO_4^{2-} = MgSO_4 \qquad \text{Rxn (7)}$$

$$2Na^+ + SO_4^{2-} = Na_2SO_4 \qquad \text{Rxn (8)}$$

Using known densities of these minerals, the collective volumes of these salts that precipitate were calculated. Assuming the salts were confined to the upper 0.6 m of the soil surface, approximately 7–9% of soil pore volumes could be clogged due to the salt formation for 90 years. This estimate represented a significant porosity reduction since soil cultivation (Table 1). This case study showed that flood irrigation greatly impact soil porosity, in addition to increasing soil salinity and sodicity. It was assumed that no drainage occurred in the soils, and water was only lost through evapotranspiration. Thus the salt buildup reported above represented the maximum amount.

The cations including Na and Ca in water leachable fraction of soils were assumed to be released from dissolution of soluble and evaporite minerals halite and gypsum, respectively. Based on the mineral stoichiometry and cation concentrations in Supplementary material, Table 1S, we estimated evaporite minerals are present at up to 1 wt%, beyond the detection limits of X-ray diffraction. As discussed below, some of the salts loaded during irrigation were retained in the shallow soils, due to low soil permeability in these clayey sediments. If the soils are predominantly by sandy particles, then the salt loading would be much smaller in magnitude. Results from our study indicated that continuous flood irrigation had deteriorated the soil quality and made these soils sodic and saline. In order to support crops of the region, appropriate management is essential.

4.2. Texture controls on salt accumulation

Soil texture controls physical, hydrological and chemical properties of soils (Brady and Weil, 2002). In this study, both soil CEC and exchangeable cation concentrations varied with soil texture, with higher values in clayey soils. Indeed, the higher percentages of clay in soils correlated with elevated CEC in surface soils, and CEC decreased when soils changed to sandy texture at depths of 40 cm in Alfalfa and 50 cm in Pecan 2 (Fig. 2A). Similarly, the dependency of exchangeable cation concentrations on soil texture was observed in soils among four sites. Concentrations of exchangeable cations at the Alfalfa and Pecan 2 sites were lower than those at Cotton and Pecan 1 sites (Fig. 2B–E). Pecan 1 and Cotton sites were more clayey and thus higher in CEC and exchangeable concentrations (Fig. 2).

Water saturation percentage is a rough measure of soil's water holding capacity, and mainly depends on soil texture (Richards, 1954; Hanson et al., 2006). Fine-grained soils from Pecan 1 and Cotton had much higher $H_2O\%$ values than those from sandy Pecan 2 and Alfalfa (Supplementary material, Table 1S). Water-soluble cations also correlated with soil texture, with higher concentrations observed on soils with finer soil texture (Fig. 3D, 3E, 3F and 3G). Lower soil permeability in clay-rich layers induces higher salt contents and higher water residence time. High affinity of water for clay holds the water and dissolved salts within soils, reducing infiltration and recharge to local groundwater aquifer or drainage canals. While water was lost quickly to evaporation, salts accumulated in soils. This observation pointed to the local hydrology, impacted by soil texture, as the dominant controls on salt loading.

Pecan 2 had similar texture as Alfalfa. Deeper soils at the Pecan 2 site were slightly sandy but still had high cation concentrations in the water-soluble fraction, probably because Pecan 2 had much higher irrigation load of cations (Table 1). In general, pecan trees require frequent irrigation every year, whereas alfalfa can lie fallow when irrigation is limited. When Rio Grande surface water is limited due to drought conditions, local groundwater was pumped as supplements for irrigation. Groundwater exhibited higher total dissolved solids than Rio Grande waters, and thus led to more salt accumulation for Pecan 2.

The application of flood irrigation increases the soil salinity in the absence of drainage (in sodium affected soils). Salts prefer to accumulate on soils with clayey texture, where water is retained longer. A positive feedback is expected that Na from flood irrigation increases soil sodicity and lowers the soil permeability by dispersing clays, and therefore drives more salt accumulation. This conceptual model indicates that local soil quality will continue to deteriorate over time, if without treatments. In recognition of salt accumulation and its detrimental effects on crop yields, farmers have mixed sandy and clayey soil for the top 3–5 m, to improve soil health temporarily approximately once every five years.

4.3. Intrinsic linkage among agricultural soils, local groundwater aquifers, and Rio Grande

It is clear that irrigation practices have diverted water from Rio Grande and extracted shallow groundwater aquifer, loading salts within surface soils (Fig. 8). Spatial and temporal variation of soil water chemistry observed in this study indicated evaporative salts were mobilized and moved to deep soils along the flow paths. Indeed, concentrations of almost all major ions measured in soil waters increased with depth: the highest levels were always observed at ~60 cm depth (deepest soil water sampled in this study) (Fig. 5). This trend suggested that existing salts in the shallow soils were dissolving during initial irrigation and moved to deep soils as soil water infiltrated. Consistent with this, all irrigation waters, with negative SI value, were undersaturated with respect to major salts (gypsum, halite, thendardite and nahcolite), and with continuous salt dissolution, SI values of deeper soil waters increased significantly and approached saturation (i.e., 0; Fig. 6; Supplementary material, Table 4S). Fluid EC (soil water EC) were estimated from bulk-soil EC data recorded by the sensors and showed increasing temporal trends at initial irrigation, also supporting the notion that salts were dissolving locally (Fig. 7D). The near 1:1 molar ratios of soil water Na^{+}:Cl^{-} and Ca^{2+}:$SO_4{}^{2-}$ were probably produced due to dissolution of halite and gypsum that were previously accumulated in soils (Fig. 5; Supplementary material, Fig. 2). Thus dissolved salt was loaded at land surface through water but some of the salt was pushed downward into the deep portion of the soil column and even deeper aquifers (Fig. 8). Evaporation could potentially concentrate the soil waters and keep the Na^{+}/Cl^{-} and $Ca^{2+}/SO_4{}^{2-}$ ratios of the irrigation waters, but soil waters were typically collected two days after flood irrigation, the field was wet, and thus evaporation alone was not enough to concentrate the soil waters by a factor 10, as observed in the soil waters.

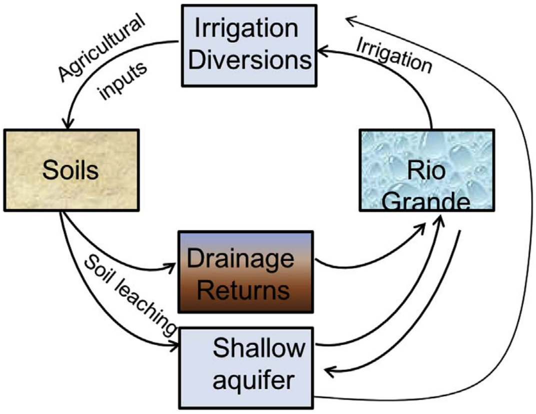

Fig. 8. Linkage among soil and water resources in the Rio Grande Valley.

Drainage water (DRW) and irrigation water (IRW) samples were similar in their elemental chemistry, and both were lower in major ion concentrations and EC values than deep soil waters. This trend suggested that a large fraction of the irrigation water bypassed the deep soils and flowed laterally and directly to the drainage canal when the field was flooded and soils were saturated. The return flow from agricultural fields to Rio Grande is an important water flux (Fig. 8). The salt loadings leached from irrigated agriculture fields have been suggested to contribute to elevated chlorite and sulfate concentrations in the Rio Grande downstream of El Paso (Rodriguez and Lougheed, 2010; Szynkiewicz et al., 2011).

Once all the standing water on the land surface had infiltrated and soils reached field capacity, water stopped draining and evapotranspiration began to dominate, lowering moisture content but increasing ion concentration of soil water continuously (Fig. 7). Indeed, fluid EC calculated from sensor data showed the concentrations of most dissolved ions in soil waters increased with time between irrigation periods (Fig. 7D). This observation suggested that between irrigation periods, soil waters became oversaturated and salts started to precipitate and accumulate in the soils. Indeed, as discussed above, the clayey soils held more water and thus potentially led to more salt buildup. This would be the case for gypsum, as soil waters, especially those collected at deeper soils, had SI values close to 0. Different from gypsum, accumulation of halite during the growing season was probably limited to soil surface that almost completely dried up one week after the onset of an irrigation event. Soil waters were unsaturated with respect to halite, with SI values < -4. Thus when farmers irrigated regularly from April to October, soils probably were never dry enough to precipitate halite until the non-growing season.

Soil and water resources are inextricably linked in the Rio Grande Valley among Rio Grande, shallow aquifers and soils through irrigation (Fig. 8). Therefore, it is important to understand the interactions among soils, irrigation/shallow groundwater and crop performance for ensuring long-term soil sustainability and maintaining environmental quality. The connection of soils and fresh waters in the region also has implications for the mobility of nutrients and water quality, beyond the salinity. In contrast to natural ecosystems, the agricultural fields in aridlands become more biologically active with the additions of water and nutrients (fertilizers). Top-soils at the two Pecan sites had the highest TOC contents, due to litter fall (pecan leaves), degradation, and growth of tree roots (Fig. 4; Supplementary material, Table 1S). Beneath the top-soils, TOC content at Pecan 1 and 2 decreased sharply. The DOC levels of the associated soil water samples were higher than those of irrigation waters, indicative of soil organic material being continuously leached (Supplementary material, Fig. 3; Supplementary material, Table 3S). Concentrations of dissolved phosphate in irrigation waters varied significantly, and were similar as those in soil waters and drainage waters, probably because of rapid dissolution of P-rich fertilizers applied to the fields (Supplementary material, Table 3S). The nitrate concentrations increased with depths, from both dissolution of fertilizers and dissolution of N-bearing salts. This observation is important for groundwater quality as nitrate is likely transported to this much deeper freshwater resource. Interestingly, nitrate concentrations were extremely low in waters from the drainage canals, possibly caused by consumption of nitrate by aquatic microorganisms in the drainage canal.

4.4. Pedogenic carbonate in agricultural soils and long-term climate feedback

Modeled calcite saturation indices of irrigation waters vary significantly, suggesting that the chemistry of Rio Grande and shallow groundwater is quite variable, ranging from slightly unsaturated to highly supersaturated (Fig. 6A and 6B). In contrast, all the soil waters and drainage waters are oversaturated for calcite, suggesting precipitation of calcite at all soil depths. Szynkiewicz et al. (2015) reached the same conclusion, as Rio Grande rivers shift from Ca-rich to Na-rich chemistry as a result of calcite precipitation out of water in agricultural soils. The transition of unsaturation in irrigation water to oversaturation of calcite in soil water at this stage is probably due to the leaching of existing gypsum, thus leading to much higher Ca^{2+} concentrations, in addition to evapotranspiration. Other sulfate salts dissolve quickly too, as observed by deviation of soil water on the $SO_4{}^{2-}$:Ca^{2+} line (Supplementary material, Fig. 2A). Calcite dissolution is limited, suggested by slow increase of soil water alkalinity with depth (Fig. 5H), relative to depth trends of soil water Ca^{2+} and $SO_4{}^{2-}$ (Fig. 5G and D). When water volumes decrease through evaporation and transpiration, remaining soil water becomes more concentrated, driving calcite to precipitate out continuously. This is in agreement with the high TIC contents (carbonate minerals) observed in these soils.

Precipitation of pedogenic carbonate is accelerated by irrigation, with addition of extra Ca^{2+} and DIC loads. Based on our rough estimates with the parameters constrained in this study, after 100 years, calcite accumulation can be up to 250 mole/m^2, or 3.5 wt% for a soil pedon with dimension of 1m wide by 1m long by 0.6 m deep, third of the value that is currently observed in the soils (Table 1). More research is greatly needed to investigate the mechanism, kinetics and controls of carbonate precipitation reactions in such managed agricultural settings to quantify their significance in the global carbon cycles. Indeed, the accumulation of calcite leads to the releases of CO_2 to atmosphere as shown by Reaction (4). It is important to quantify how carbonate dissolution and re-precipitation respond to changes in soil properties relevant to water penetration and moisture holding capacity caused by agricultural practices. It is also important to explore how the sequestration of C will be likely to change in this region and other similar dryland irrigated fields in the future based on changing climates and continued salinization of water resources.

4.5. Environmental implication and future research directions

Climate variability is predicted for American Southwest with less snowfall expected in the Colorado headwater regions (Seager and Vecchi, 2010; MacDonald, 2010; Rehfeldt et al., 2012; Hargrove et al., 2013), and extremely low storage levels in Elephant Butte Lake reservoir is observed, and thus irrigation allotments have decreased dramatically from 1.2 m (48 inches) to 0.5 m (18 inches) of water after 2011 (Jackson et al., 2001; Ganjegunte et al., 2017). Because of this, many farmers in El Paso County have been drilling and reopening existing wells, relying on groundwater with a higher TDS than the Rio Grande river water. However, irrigation with higher salinity groundwater will impact soils more severely than the less saline river water.

The spatial variation in soil texture and associated hydrological conditions exert a great control on mobility of salts and nutrients and thus the water quality of Rio Grande and underlying shallow groundwaters as observed in other agricultural fields of arid southwest (Scanlon et al., 2012; Rengasamy, 2006). Indeed, pathways and residence time of water within the heterogeneous soil substrates are critical for identifying efficient and effective irrigation strategies, assessing the water connection among Rio Grande, groundwater and agricultural return flows, and examining the variations in the groundwater level by pumping and recharge during intensive irrigation. Thus, the characterization of fluvial sediments with layers of contrasting particle sizes and permeability is needed at regional scales. This study clearly identified connection of irrigation, soil water and shallow aquifers with a geochemical perspective. It is critical to understand how irrigation alters the surface and subsurface hydrologic regimes of agricultural fields with consequences on the regional recharge of the underlying aquifers in arid climate. Combining hydrological, geochemical and hydrogeophysical tools (e.g., resistivity, GPR) to study these managed agricultural systems has great implications for soil sustainability and water resources management (Metternicht and Zinckb, 2003; Huang et al., 2014).

5. Conclusions

Characterization of soil and water samples at four agricultural sites in the El Paso region, covering three major crops with different irrigation intensity, indicates flood irrigation has led to salt accumulation on agricultural soils. The mass balance calculation quantified maximum amount of salt buildup at 4–5 tons/acre every year. This reveals after 90 years of soil cultivation, up to 7% of pores could have been blocked due to salt accumulation, significantly reducing water infiltration and leading to more salt accumulation. In addition, high amounts of Na in irrigation waters make soil sodic, and cause a decrease in permeability in relatively clayey soils. Indeed, SAR values will increase making water infiltration near impossible and salinity values will increase in soils rendering them uninhabitable for plants with low salt tolerance such as alfalfa and pecan. When soils are poor in permeability and high salinity, crop yields will be lower due to reduced water flow and decreased nutrient availability. Ion concentrations, nutrient loads, salinity, and sodicity values indicate poor soil health at almost all depths in all locations in our study, especially deeper soils. If current practices are maintained without remedial help to have better soil heath, soil conditions will continue to diminish.

Pedogenic carbonate is a major secondary salt that accumulates in the soils. We only quantified inorganic carbon concentrations in Alfalfa site, and as much as 10 wt% of the calcite is observed. After 100 years of soil cultivation, a maximum of 3.5 wt% of calcite can be accumulated based on loading of bicarbonate since Ca^{2+} is much higher in concentrations. This exercise reveals the faster rates of calcite accumulation in agricultural soils than in arid ecosystems. As illustrated by Reaction (4), calcite is formed accompanied by release of CO_2. Future work is needed to quantify this flux, maybe an important feedback among soil-air-climate.

Now, more than ever, water availability for irrigated agriculture, water flow paths through the soil profile and underlying aquifer, linkage between soil salinity and water quality needs to be assessed for highly stressed arid ecosystems. In addition, 3-dimensional hydrological framework and water mass balance with the agricultural fields are much needed, to determine the effectiveness of flood irrigation, evolution of Rio Grande for TDS, long-term viability of soils to support crop growth, adaptability to extreme weather conditions and potential climate change predicted for U.S. Southwest. The difference in soil texture between soil mapping and field observation highlights the heterogeneous nature of fluvial sediments, sensitive to depositional environments related to changing courses of Rio Grande in the geological past. Soil mapping available through USDA Websurvey was at low spatial resolution, and regional survey using geophysical tools should be used in future studies to reveal the variation of hydrogeological properties of these sediments and quantify mobility of water and salts. Regional studies of salt buildup in drylands therefore entail comprehensive analyses by combining geochemical and geophysical tools.

Acknowledgments

This work was sponsored by the Southwest Consortium for Environmental Research and Policy (SCERP) through a cooperative agreement with the U.S. Environmental Protection Agency (EM-834861-01). The owners of our study sites, the Ivey family, are greatly acknowledged for their support and collaboration. We thank Ryan Reeves, Crystal Subia, Alyssa Le Mar, and Pat Rea from UTEP for their assistance in the laboratory and field.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.apgeochem.2017.12.019.

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