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Impact of brackish groundwater and treated wastewater on soil chemical and mineralogical properties

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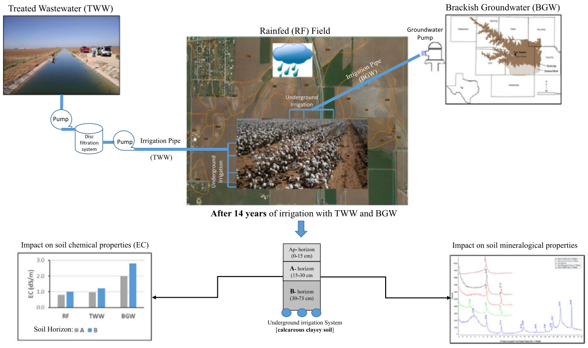
HIGHLIGHTS

- Treated wastewater has a better quality than the brackish groundwater of the local aqufer
- Calcareous clayey soil showed no salinity or sodicity problems after long-term (15 years) irrigation with non-freshwater
- Clay mineralogy in this soil type is fairly stable and plays a major role in the fertility of the soil
- Treated wastewater and brackish groundwater are viable substitutes for freshwater irrigation in semi-arid and arid regions

GRAPHICAL ABSTRACT



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ABSTRACT

The long-term effect of using treated wastewater is not clearly defined: some researchers argue that it is better than freshwater for the soil health; others disapprove, claiming that irrigation with unconventional water resources causes soil degradation. This study assesses the impact of irrigation with non-traditional water on the chemical and mineralogical properties of a calcareous clayey soil from West Texas. The exponential rise in population and the realities of climate change contribute to the global increase in freshwater scarcity: non-conventional water sources, such as treated wastewater (TWW) and brackish groundwater (BGW), offer potentially attractive alternative water resources for irrigated agriculture. For this research, the differences between TWW and BGW were addressed by collecting and analyzing water samples for salt and nutrient content. Soil samples from three horizons (Ap, A, and B) were obtained from three different fields: Rainfed (RF), BGW irrigated, and TWW irrigated. Soil was analyzed for texture, salinity, sodicity, and carbon content. Clay mineralogy of the three different fields was analyzed using the B-horizons. The outcomes from the analysis showed that the BGW from the Lipan aquifer has higher salinity and is harder compared to TWW. Although the exchangeable sodium percentage (ESP), sodium adsorption ratio (SAR), and electroconductivity (EC) increased marginally compared to the control soil (RF), the soils were in good health, all the values of interest ($SAR < 13$, $ESP < 15$, $pH < 8.5$, and $EC < 4$) were low, indicating no sodicity or salinity problems. Smectite, illite, and kaolinite were

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identified in the three B-horizon samples using bulk X-ray diffraction (XRD). Overall, no major changes were observed in the soil. Thus, TWW and BGW are viable replacements for freshwater irrigation in arid and semi-arid regions.

1. Introduction

Water scarcity is one of the major threats facing humanity as competition for resources increases with population growth. As various sectors compete to supply the fundamental human needs, demand for water has increased. Globally, the agriculture sector consumes the greatest amount of water, nearly 70% compared to 10% for domestic use and 20% for industry (Food and Agriculture Organization (FAO), 2010). The impacts of climate change add to the burden of the deficit between demand and supply for water. In 2030, with a “business as usual model”, the projected global water gap (shortage) will be 40% and one third of the population will live in water stressed regions (WEF-WRG, 2012). The projected increase in frequency of drought conditions (Intergovernmental Panel on Climate Change (IPCC), 2013) and the demand for freshwater (FW), will surely lead to rising prices, spurring the use of non-traditional water.

Wastewater (WW) is an untapped resource in a world where FW depletion rates are unprecedented. Yearly, 40 million ha (400,000 km^2) or 15% of all irrigated lands can be irrigated with the 330 km^3 (267.5 million acre-feet/year) municipal wastewater produced around the world (Mateo-Sagasta et al., 2015). Treated wastewater (TWW) has gained attention globally, especially in the agriculture sector. TWW is a highly valued resource in the face of this projected water shortage. TWW could be used to alleviate or prevent further exhaustion of the natural FW resources by helping to overcome shortages and mitigating the severe impact of drought on the underlying aquifer. Irrigation with TWW has been successfully applied in several countries: it contains nutrients that can replace fertilizers and soil conditioners (Jimenez-Cisneros, 1995; Qadir et al., 2007). In a study on the impact of TWW on grape yields and quality, the drip irrigation with treated municipal water increased grape production with no adverse effect on the soil (Mendoza-Espinosa et al., 2008). TWW is therefore a means to conserve resources, and potentially reduce fertilizer use.

Conversely, some researchers rejected replacing FW with TWW due to the risk of degradation of the soil's physical properties as a result of increased salinity (Klay et al., 2010; Hasan et al., 2014). Qian and Mecham studied the effects of long term application of TWW on golf courses, which resulted in increased soil salinity due to the higher salinity of the reclaimed water (Qian and Mecham, 2005). The most common problem in arable land is soil salinization, particularly in arid and semiarid areas where precipitation is insufficient to prevent salt accumulation that leads to reduced yield (Francois and Maas, 1994; Munns, 2002). However, in semiarid regions with an annual precipitation >20 in (508 mm), the rain is sufficient to prevent long-term salt accumulation in the root zone when irrigated with secondary TWW (Lado et al., 2012).

Public health and safety are among the major issues when applying marginal quality water in countries with unenforced regulations. In developed countries, such as the United States, the use of TWW is regulated through governmental (US Environmental Protection Agency) and local agencies. The Texas Commission on Environmental Quality (TCEQ) regulates places constraints on the use of treated wastewater, classified into either Type I or Type II (Table 1). The end use of the categories differs according to the quality of each type. Type I can be applied where public contact is likely; Type II is restricted to areas where human contact is unlikely, thereby ensuring that health risks are minimal to nonexistent.

Brackish groundwater (BGW) contains from 1000 to 10,000 milligrams per liter (mg/l) of dissolved solids. The classification of water based on TDS is: Freshwater < 1000 mg/l, Slightly Saline (Brackish) 1000–3000 mg/l, Moderately Saline (Brackish) 3000–10,000 mg/l, Highly Saline > 10,000 mg/l, Seawater ≈ 35,000 mg/l, and Brine > 100,000 mg/l (Stanton et al., 2017). Desalination methods are expensive and produce highly saline concentrate (brine). BGW has been successfully used for irrigation and proved helpful for crop production. An 8-year study of field experiments using BGW to irrigate winter wheat and maize established that slightly brackish water was the most beneficial irrigation scheme, although freshwater (FW) is needed for leaching accumulated salt if precipitation events are rare (Ma et al., 2008). Some researchers have shown the promising potential of brackish water irrigation during the dry season and in climatic conditions with an average annual rainfall of 15 in–24 in (381 mm–609.6 mm) in which accumulated salt is leached with the rain (Hamdy et al., 2005; Kiani and Mirlatifi, 2012).

The main issue with BGW is salt build-up in the soil: it can be harmful for sensitive crops (Rengasamy, 2010; Ramos et al., 2012; Wang et al., 2015). However, BGW can be used and salt accumulation avoided with a proper irrigation schedule. The main crop in the area of interest is cotton, a highly salt tolerant crop with a soil of 7.7 deci-Siemens per meter (dS/m) EC threshold (Bernstein and Ford, 1959). Cotton is also the most valuable crop in Texas, which leads the US with sales of $1.6 billion in cotton and cottonseed (United States Department of Agriculture (USDA), 2015).

The state of Texas has a massive BGW reserve, found in nearly all its 30 aquifers. According to a study done by LBG-Guyton Associates in 2003, for the Texas Water Distribution Board (TWDB), the estimated amount of BGW is >2.7 billion acre-feet (ac ft) (3330.396 km^3), particularly widespread within the major and minor aquifers (LBG-Guyton Associates, 2003).

Several components may influence soil function, but its texture and mineralogy dominate the reaction to unusual additions, such as irrigating with TWW or BGW. The impact of marginal water quality on soils differs with the clay content and mineralogy, particle surface charge characteristics, pH, and organic matter content (Huang et al., 2012). Researchers argue that sodic conditions are more likely to occur in soils with a higher clay content (Leal et al., 2009; Chen et al., 2013). Also,

Table 1
Water quality parameters for using reclaimed water adapted from 30 Tex. Admin. Code § 210.33–210.34.

	Type I	Type II
Quality standards (30 day average)	• $BOD_5/CBOD_5 = 5$ mg/l • Turbidity = 3 NTU • Fecal coliform < 20 or <75 CFU/100 ml (single grab)	• $BOD_5 = 20$ mg/l • $CBOD_5 = 15$ mg/l • Fecal coliform < 200 or <800 CFU/100 ml (single grab) • For a pond system: $BOD_5 = 30$ mg/l, fecal coliform < 20 or <800 CFU/100 ml (single grab)
Sampling/analysis frequency	Twice per week	Once per week

irrigation methods play a key role in the modification of soil chemical properties that might occur when applying recycled domestic water (Maas and Grattan, 1999; Malash et al., 2007) and saline water (Kang et al., 2010; Zhao et al., 2015).

Changes in the soils clay mineralogy over short periods and due to anthropogenic actions such as irrigation with TWW or BGW have rarely been documented. It has been thought that such alterations could only occur at geological time scales. Although, burial diagenesis is the most common for the conversion, this process can happen at or close to the earth's surface in the upper horizons of soils under very different environmental conditions, such as low pressure and temperature (Barré et al., 2008). Thus, the phenomenon can transpire in geological and artificial settings especially where high pH K-solutions are present (Drief et al., 2002; Marchuk et al., 2016). Time, chemical composition, and temperature are the major components for this transformation. On the other hand, some studies have found no significant effects on soil mineralogy composition as a result of long-term irrigation with TWW (Tarchouna et al., 2010; Rezapour and Samadi, 2011).

Crops irrigated with TWW or BGW become more vulnerable because these sources contain higher levels of salts. Most previous studies on irrigation with non-traditional water have mainly targeted the physico-chemical alterations of soils: very few studies have focused on the modifications of clay minerals. This study addresses the following research question: does the long–term application of non-conventional water (BGW or TWW) have an impact on soil chemistry and clay mineralogy? While keeping in view the importance of alternative water sources and soil health, this study addresses two objectives:

1. Quantification of the changes that occur in the chemical properties of the clayey soil from BGW and TWW irrigation.
2. Assessment of the response of the soil's clay mineralogy to long term BGW and TWW irrigation.

The outcome of this research provides scientific proof of the benefits of using alternative water resources in arid and semi-arid areas. The use of non-conventional water sources for agriculture purposes lessens the pressure on freshwater supplies. The results can be used to motivate decision makers to allocate non-traditional water for irrigation. In addition, it will give hesitant farmers greater confidence in using alternative water resources to irrigate their land. The paper first discusses the methodology of the research, explaining the general procedure, study location, sampling and analyses. The results and discussion section present the data from the experiments in tables and graphs and discuss the significance of the results. The importance of the study in the context of the Water-Energy-Food (WEF) Nexus is also discussed. The final section of the paper summarizes the main points of the study and suggests ideas for future research.

2. Materials and methods

2.1. Overall approach

The sampling was carried out in 2017 in an area chosen for its scarcity of FW sources and its long-term use of TWW for irrigation. Fig. 1 outlines the general procedure of the work. The Web Soil Survey tool from the Natural Resources Conservation Service (NRCS) was used to determine that the Angelo series is the dominant soil series of the study area (Web Soil Survey - Home, 2017). Angelo soils are fine-silty, mixed, superactive, thermic Aridic Calciustolls and consist of deep or very deep, well drained, moderately slowly permeable soils formed in calcareous loamy and clayey alluvium derived from limestone. The Angelo series occupies 23.4% of Tom Green County prevailing over other soil types there. Furthermore, Angelo clay loam, 0 to 1% slopes (AnA) is the main mapping unit from the Angelo series covering 16.2% of the county (Wiedenfeld and Flores, 1976). Water samples were collected from the different sources used for irrigation, using 16-oz (500 ml) plastic bottles. The chemical analysis of the water samples was performed at Texas A&M University Soil, Water, and Forage Laboratory in College Station. In total, 10 different soil samples were taken from the three top horizons of the different fields, except the filter-flush (FF) in which only the Ap horizon was sampled. The samples were obtained using a trowel and were placed in gallon Ziploc bags and air-dried. The RF field was used as a control as it has not been irrigated; the FF was sampled because it portrays an intensive case of TWW irrigation. The texture, chemical, and mineralogical properties of the soil were investigated at the Heep Center in Texas A&M University. After all the data was obtained, it was analyzed to answer the hypothesis and complete the objectives.

2.2. Study area

The area of interest is located in a rural setting of Tom Green County, West Central Texas (Fig. 2), in the southeast portion of the city of San Angelo. A drip irrigation system using TWW has been used to irrigate cotton for >10 years and could have led to changes in the soil's chemistry. The cotton farm is divided into three agriculture practices, and most of the land is irrigated: 70 acres (283,280 m^2) of rainfed/dryland, 115 acres (465,388 m^2)

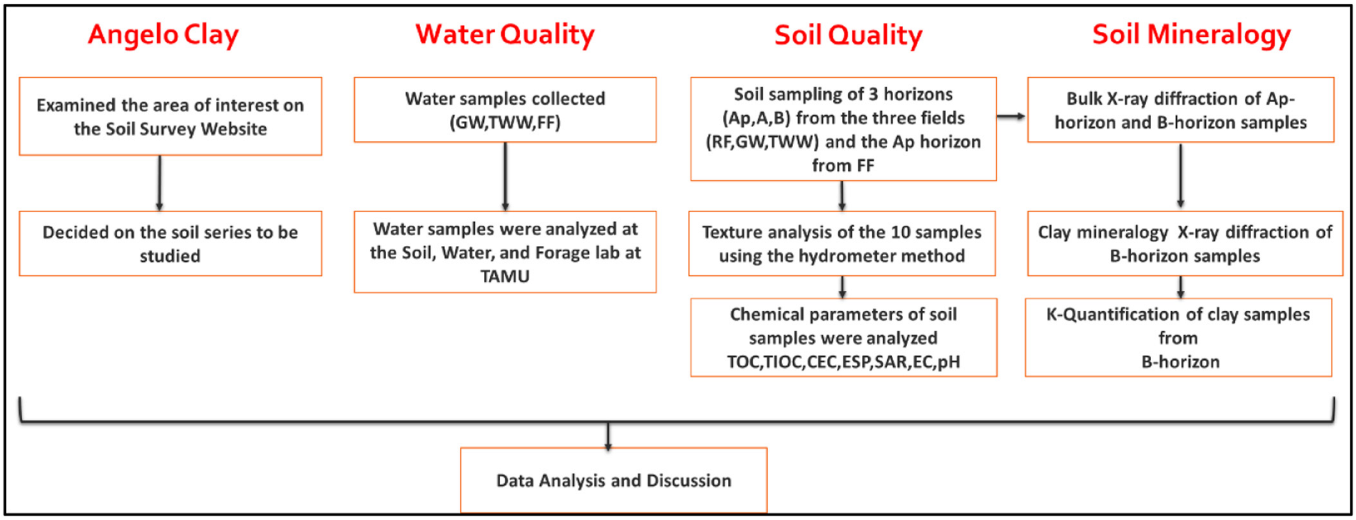
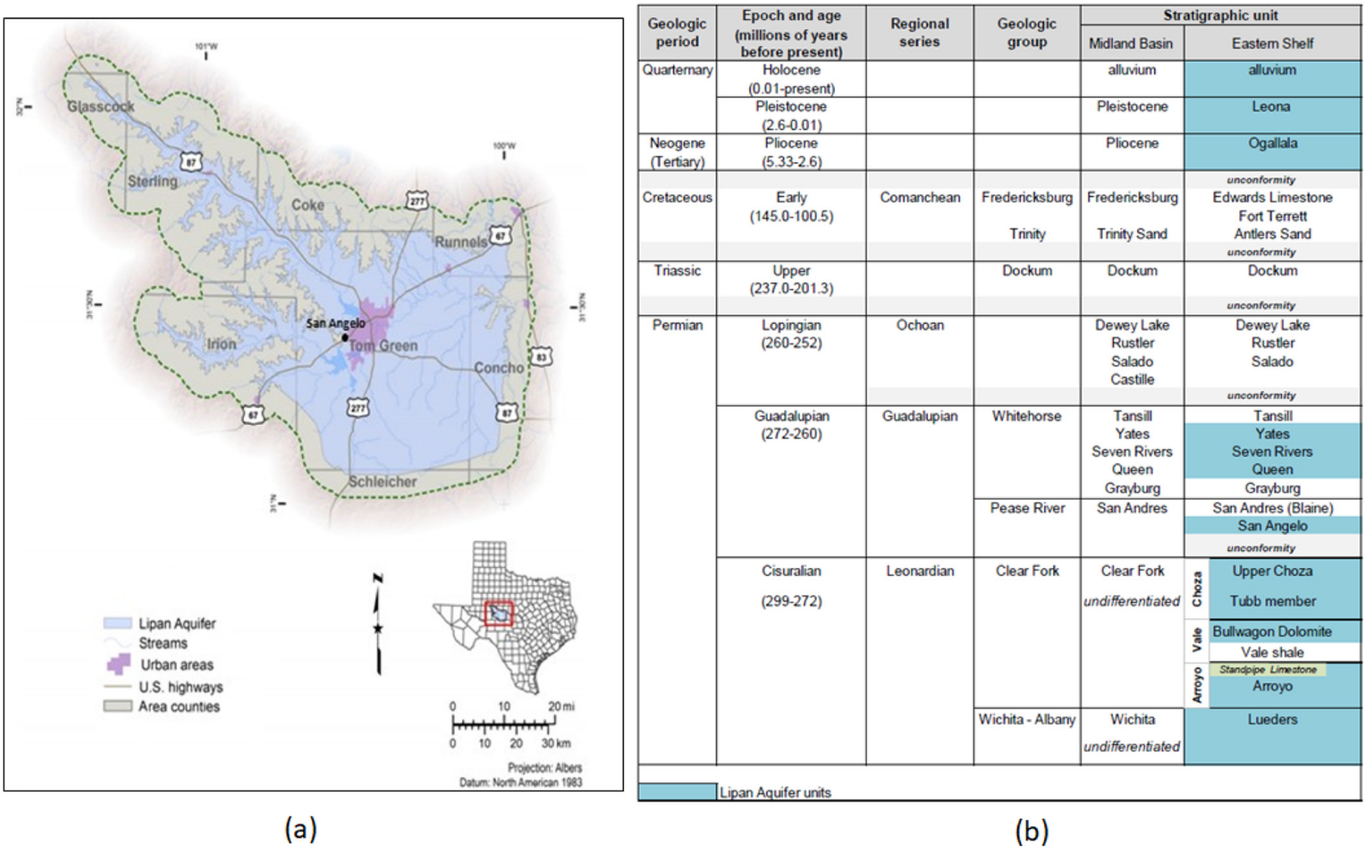


Fig. 1. Chart summarizing the methods.



Geologic period	Epoch and age (millions of years before present)	Regional series	Geologic group	Stratigraphic unit: Midland Basin		Stratigraphic unit: Eastern Shelf
Quaternary	Holocene (0.01-present)			alluvium		alluvium
	Pleistocene (2.6-0.01)			Pleistocene		Leona
Neogene (Tertiary)	Pliocene (5.33-2.6)			Pliocene		Ogallala
						unconformity
Cretaceous	Early (145.0-100.5)	Comanchean	Fredericksburg Trinity	Fredericksburg Trinity Sand		Edwards Limestone Fort Terrett Antlers Sand
						unconformity
Triassic	Upper (237.0-201.3)		Dockum	Dockum		Dockum
						unconformity
Permian	Lopingian (260-252)	Ochoan		Dewey Lake Rustler Salado Castille		Dewey Lake Rustler Salado
						unconformity
	Guadalupian (272-260)	Guadalupian	Whitehorse	Tansill Yates Seven Rivers Queen Grayburg		Tansill Yates Seven Rivers Queen Grayburg
			Pease River	San Andres		San Andres (Blaine) San Angelo
						unconformity
	Cisuralian (299-272)	Leonardian	Clear Fork	Clear Fork *undifferentiated*	Choza	Upper Choza Tubb member
					Vale	Bullwagon Dolomite Vale shale
					Arroyo	*Standpipe Limestone* Arroyo
			Wichita - Albany	Wichita *undifferentiated*		Lueders

🟦 Lipan Aquifer units

Fig. 2. Study area: (a) location of the study area and Lipan aquifer, and (b) stratigraphic column of the geologic units within the study area (TWDB, 2018).

of BGW drip irrigation, and 250 acres (1,011,714 m^2) of TWW drip irrigation. The region is classified as semi-arid; its average annual precipitation is 21.25 in (539.75 mm); it is on the edge of being classified as humid temperate due to its considerable humidity (West Central Texas Climate Data, 2017). The fluctuations in the weather add pressure on farmers, who receive less water from rain. The city of San Angelo is located on top of the Lipan aquifer (Fig. 2a), considered to have high available BGW and very shallow with a moderately transmissive alluvial stratigraphy. The aquifer is composed of Quaternary and Neogene sediments found outcropping or near the surface and the underlying hydraulically connected Permian formations (Fig. 2b). The FW is only found in the younger formations (Quaternary-Neogene and Cretaceous), whereas the formations at the base of the aquifer (Permian) hold the slightly and moderately saline water (TWDB, 2018). The groundwater flow is not structurally controlled. The aquifer has approximately 1.3 million ac ft (1.6035 km^3), with most of the water ranked as slightly saline (LBG-Guyton Associates, 2003).

Since 1958, the city of San Angelo has disposed of primary treated municipal wastewater onto agricultural land as solution to the marginal quality water. Municipal wastewater was further treated to decrease water pollution, per the October 1972 Clean Water Act (Public Law 92-500). By 1983, all wastewater treatment facilities owned by the government were required to meet secondary treatment effluent standards (FEDERAL WATER POLLUTION CONTROL ACT). As a result, the reclamation plant in San Angelo upgraded to secondary treatment using an activated sludge process. Currently, the treated effluent water is seen as a solution to cope with demographics and the harsh climate in meeting irrigation requirements. According to the Texas Water Development Board's (TWDB) 2017 State plan, by 2020 San Angelo will use 8300 ac ft (0.01024 km^3) of TWW for irrigation purposes (TWDB, 2017).

2.3. Water sampling and analysis

The wastewater is treated to Type II standard at the water reclamation facility in San Angelo. It then is transferred to holding lagoons for further treatment and finally sent to contracted farmers in accordance with the Texas Commission on Environmental Quality (TCEQ) regulations (30 Tex. Admin. Code §210.33) (Table 2).

The composition of the wastewater changes, even on a local scale, depending upon the source. The most common source for previous studies has been treated municipal effluent. Prior research reflects that TWW always had higher salinity levels compared to the local water source used to run the experiment. In this work, the case is reversed because the groundwater (GW) quality in the alluvial Lipan aquifer was degraded via anthropogenic and natural sources of salinity (Ashworth and Hopkins, 1995). The water quality starts to decline at the top of the Permian formations and becomes very hard, ranging from marginally fresh to moderately saline (Lee, 1986).

The treated wastewater used by the farmer was sampled from the man-made canals where the water is held before it is pumped for

Table 2
Minimum water quality of Type II reclaimed water adapted from 30 Tex. Admin. Code.

Type II reclaimed water use, for a system other than pond system	
BOD_5	20 mg/l
Or $CBOD_5$	15 mg/l
Fecal coliform or *E. coli*	200 CFU/100 ml[a]
Fecal coliform or *E. coli*	800 CFU/100 ml[b]
Enterococci	35 CFU/100 ml[a]
Enterococci	89 CFU/100 ml[b]

[a] 30 day geometric mean.
[b] Maximum single grab sample.

irrigation. The BGW was sampled from three different wells present on the land (Fig. 3). The wells were purged for 15 min prior to taking the samples to remove stagnant water from the well and obtain a sample representative of the groundwater of the Lipan aquifer. The described procedure for sampling groundwater was obtained from the Soil, Water and Forage Testing Laboratory in College Station. Well B is the most representative of the water used for the BGW irrigated soils for this study.

The FF water sampling was done from the ponding caused by the pipe that dumps out the backflush water from the filter flush system. The Arkal Spin Klin is a modular, automatic, self-cleaning, polymeric disc filter that is highly suitable for corrosive water application. It captures suspended solids with a size of 130 μm or larger before then the filtered water is sent to the drip system for irrigation. The accumulation of particulates on the filter causes a buildup of pressure that triggers the pressure sensor and activates the self-cleaning process. The filters are flushed by TWW and the highly concentrated water is pumped out using an automatic backflush system. The FF water is full of suspended solids and sampled as concentrated TWW. Routine water analysis was carried out by the lab at Texas A&M University using standard methods such as inductively coupled plasma, titration, ion selective electrode, and cadmium reduction. The analysis included the following tests: electroconductivity (EC), pH, sodium (Na), calcium (Ca), magnesium (Mg), potassium (K), carbonate (CO_3), bicarbonate (HCO_3), sulfate (SO_4), chloride (Cl), boron (B), nitrate (NO_3-N), phosphorus (P), total dissolved salts (TDS), alkalinity, hardness and SAR.

2.4. Soil sampling and physicochemical parameters analysis

After determining the major soil series in the area, the three soil horizons (Ap, A, and B) from the AnA were sampled from three different fields: RF, BGW irrigation, TWW irrigation. In addition, the Ap horizon was sampled from the FF field to be used as an accelerated effect of TWW irrigation (Fig. 4). The fields are drip-irrigated with the drip rows at 12–14 in (30.48–35.56 cm) deep.

The physicochemical and mineralogical parameters of the soils were analyzed in the Soil and Crop Sciences Department at Texas A&M University. The texture of the soil was analyzed using the hydrometer method (Gee and Bauder, 1979). The CEC was calculated using potassium saturation; the exchangeable bases (Ca, Mg, and Na) were determined by ammonium acetate (NH_4OAc) extraction; exchangeable sodium percentage (ESP) and exchangeable sodium ratio (ESR) were calculated based on the exchangeable cations data (Eqs. (1) and (2)). The saturated paste method was used to determine the EC, soluble cations, and pH. The SAR was calculated using Eq. (3) based on the soluble cations. The Gapon equation showing the relationship between ESR and SAR is demonstrated in Eq. (4), where X is the soil, the exchangeable ion concentrations are in millimoles (+) per kilogram, and K_G is the Gapon exchange constant ranging from 0.010 to 0.015 $(\mathrm{L\ mmol})^{-1/2}$ (Stewart and Lal, 1992).

$$ESP(\%) = 100 \times \frac{[Na]^{+}}{\left[Ca^{2+}\right] + \left[Mg^{2+}\right] + \left[Na^{+}\right] + \left[K^{+}\right]} \tag{1}$$

$$ESR = \frac{[Na]^{+}}{\left[Ca^{2+}\right] + \left[Mg^{2+}\right]} \tag{2}$$

$$SAR = \frac{[Na]^{+}}{\sqrt{\frac{\left[Ca^{2+}\right] + \left[Mg^{2+}\right]}{2}}} \tag{3}$$

$$ESR = \frac{[NaX]^{+}}{[CaX + MgX]} = \frac{K_G\left[Na^{+}\right]}{\left[\frac{\left[Ca^{2+}+Mg^{2+}\right]}{2}\right]^{1/2}} = K_G SAR \tag{4}$$

2.5. Soil clay mineralogy analysis

The overall mineralogy of the soil was examined using a bulk X-ray diffraction (XRD) on the B-horizons of the different fields (TWW, BGW, and RF). Bulk XRD provides an initial survey of the whole sample (sand, silt, clay). Then, powder XRD was used to identify clay minerals in the soil. The B-horizon has the highest clay content and the lowest erosion compared to A and Ap because it is the deepest. Therefore, if any mineralogical changes have occurred with the introduction of TWW or BGW it would appear in the deepest horizon. The clay was separated from sand by sieving and from silt by size using the centrifugation method, based on Stokes' Law. A clean, dry clay sample was obtained

Fig. 3. Water sampling location: A, B, and C: Groundwater Wells, W: Wastewater Canal, and F: Filter Flush.

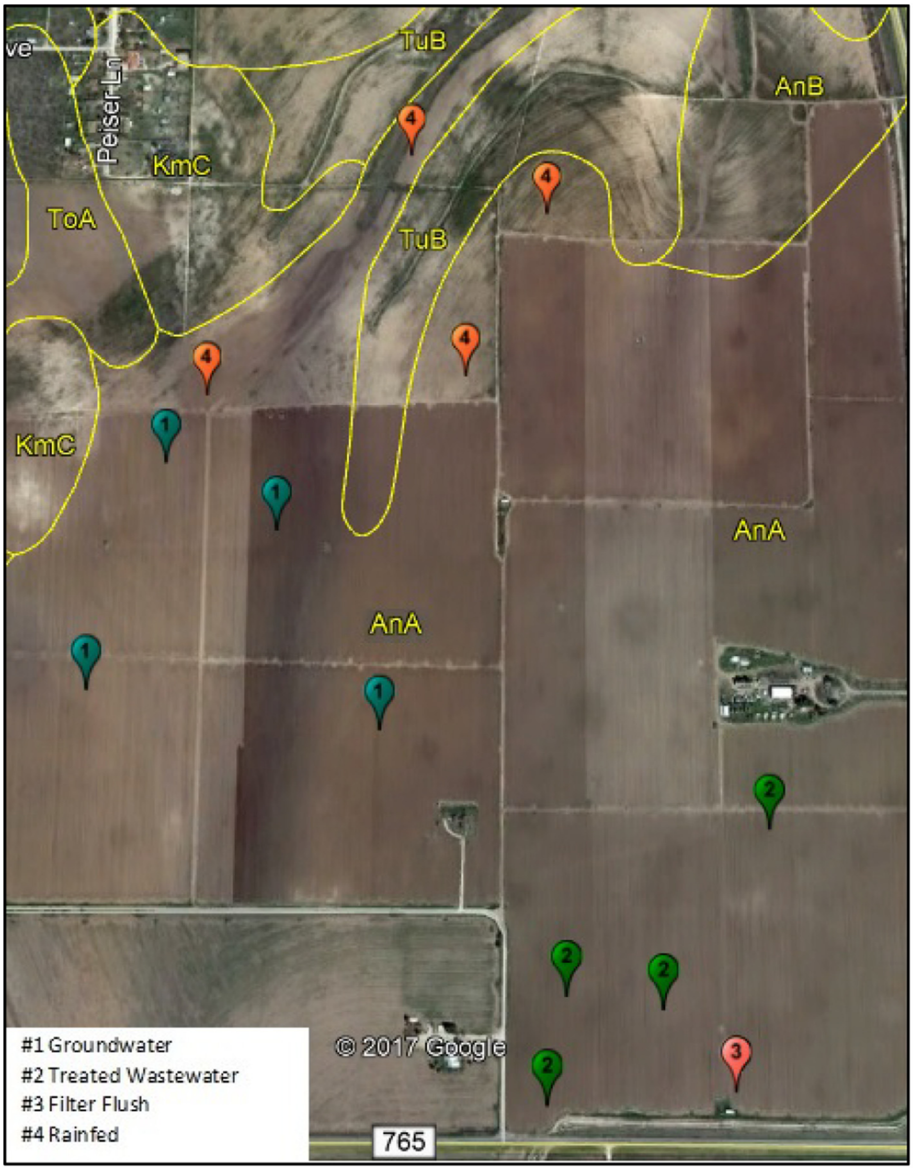


Fig. 4. Soil map and sampling locations based on the type of water used for irrigation: #1 Groundwater, #2 Treated Wastewater, #3 Filter Flush, and # 4 Rainfed.

from the centrifugation procedure following dialysis of the condensed clay suspensions to remove any surplus of electrolytes. Afterwards, the clay samples were oven-dried at 60 °C and finely grounded for XRD analysis. The clay fractions were further treated, some subsamples were saturated with Mg and K. Additionally, after the first diffraction pattern of the Mg saturated sample, it underwent a glycerol treatment to aid in the detection of smectite. The K treated subsample underwent several heat treatments to detect kaolinite and mica. The final procedure for clay samples was quantification of mica by total K determination. The HF method (acid dissolution technique), a modification of the Bernas (1968) method that measures the solutions and clay sample directly into a Nalgene volumetric flask, allowed the digestion to continue occurring at room temperature.

3. Results and discussion

3.1. Characterization of the irrigation water

The results from the inorganic chemical analysis of the groundwater (GW) samples and other water used for irrigation in the study area are represented Table 3. The GW wells increase in depth from A to C, leading to the increase in salinity levels due to penetrating deeper formations. The treated wastewater in the study area differs greatly from the GW for many reasons. First, the sodium (Na) concentration for BGW is higher than 400 mg/l and not recommended for use in irrigation (Provin and Pitt, 2002) as it may lead to significant burning of the foliage. In addition, the high Na concentration in irrigation water may cause poor soil structure as a result of sodicity in the soil. The chloride (Cl^-) levels for BGW are very high, exceeding the suggested concentration for maximum Cl^- content (900 mg/l): the water is considered unsuitable for all agronomic crops as it inhibits plants growth by reducing phosphorus availability (Provin and Pitt, 2002). The sulfate (SO_4^{2-}) concentration for the BGW is higher than the levels recommended by FAO (Table 3), which could have the same effect as Cl^- for plants, leading to potential acidification of the soil. BGW and TWW have high TDS, but the former's moderate salinity is more than triple that of slightly saline TWW, which increases the risks of damaging the soil and plants by salt accumulation. The TWW and FF have similar water chemistry because TWW is used as the backflush for the FF system. Water quality with EC higher than 3.0 dS/m and TDS above 1920 mg/l means high salinity hazard, the water is generally unacceptable for irrigation, except for very salt-tolerant plants where there is excellent drainage, frequent

Table 3
Depth and chemical characteristics of the different brackish groundwater wells, and the chemical characteristics of the other types of water used for irrigation.

Parameters	BGW			TWW	FF	Irrigation water quality criteria (Ayers and Westcot, 1985, 1989, 1994)
	GW A	GW B	GW C			
Depth (ft)	120	230	280	–	–	–
pH	6.73	7.09	6.98	7.7	8	6.5–8.5
EC (dS/m)	6.93	7.02	7.595	2.135	2.455	3
Hardness (mg/l CaCO3)	2330	2671	2900	454	503	–
Alkalinity (mg/l CaCO3)	176	177	187	241	227	–
SAR	4.3	4.2	4.2	4.7	5.2	12–20
Calcium (mg/l)	618	739	803	101	111	400
Magnesium (mg/l)	191	200	218	49	55	60
Sodium (mg/l)	479	495	514	229	266	920
Potassium (mg/l)	6	8	8	25	29	2
Boron (mg/l)	0.32	0.365	0.49	0.49	0.55	3
Bicarbonate (mg/l)	215	215	228	295	271	610
Sulfate (mg/l)	910	1280	1006	212	262	960
Chloride (mg/l)	1306	1339	1701	431	516	355
Nitrate-N (mg/l)	34.35	34.61	41.52	11.06	3.65	40
Phosphorus (mg/l)	0.07	0.07	0.07	2.5	1.25	5
Total dissolved salts (mg/l)	3760	4312	4520	1356	1518	2000

leaching, and intensive management (Provin and Pitt, 2002). The main crop in the study area is cotton, which can handle water with EC up to 5.1 dS/m without yield reduction (Ayers and Westcot, 1976). In the case of BGW, reduction of yield occurs at a rate of approximately 20%, as stated by the farmer in the area of interest. Excess salts from water accumulate in the soil and increase the osmotic pressure of the soil solution leading to plant wilting. In addition, the farmer claims that the yield from TWW irrigation is around 3.5–4 bales per acre compared to 3 bales for BGW and 3/4 bales for RF.

In summary, the TWW has a much better quality and provides higher yields compared to the GW; further, as a result of the high salinity levels, BGW could prove detrimental to the soil and crop yields (Halliwell et al., 2001).

3.2. Impact on soil physicochemical parameters

The chemical characteristics and texture of the different horizons are documented in Tables 4 and 5. The high CEC values observed in all the samples could be attributed to the high clay content and the organic carbon of the soil. The EC values of the irrigated soils are marginally higher when compared to RF soils because the irrigation water introduces soluble salts to the soil. Furthermore, the highest EC value was in the FF soil (Fig. 5a) because the water is highly concentrated with salts and the soil is rarely surface flood irrigated by the FF system. The SAR values follow a similar trend with a marginal rise in the irrigated soils (Fig. 5b). In this case, TWW soils have higher SAR numbers than BGW irrigated soils as a result of the TWW having a higher Na^+ concentration compared to Ca^{2+} concentration (Table 3). Fig. 5c shows the ESP response of the soils and the results follow the same trend as the SAR. The ESR in the soils and SAR in the extracts (soluble cations) are highly correlated, further solidifying the accuracy of the data (Fig. 5d). According to the Natural Resources Conservation Service (NRCS), a soil is classified as sodic when pH is above 8.5, SAR and ESP are >13 and 15 respectively. In the case of the Angelo series samples, all the values of interest (SAR, ESP, and pH) are low. This indicates no sodicity problems (Table 6). Saline soils are characterized by having an EC >4 dS/m, all the samples have low numbers, which means salinity problems are not an issue for this soil and the cotton crop (Table 5). The situation is ideal because the main crop in the study area is cotton, a high salt tolerant crop (Maas and Hoffman, 1977). The TOC slightly increases because of TWW and

Table 4
Physiochemical properties of Angelo clay loam soil.

Physiochemical properties of Angelo clay loam soil											
Soil physical properties						Concentration in saturated extract					
						EC	K	Na	Ca	Mg	SAR
Irrigation water	Soil horizon	Depth (cm)	Clay content (%)	Texture		dS/m	(mmol(+)/L)				
Rainfed (RF)	Ap	0–15	33.40	Clay loam	Mean	0.47	0.49	0.62	4.53	0.31	0.58
					SD	0.19	0.41	0.39	1.26	0.54	0.47
	A	15–30	42.92	Clay	Mean	0.60	1.03	0.62	5.61	0.29	0.50
					SD	0.17	1.28	0.25	1.27	0.49	0.25
	B	30–72	49.68	Clay	Mean	0.97	0.41	1.38	9.66	0.30	0.99
					SD	0.59	0.30	0.72	7.86	0.51	0.48
Brackish groundwater (BGW)	Ap	0–15	35.26	Clay loam	Mean	1.43	1.05	1.68	11.61	0.59	0.89
					SD	0.33	0.13	0.53	1.90	0.98	0.29
	A	15–30	45.31	Clay	Mean	1.02	0.61	0.86	7.78	0.65	0.68
					SD	0.58	0.37	0.44	3.57	1.11	0.41
	B	30–72	49.52	Clay	Mean	1.13	0.38	3.66	6.47	1.27	1.89
					SD	0.97	0.20	4.02	4.65	2.20	0.88
Treated wastewater (TWW)	Ap	0–15	47.17	Clay	Mean	1.69	1.71	5.27	8.91	2.49	3.74
					SD	1.19	1.86	3.23	8.13	4.29	2.74
	A	15–30	50.90	Clay	Mean	2.33	0.82	9.92	10.24	0.59	5.20
					SD	2.03	0.27	9.31	8.30	0.95	3.58
	B	30–72	54.51	Clay	Mean	1.79	0.56	8.11	6.83	0.54	5.35
					SD	0.77	0.10	4.07	2.95	0.87	2.41
Filterflush (FF)		0–15	48.15	Clay		3.5	1.86	12.85	11.57	4.20	4.57

Table 5
Exchangeable bases and organic content of Angelo clay loam soil.

Exchangeable bases and organic content of Angelo clay loam soil											
Irrigation water/soil horizon			Exchangeable cations				CEC	ESR	ESP	OM	TOC
			K	Na	Ca	Mg					
Irrigation water	Soil horizon		cmol(+)/kg						%	%	
Rainfed (RF)	Ap	Mean	1.08	0.28	38.63	1.84	43.69	0.69	0.67	3.39	1.73
		SD	0.32	0.04	5.84	0.74	4.55	0.05	0.05	0.63	0.32
	A	Mean	0.95	0.31	39.89	1.82	46.31	0.74	0.72	3.53	1.80
		SD	0.23	0.03	5.42	0.82	5.36	0.02	0.02	0.49	0.25
	B	Mean	0.73	0.43	39.66	1.89	45.91	1.01	0.98	3.38	1.72
		SD	0.14	0.16	4.60	0.85	4.26	0.28	0.27	0.67	0.34
Brackish groundwater (BGW)	Ap	Mean	1.74	0.40	39.86	3.30	48.08	0.93	0.88	4.15	2.12
		SD	0.18	0.06	3.50	0.71	3.12	0.09	0.08	0.48	0.25
	A	Mean	1.27	0.40	39.92	2.93	48.33	0.92	0.89	4.35	2.22
		SD	0.37	0.10	2.89	0.67	3.48	0.19	0.18	1.00	0.51
	B	Mean	1.03	0.75	39.73	3.52	49.22	1.70	1.63	4.47	2.28
		SD	0.33	0.44	2.22	0.82	2.47	0.90	0.85	0.47	0.24
Treated wastewater (TWW)	Ap	Mean	1.88	0.84	36.55	5.41	47.33	2.01	1.89	4.26	2.17
		SD	0.22	0.27	3.00	1.27	1.59	0.68	0.63	0.26	0.13
	A	Mean	1.53	1.15	37.39	5.81	50.02	2.71	2.53	4.02	2.05
		SD	0.29	0.60	3.00	1.47	1.77	1.47	1.35	0.24	0.12
	B	Mean	1.18	1.29	36.72	5.94	48.82	3.02	2.84	3.54	1.80
		SD	0.33	0.39	3.27	1.29	1.47	0.90	0.81	0.23	0.12
Filterflush (FF)			1.33	1.86	39.86	4.68	52.00	4.17	3.89	4.99	2.54

BGW application for irrigation, increasing yields and resulting in high organic material deposited on the soil from the crops compared to RF agriculture (Fig. 6). The FF irrigated soil has the highest TOC because it contains all the materials filtered from TWW. In summary, soil salinization was not a factor after 14 years of irrigation with TWW nor irrigation with BGW.

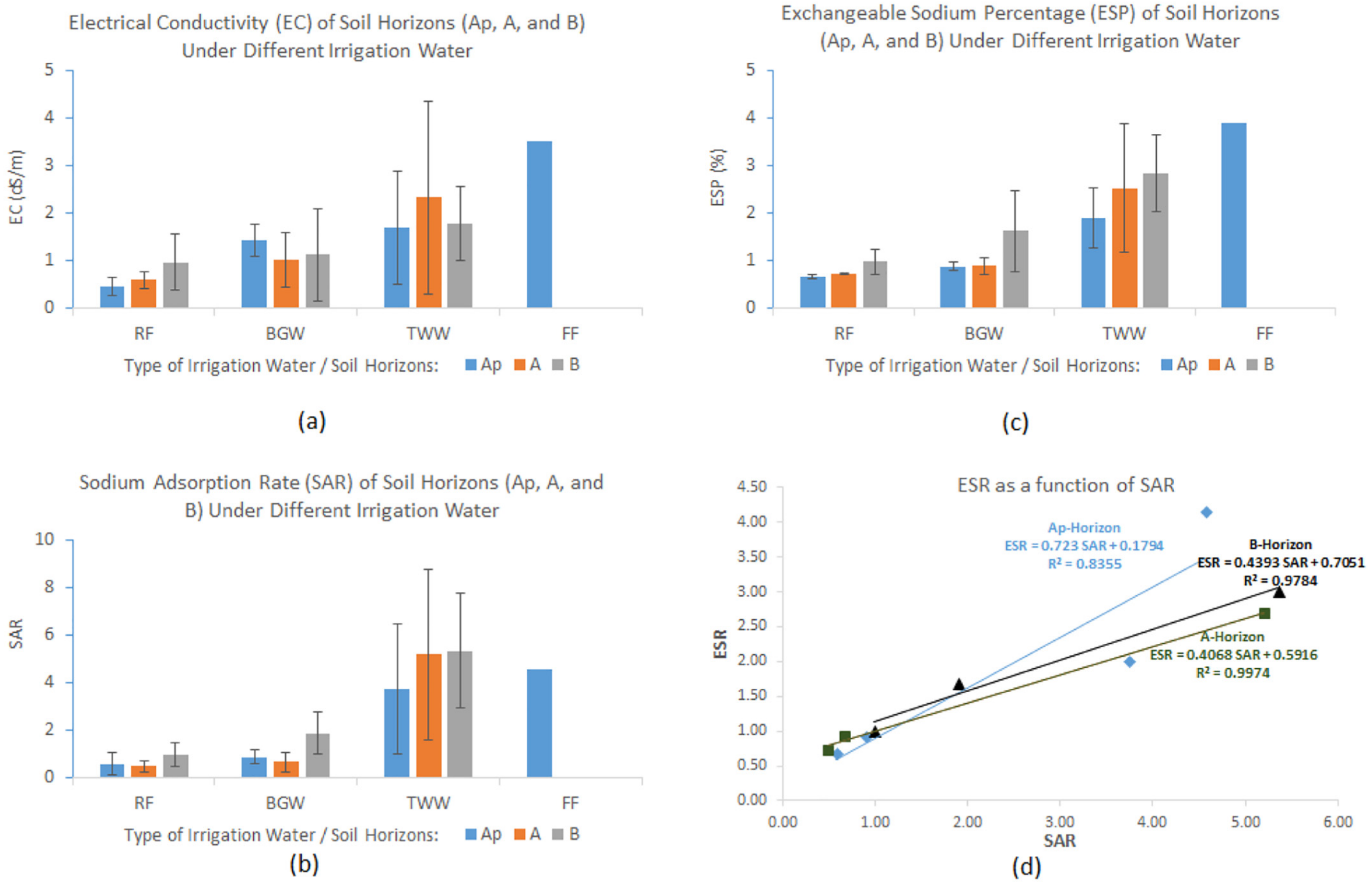


Fig. 5. Chemical properties of soil horizons under different irrigation water types: (a) electrical conductivity (EC), (b) sodium adsorption rate (SAR), (c) exchangeable sodium percentage (ESP), and (d) ESR as a function of SAR.

Table 6
Classification of salt-affected soils according to NRCS reprinted from Richards (1954).

Class	EC (dS/m)	SAR	ESP	Typical soil structural condition[a]
Normal	<4	<13	<15	Flocculated
Saline	>4	<13	<15	Flocculated
Sodic	<4	>13	>15	Dispersed
Saline-sodic	>4	>13	>15	Flocculated

[a] Soil structural condition also depends of other factors not include in the NRCS classification system, including soil organic matter, soil texture and EC of irrigation water (Horneck et al., 2007).

3.3. Impact on soil clay mineralogy

The results from the bulk XRD showed identical peaks for the three treatments (Fig. 7a). The minerals present in the overall samples are quartz (3.34 Å), calcite (3.03 Å), and minor feldspars (albite and microcline) between the quartz and calcite peaks. The dominant mineral is quartz followed by calcite in the bulk samples. For the powdered XRD (Figs. 7b, c, and d), all the samples had similar peaks with intensity and shape alike: Peak at 15.1–15.5 Å on the Mg-saturated XRD pattern slightly collapses upon glycerol solvation indicating a slight random mica-smectite interstratification. Mica is observed in the sample, it is indicated by peaks 10, 5, 3.3 Å. Kaolinite is shown by peaks 7.15 and 3.6 Å. Quartz and calcite are observed at 4.26 and 3.03 Å respectively.

The K-quantification technique provided the amount of mica present in each sample (Table 7). Illite/mica constitutes about 20% of the clay minerals in each sample. Smectite is the dominant mineral; it is assumed that it constitutes around 50% of the clay samples because it has broad peaks with a large surface area and the high CEC shown in the chemical analysis data (Table 5). Furthermore, kaolinite is the least dominant making up around 10% of the clay sample. Each clay sample is composed of approximately 15–18% of calcite depending on the presence of quartz.

The soil bulk and clay mineralogy are not altered because the water sources used for irrigation are close to regular conditions and don't hold extreme concentrations of salts. However, the trends of illite percentages are showing that perhaps on a long-run BGW irrigated soils would become richer in illite and decrease in smectite content via illitization.

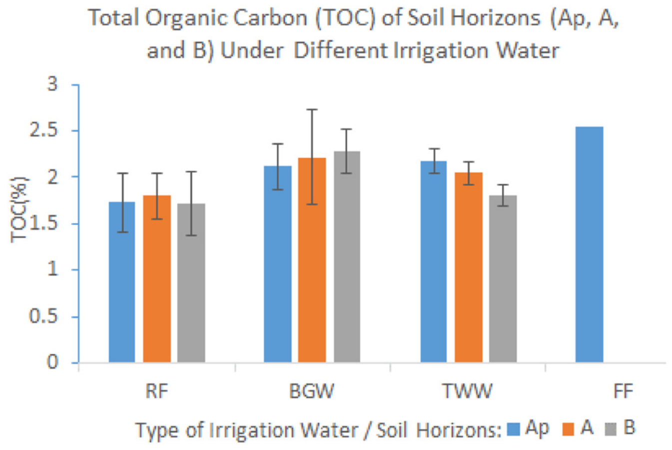


Fig. 6. Total organic carbon (TOC) of the different soil horizons under different irrigation water types.

3.3.1. Water-Energy-Food Nexus

The Water-Energy-Food Nexus concept was addressed by observing the benefits provided to agriculture while saving valuable FW and energy: crops are produced at a regular or even superior rate. When WW is treated to be used for irrigation it will decrease the use of fertilizers and lead to energy savings for spreading the fertilizer on a local scale. Energy will be conserved if the level of WW treatment decreases, leaving a higher nutrient concentration in the irrigation water, which in turn will help with nutrient recycling and may further reduce the demand for fertilizers. The second goal of the Sustainable Development Goals (UN General Assembly, 2015) is addressed by irrigating with TWW because higher yields would be anticipated compared to those with traditional irrigation. Given that the use of TWW helps the agriculture sector decrease its large FW consumption, water conservation will be accomplished. WW should be treated with regard to the intended use and should meet standards and regulations to protect human and soil health.

4. Conclusions

The use of treated wastewater for agriculture can be traced back many centuries and across the world, including to the late 19th century Texas. Reclaimed water use is on the rise with growing water scarcity due to the demands of growing populations. A by-product of population growth will be an increase in quantities of wastewater that can be channeled for use in irrigation. This study shows that unconventional water sources (TWW and BGW) are a viable substitute for FW irrigation in semi-arid and arid regions: there was no significant change in the soil chemistry nor any sign of salinity or sodicity problems. TWW has a better quality (pH, salinity, chloride, sodium, and sulfate) than the saline groundwater of the Lipan Aquifer. Soil health reflects the quality of the irrigation water: in the long term, BGW could lead to salinity problems. Therefore, TWW should be used instead of BGW to decrease the stress on the Lipan Aquifer that is shared by 8 counties. In addition to the reduction of groundwater pumping, the use of TWW could help the aquifer to replenish properly and lead to enhanced groundwater quality. Soils with high clay content, organic carbon, and smectite lead to high CEC values which provides a large nutrient reserve. Clay mineralogy is stable and plays a major role in the fertility of the soil. Although, a minor (insignificant) increase in illite content under BGW irrigation was observed, clay mineralogy is not easily changed over a short time period during which close to regular conditions occur. An artificial setting that imitates geological conditions is needed for such a change (high pH K-solutions, seawater at high temperatures 50 °C).

Future work should focus on correlating soil chemistry and clay mineralogy results with the hydrostructural properties of the soil and using the pedostructure theory model (Braudeau et al., 2014). Pedostructure, soil aggregate structure, can be characterized through a set of physical parameters extracted from the soil shrinkage curve (ShC) and water retention curve (WRC). Each of these parameters characterizes specific hydro-structural properties of soil medium (Assi et al., 2014), and thus, can be used to track the impact of water reuse on soil aggregate structure and soil health. Soil microbiology and yield alterations when using TWW compared to BGW and RF agriculture should be evaluated. The chemistry and mineralogy of the soil showed no apparent changes resulting from the use of alternative water sources. Therefore, exploring the other properties of the soil (microbiology and pedostructure) is needed to conclude the overall impact of non-traditional water irrigation. The impact of BGW irrigation can be further explored by observing the effect on different soil series from the area such as the Mereta series and the Tarrant series. Another beneficial work would be the comparison of Angelo soils

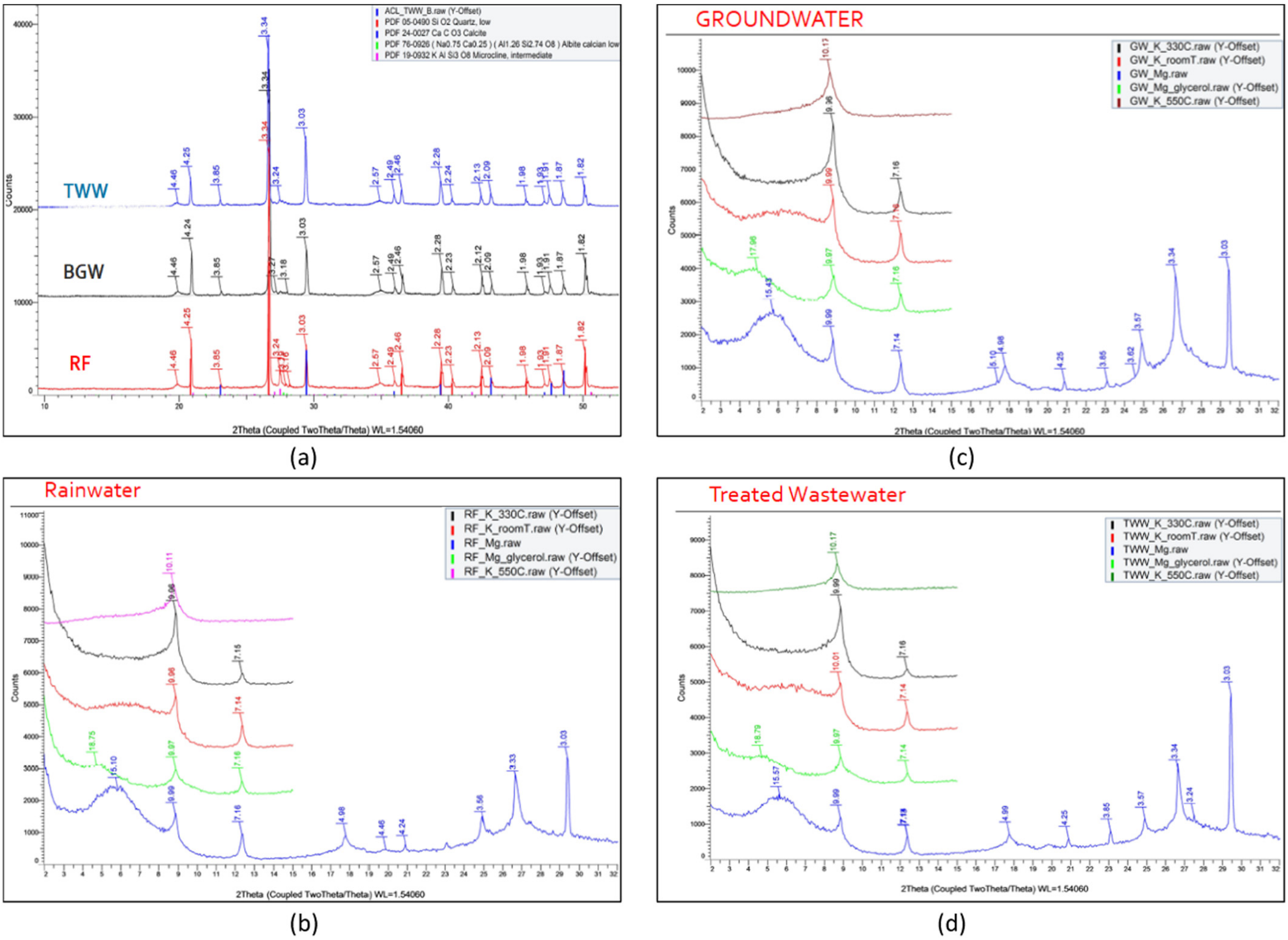


Fig. 7. Mineralogical properties of soil horizon B under different irrigation water types: (a) Bulk X-ray diffraction, (b) X-ray powder diffraction of Rain-fed clay sample, (c) X-ray powder diffraction of brackish groundwater clay sample, and (d) X-ray powder diffraction of treated wastewater clay sample.

irrigated with FW to the soils from this study. The main subject to consider when comparing other studies where domestic reclaimed water has been used for agriculture is that TWW allocated for irrigation in Texas has a high quality.

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Table 7
Quantification of mica in clay samples.

Samples	% K	% mica	Average % mica
RF1	1.5	18.1	19.1
RF2	1.7	20	
GW1	1.8	21.8	21.3
GW2	1.7	20.9	
TWW1	1.6	19.5	19.8
TWW2	1.7	20.1	

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