

Effects of irrigated agroecosystems: 2. Quality of soil water and groundwater in the southern High Plains, Texas

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[1] Trade-offs between water-resource depletion and salinization need to be understood when promoting water-conservative irrigation practices. This companion paper assesses impacts of groundwater-fed irrigation on soil water and groundwater quality using data from the southern High Plains (SHP). Unsaturated zone soil samples from 13 boreholes beneath irrigated agroecosystems were analyzed for water-extractable anions. Salt accumulation in soils varies with irrigation water quality, which ranges from low salinity in the north (median Cl: 21 mg/L) to higher salinity in the south (median Cl: 180 mg/L). Large Cl bulges under irrigated agroecosystems in the south are similar to those under natural ecosystems, but they accumulated over decades rather than millennia typical of natural ecosystems. Profile peak Cl concentrations (1200–6400 mg/L) correspond to irrigation efficiencies of 92–98% with respect to drainage and are attributed to deficit irrigation with minimal flushing. Perchlorate (ClO₄) also accumulates under irrigated agroecosystems, primarily from irrigation water, and behaves similarly to Cl. Most NO₃-N accumulation is below the root zone. Groundwater total dissolved solids (TDS) have increased by ≤960 mg/L and NO₃-N by ≤9.4 mg/L since the early 1960s. Mobilization of salts that have accumulated under irrigated agroecosystems is projected to degrade groundwater much more in the future because of the essentially closed-basin status of the aquifer, with discharge occurring primarily through irrigation pumpage. TDS are projected to increase by an additional 2200 mg/L (median), ClO₄ by 21 μg/L, and NO₃-N by 52 mg/L. Water and salt balances should be considered in irrigation management in order to minimize salinization issues.

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1. Introduction

[2] As with the quantity of available water resources, water quality can also be a limiting factor in agricultural productivity and sustainability of land and water resources. Soil salinization impacts ~20–25% of irrigated land in the United States. [Ghassemi *et al.*, 1995]. Many irrigation studies over the last several decades have emphasized the importance of salt management and leaching requirements for crop production [Rose *et al.*, 1979; Smith and Hancock, 1986]; however, recent emphasis on decreasing irrigation applications to reduce water resource depletion may not provide sufficient irrigation water to leach salts through the system. In addition, there has been considerable debate in

recent years about whether proposed water conservative irrigation practices based on improved irrigation technologies actually conserve water at the basin scale [Huffaker and Whittlesey, 2003; Scheierling *et al.*, 2006]. Although runoff and recharge may be considered losses to the system at the field plot scale, these flows would not be considered true losses at the basin scale [Perry, 2007]. More efficient irrigation technologies often increase crop-water consumption because water is applied more uniformly to crop root zones, and crop yield also increases. For example, Ward and Pulido-Velazquez [2008] showed that for the Rio Grande basin, increasing application of drip irrigation technology would result in increased water depletion at a basin level because of increased crop evapotranspiration (ET) and reduced runoff and recharge. It is essential that leaching requirements for crop production not be overlooked in proposed water conservative irrigation practices. It has also been suggested that salt rights need to be considered, along with water rights, for irrigation [Oster and Wichelns, 2003].

1.1. How Does Irrigation Salinize Soils and Groundwater?

[3] Irrigation adds a considerable amount of salts to soils relative to precipitation in nonirrigated cropland. Crop ET is

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similar to desalinization in that root-water uptake excludes most salts, and soil water salinity levels, which are harmful to crops, may build up when water drainage or percolation through the root zone is insufficient to flush accumulated salts [Richards, 1954]. Concentrations of salts in soils depend on the water balance of the system. Assuming steady state with no change in water storage:

$$Pe = R = I + P - ET - Ro \quad (1)$$

where Pe is percolation below the root zone, R is recharge at the water table, I is irrigation, P is precipitation, ET is evapotranspiration, and Ro is runoff, with all units expressed in mm/a. Considering a salt balance using Cl as an example and assuming no runoff:

$$PeCl_{sw} = RCl_{sw} = ICl_I + PCl_P - ETCl_{ET} \quad (2)$$

where subscripts associated with Cl refer to Cl concentrations in those media and sw is soil water. In irrigation systems that are 50% efficient with respect to drainage, i.e., $ET = 50\%$ of $I + P$, Cl_{sw} will double relative to Cl in irrigation and precipitation, assuming crops do not take up any Cl. In contrast, for an irrigation system that is 95% efficient, which is approximately the upper limit of sprinkler systems, $ET = 95\%$ of $I + P$ and Cl_{sw} will increase by a factor of 20 relative to Cl in irrigation and precipitation. Although it is generally assumed that recharge is greater beneath irrigated versus nonirrigated cropland because of additional water input to the system through irrigation, crop yields and associated ET rates are generally much higher in irrigated cropland and can greatly reduce percolation in the system and increase salinity of percolation water. In addition to soil salinization, groundwater salinity can increase under irrigated agroecosystems by mobilizing salts that accumulated under natural ecosystems [Stonestrom *et al.*, 2003; McMahon *et al.*, 2006] through increased recharge caused by conversion of deep-rooted perennial native vegetation to shallow-rooted annual crops [Scanlon *et al.*, 2007]. Assessing nutrient buildup beneath irrigated cropland is much more complicated than that of salts with inputs, in addition to irrigation water, from fertilizers and mineralization and nitrification of soil organic nitrogen (SON) and additional sinks in crop uptake and volatilization.

1.2. What Controls Salinity Buildup Under Irrigated Cropland?

[4] Controls on salinity buildup include irrigation water quality, ET, root-zone depth, soils, and climate. As discussed previously, irrigation water quality can vary from fresh water to brackish water, depending on the source [Stonestrom *et al.*, 2003; Oren *et al.*, 2004; Schoups *et al.*, 2005]. Irrigation application rates relative to crop ET determine the concentration factor in the crop root zone. Annual crops have limited time to develop deep roots that would remove more water and increase salinity buildup. Soil types can also impact salinity buildup. Finer grained soils retain irrigation water within the root zone for longer periods, allowing more time for ET and salinity buildup. Seasonal distribution of precipitation can also play an important role in controlling salinization. Precipitation coincident with crop demand should result in greater soil salinization versus precipitation that is not. In the saturated

zone, the volume of water impacts the capacity to dilute or assimilate salts introduced from the unsaturated zone, with salinity in mg/L increasing linearly as aquifer saturated thickness decreases.

1.3. How Can Irrigation Be Managed Sustainably With Respect to Soil Water and Groundwater Quality?

[5] Approaches to achieve sustainability with respect to water quality may differ from those required for water quantity. Minimizing soil salinization requires irrigation with sufficient water to flush salts through the profile; however, this approach runs counter to water-conservative irrigation approaches promoted in recent decades to reduce groundwater depletion. Rotating between irrigated and rain-fed agriculture would reduce salinization because of extremely low salt concentrations in precipitation in rain-fed agriculture. Ideally salts could be flushed through the soil and groundwater to discharge from the system through surface water bodies. However, in many groundwater-fed irrigation systems, the primary discharge mechanism is through irrigation pumpage, and salts are continually recycled through the system. Once salt bulges accumulate in soil profiles, they need to be managed to minimize negative impacts on crop productivity and groundwater quality. One approach would be to irrigate with water sufficient to maintain the salt bulge below the root zone but not to mobilize the bulge into the aquifer. Salinity issues may pose a much greater problem for irrigated agriculture than water-quantity issues because salinization may be irreversible.

[6] The High Plains aquifer is one of the largest freshwater aquifers in the United States and in the world. Under predevelopment conditions, i.e., prior to large-scale irrigation pumpage, groundwater discharge balanced groundwater recharge [Sophocleous, 2000]. Salts in the High Plains aquifer were originally derived primarily from underlying high-salinity aquifers, as shown by the earliest groundwater sampling in the 1930s and by stable isotope data [Nativ, 1988]. With intensive groundwater development for irrigation, water for pumpage was initially derived from groundwater storage, as evidenced by declining water tables, and also from reduced discharge, and increased recharge [Blandford *et al.*, 2003]. Discharge to springs along streams and along the margins of the SHP has been greatly reduced with groundwater development for irrigation [Blandford *et al.*, 2003]. The aquifer under current conditions can essentially be considered a closed system, with the primary discharge mechanism being irrigation pumpage.

[7] Recharge beneath natural ecosystems is focused beneath ephemeral lakes or playas and averages ~6 to 11 mm/year, on the basis of groundwater Cl data in the SHP-N region [Wood and Sanford, 1995; Scanlon *et al.*, 2008a]. Salt loading from playas is negligible. There has been no recharge in interplaya areas since Pleistocene times ~10,000–15,000 years ago, and salts have accumulated in soil profiles during that time [Scanlon *et al.*, 2003]. Conversion of natural ecosystems to rain-fed agroecosystems did not change recharge in areas of low-permeability fine-grained soils, such as the SHP-N region [Scanlon *et al.*, 2008a], but increased recharge in sandier soils in the SHP-S region (median 24 mm/year) [Scanlon *et al.*, 2007]. This increase in recharge mobilizes salts that accumulated under natural ecosystems and results in a transient input of

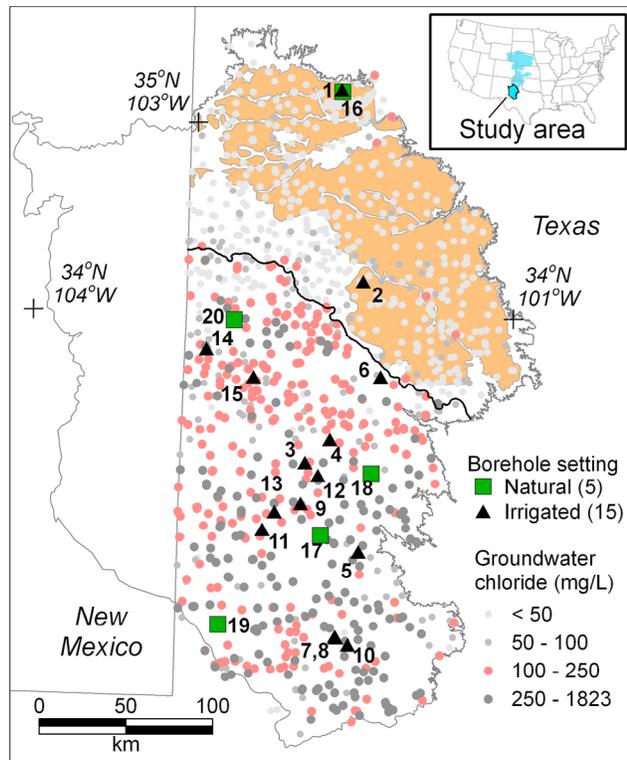


Figure 1. Borehole locations and groundwater chloride concentrations in the study area. Map reference numbers are shown for irrigated and natural setting boreholes (Table 1). Groundwater chloride data are from the Texas Water Development Board groundwater database (www.twdb.state.tx.us) and represent the latest samples (1996–2008) for 1100 wells completed in the Ogallala Formation. Black line represents the 500 mg/L groundwater total dissolved solids (TDS) contour that defines the northern low TDS (SHP-N) and southern high TDS (SHP-S) regions in Texas. Shaded areas in the SHP-N region indicate the extent of Pullman clay loam soils. Irrigated boreholes 14 and 15 and natural borehole 20 represent *McMahon et al.* [2006] irrigated boreholes MPL and JRW and natural borehole MWR, respectively.

salts to the High Plains aquifer. Previous studies indicate that mobilization of salt inventories that accumulated under natural ecosystems, approximated by profile 18 (Figure 1), into the underlying aquifer would increase median values of Cl by ≤ 150 mg/L, SO_4 by ≤ 480 mg/L, and ClO_4 by ≤ 14 $\mu\text{g/L}$ [Scanlon *et al.*, 2008c, 2009b]. Mobilizing $\text{NO}_3\text{-N}$ that was created during initial cultivation would increase $\text{NO}_3\text{-N}$ in groundwater by up to 17 mg/L [Scanlon *et al.*, 2008b]. Because the groundwater system is essentially a closed basin, transient inputs of salts from external sources, such as the bulges that accumulated under natural ecosystems, that are mobilized by increased recharge under cropland, increase salt concentrations in the aquifer.

[8] Irrigation essentially redistributes salts from groundwater to soils but may also result in the addition of salts to the aquifer from external sources, such as through mobilization of salt bulges that accumulated under natural ecosystems or through application of treated wastewater and/or recycled water [Beltrán, 1999; Kalavrouziotis *et al.*, 2006].

If salts that were originally derived solely from the aquifer are mobilized back into the aquifer, the concentration on a mass basis (mg salt/kg of sediment) should not change in the aquifer if there are no external inputs; however, salt concentration on a volume basis (mg salt/L of water) in the aquifer would increase linearly as the amount of water in the aquifer is depleted and the assimilative capacity of the aquifer is reduced. Nutrients, such as $\text{NO}_3\text{-N}$, are continually added to the system from fertilizers and $\text{NO}_3\text{-N}$ concentrations should increase continually in the aquifer. An artificial drainage system cannot be used to remove salts below the root zone in groundwater fed irrigation systems because the soil zone is generally unsaturated.

[9] *McMahon et al.* [2007] noted that availability and sustainability of water resources in the High Plains aquifer are affected by water quality and that processes that promote recharge in this semiarid region, such as irrigation, increase aquifer vulnerability to contamination by increasing chemical fluxes through the unsaturated zone and reducing transit times to the water table. This study also notes that the SHP had the poorest groundwater quality within the entire High Plains aquifer, with maximum contaminant level (MCL) exceedances of TDS, NO_3 , As, and F. Chemical inventories were quantified in three natural ecosystem sites and two adjacent irrigated sites, in the northern (NHP), central (CHP), and southern (SHP) High Plains [McMahon *et al.*, 2006]. Salts that accumulated under natural ecosystems account for 60–80% of Cl and NO_3 inventories under irrigated agroecosystems, whereas KCl fertilizer contributed to some Cl at one site. Higher recharge rates under irrigated agroecosystems versus natural ecosystems sites by factors of ~ 1.5 in the NHP, 8–11 in the CHP, and 85–160 in the SHP are mobilizing salt reservoirs that accumulated under natural ecosystems. Groundwater quality is projected to degrade when these salt inventories reach the water table. Similar results were found beneath irrigated sites in the Amargosa Desert, where increased percolation under irrigated sites mobilized Cl and NO_3 bulges that accumulated under natural ecosystems [Stonestrom *et al.*, 2003; Scanlon *et al.*, 2005]. Increased percolation/recharge under cropland is not considered important for groundwater pesticide contamination according to studies in the High Plains because 80–100% of pesticide inventories were found in the upper 2 m of the soil profile, indicating significant retention and degradation of pesticides [McMahon *et al.*, 2006]. Although As has been applied to defoliate cotton in the past and F can be derived from precipitation, previous studies show that As and F are readily sorbed onto soils in the SHP and are generally not mobilized by increased percolation/recharge [Reedy *et al.*, 2007; Scanlon *et al.*, 2009b].

[10] Perchlorate (ClO_4) is another salt that can degrade groundwater and has been found at concentrations of up to 200 $\mu\text{g/L}$ in groundwater in the SHP [Rajagopalan *et al.*, 2006]. Although there is no established MCL for ClO_4 in groundwater, a National Research Council panel in 2005 suggested that a reference dose of 0.7 mg/kg body weight (bw) per day would be appropriate, which translates into a drinking-water equivalent level of 24.5 $\mu\text{g/L}$ [National Research Council, 2005]. Perchlorate adversely affects human health by competitively inhibiting iodide uptake into the thyroid, resulting in reduced thyroid hormone production, which is required for normal development of the central nervous system of fetuses and infants, normal skeletal

development and growth, and metabolic activity of infants and adults [Gullick *et al.*, 2001]. Although ClO_4 was originally thought to be derived from NO_3 fertilizers from Chile, studies in the SHP indicate that ClO_4 is derived from bulk precipitation [Rajagopalan *et al.*, 2006; Rao *et al.*, 2007]. Previous studies show that ClO_4 is mobilized by increased recharge under rain-fed agriculture in the SHP [Scanlon *et al.*, 2008c] and under irrigated agriculture in the Amargosa Desert, Nevada [Rao *et al.*, 2007]. In addition, buildup of ClO_4 in the soil zone and its uptake in crops can result in large concentrations in feed for animals and in milk, providing another exposure pathway for humans [Jackson *et al.*, 2005].

[11] The objective of this study was to assess long-term impacts of groundwater-fed irrigation on the quality of soil water and groundwater, to evaluate controls on these impacts, and to examine approaches toward sustainable irrigation with respect to water quality. This study focuses on salts and nutrients, including Cl, ClO_4 , SO_4 , and NO_3 -N in irrigated areas in the SHP (Figure 1). This paper is the second of a two-part series, the first part focusing on irrigation impacts on the quantity of soil water and groundwater. Lack of monitoring information on the quantity (pumpage) and quality of irrigation water and large uncertainties in fertilizer application rates make it difficult to assess impacts of irrigation on soil water and groundwater quality on the basis of chemical loading to the system. Therefore, we evaluate the outputs from irrigation processes using hydrostratigraphic records of salts and nutrients preserved in thick unsaturated zones in a semiarid region and in time series of groundwater quality changes. We also evaluate these outputs as they relate to estimates of inputs from chemical loading and transport processes. Predominantly piston-type flow in the SHP provides an invaluable archive of past impacts of land use on subsurface flow and transport in the form of stratified chemical inventories, as shown in previous studies related to natural ecosystems and rain-fed agroecosystems [Scanlon *et al.*, 2003, 2007]. Measured concentrations of unsaturated zone solutes link surface application rates of irrigation water and fertilizers to soil water and groundwater quality. The study area allows different potential controls on water quality to be examined, including varying soil texture and irrigation water quality. Because impacts of irrigation on water quality may be irreversible, it is important to consider different approaches toward sustainable irrigation practices with respect to water quality and to consider trade-offs in terms of water quantity and water quality.

2. Materials and Methods

2.1. Site Characteristics

[12] Physical characteristics of the SHP have been described in the companion to this study [Scanlon *et al.*, 2010]. Irrigation water is abstracted primarily from the High Plains (Ogallala) aquifer. Previous studies have characterized groundwater quality in the SHP region according to variations in TDS, with a 500 mg/L TDS contour line trending from northwest to southeast that divides the aquifer into a low TDS northern region (SHP-N, median 390 mg/L) and a high TDS southern region (SHP-S, median 890 mg/L) (Figure 1) [Scanlon *et al.*, 2009b]. Differences in TDS are associated with variations in concentrations of other ions, including

median values of Cl (north median 21 mg/L, south median 80 mg/L), ClO_4 (north < 0.5 $\mu\text{g/L}$, south 3.2 $\mu\text{g/L}$) and SO_4 (north 334 mg/L, south 220 mg/L). These variations in groundwater quality also correspond to physical characteristics of the aquifer: the north generally corresponds to a paleovalley where the aquifer-saturated thickness was originally high (median predevelopment 45 m) and the water table is currently deeper (median 63 m), whereas the south corresponds to a paleoplain where the saturated thickness of the aquifer was much less (median 16 m) and the water table is currently shallower (median 25 m). The regional TDS boundary also generally corresponds to the northern subcrop limit of Cretaceous sediments [Scanlon *et al.*, 2007]. The High Plains aquifer is directly underlain by the Triassic Dockum aquifer in the north, whereas the SHP and Dockum aquifers are separated by the Edwards Trinity High Plains and other Cretaceous aquifers in the south-central region of the SHP. High-TDS water in the south was found in the earliest groundwater sampling in the 1930s (Texas Water Development Board (TWDB), www.twdb.state.tx.us) and has been attributed to upward movement of groundwater from the underlying, more saline Dockum aquifer [Nativ, 1988; Scanlon *et al.*, 2009a].

2.2. Physical and Chemical Measurements

[13] Most of the methods used in this study are described in the companion paper and in previous studies [Scanlon *et al.*, 2007, 2010]. Irrigation water and borehole soil samples were collected from 13 locations in the SHP. Soil samples were leached using 40 mL of double deionized water and 25 g of soil, placing soil samples in a reciprocal shaker for 4 h, centrifuging at 7000 rpm for 20 min, and filtering the resultant supernatant (0.2 μm filter). Irrigation and supernatant water sample concentrations of Cl, SO_4 , and NO_3 were measured by ion chromatography (Dionex ICS2000; EPA Method 300.0). Water samples for ClO_4 analyses were filtered through 0.1 μm Supor (PES) membrane IC certified Acrodisc syringe filters. Analysis of ClO_4 was conducted using a sequential ion chromatography-mass spectroscopy (IC-MS/MS) technique, with a detection limit of 0.05 $\mu\text{g/L}$ in the supernatant and an analytical uncertainty of ~20% [Rajagopalan *et al.*, 2006]. Concentrations of ClO_4 were also measured in cotton leaves from three sites by grinding the leaves and extracting ClO_4 .

[14] Water-extractable ion concentrations are expressed on a mass basis as mg ion per kg of dry soil and were calculated by multiplying ion concentrations in the supernatant by the extraction ratio (g water/g soil). Ion concentrations expressed as mg ion per L of soil pore water were calculated by dividing concentrations in mg/kg by gravimetric water content and multiplying by water density. Subsurface solute inventories (S_I , kg/ha or g/ha) were calculated as follows:

$$S_I = \sum_{i=0}^z S_{s,i} \rho_b i 10^4 dz_i \quad (3)$$

where S_s is depth-weighted solute mass concentration in soil (mg ion/kg dry sediment or $\mu\text{g/g}$), ρ_b is soil dry-bulk density (kg/m^3), dz is interval thickness (m), z is depth of interest, and 10^4 (m^2/ha) is for units conversion [McMahon *et al.*, 2006]. Total inventory values (kg/ha) are normalized by

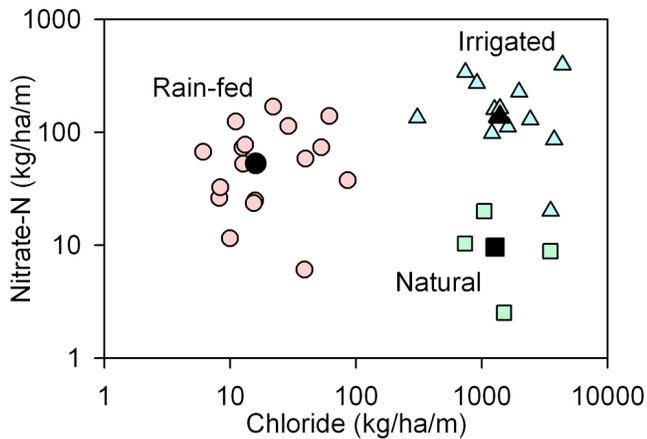


Figure 2. Relationship between inventories of chloride and nitrate-N normalized by profile depth for boreholes located in irrigated (triangles, 13 profiles), natural (squares, 4 profiles), and rain-fed (circles, 19 profiles) settings. Black symbols represent median values (Irrigated: Cl = 1400 kg/ha/m, NO₃-N = 140 kg/ha/m; Natural: Cl = 1600 kg/ha/m, NO₃-N = 9.4 kg/ha/m; Rain-fed: Cl = 16 kg/ha/m, NO₃-N = 53 kg/ha/m) (Table 1). Natural and rain-fed data are from previous studies [Scanlon *et al.*, 2008a, 2008b].

profile depths (kg/ha/m) for comparison among boreholes and ecosystem settings. Values for inventories, depth-weighted concentrations, and relationships between different ion species represent those for sampled intervals below the root zone (≥ 1 m depth), unless otherwise noted. The maximum impact of flushing salts on groundwater quality (e.g., S_{gw} , salt concentration in groundwater, mg/L) can be evaluated by mixing the entire inventory of salt (S_I) from the unsaturated zone with a specified saturated thickness of aquifer (the mixing zone, z_{mix}) with porosity n :

$$\frac{S_I}{n} \frac{1}{z_{mix}} = S_{gw} \quad (4)$$

For example, if a Cl inventory of 1000 kg/ha is transferred into a 10 m thick aquifer mixing zone with a porosity of 0.3 m³/m³, the increase in groundwater Cl concentration would be 33 mg/L. This approach provides an upper bound on the increase in groundwater salt concentration because only the salt, and not the associated water, is moved into the aquifer (equation (4)). Temporal changes in regional groundwater quality were evaluated using solute hydrographs from the TWDB database (www.twdb.state.tx.us). Median concentrations within selected regions of TDS, Cl, NO₃-N, and SO₄ were calculated for sequential multiyear intervals that span the SHP irrigation period.

3. Results and Discussion

[15] Profiles under irrigated agroecosystems have higher NO₃-N inventories (median 140 kg/ha/m) than those under natural ecosystems (median 9.4 kg/ha/m) and higher Cl inventories (median 1400 kg/ha/m) than those under rain-fed agroecosystems (16 kg/ha/m) (Figure 2 and Table 1) [Scanlon *et al.*, 2008b]. Irrigation water quality is one of the primary controls on variations in salt inventories beneath irrigated agroecosystems, as shown by the high correlation

($r = 0.94$) between Cl inventories and Cl in irrigation water (auxiliary material Table S1).¹

3.1. Impacts of Irrigation on Soil Water Quality in Area of High-Quality Irrigation Water

[16] The northernmost profiles (1 and 2) are located in the area of higher quality irrigation water (Cl: 8.6 and 83 mg/L) (Figure 1 and Table 2). Increased percolation related to irrigation mobilized Cl bulges that accumulated under natural ecosystems (Figures 3b, 3g, and 3l). These Cl bulges are associated with low NO₃-N concentrations, and peak Cl concentrations were displaced from 1.6 m (estimated from profile 16, which is a nearby profile drilled under a natural ecosystem) to 5.6 m (profile 1) and 15.6 m (profile 2). These natural Cl bulges required 9200–12,500 years to accumulate. Inventories of Cl, ClO₄, and SO₄ in the deeper bulges of profiles 1 and 2 are similar to those in profile 16, which represents the natural ecosystem (Figure 3 and Table 1). Pore water in the shallow parts of profiles 1 and 2 (3.7 and 6.1 m zones) is attributed to irrigation return flow as shown by associated high NO₃-N concentrations (Figures 3i and 3n). Chloride inventories in this zone are low (310 and 740 kg/ha/m; Table 1). Because ET is similar to desalinization with pure water evapotranspired, all the salts are concentrated in the small amount of water draining below the root zone. Chloride concentrations are used to estimate ET concentration factors (CF) because Cl is highly conservative and plant uptake is negligible. Maximum ET concentration factors, based on peak profile Cl concentration divided by mean Cl concentration in irrigation plus precipitation input, are similar in these two profiles (40 and 41) (CF_{Cl} , Table 3). The similarity in Cl concentration factors indicates that differences between Cl inventories in the two profiles reflect the order of magnitude difference in Cl input in irrigation water (Table 2). Concentration factors can also be estimated from the ratio of water input (I + P) to the average percolation rate and results in slightly lower values for these two profiles (26 and 39, CF_{Pe} , Table 3). The range in ET concentration factors suggests irrigation efficiencies (1–1/concentration factor) ranging from 96 to 98% with respect to percolation. Tracer data provide information on cumulative impacts of irrigation on subsurface water movement. However, the Cl bulge associated with irrigation in profile 2 suggests transient conditions that may reflect decreasing irrigation water quality with the large water table decline (26–81 m) that occurred at this site and/or changing percolation related to conversion from gravity fed irrigation with a mean application rate of 540 mm/year to a sprinkler system with a mean application rate of 280 mm/year [Scanlon *et al.*, 2010].

[17] Concentrations of ClO₄ and Cl are highly correlated in profiles 1 and 2 in the irrigation-impacted zones and in the deeper zones that reflect salt accumulation under natural ecosystems (auxiliary material Table S1). These data indicate that ClO₄ is behaving conservatively, similar to Cl. Mean NO₃-N concentrations are high in the irrigation-impacted zone (48 and 120 mg/L, Table 1) and low correlations with Cl may reflect additional NO₃-N inputs from fertilizers and possible mineralization and nitrification of soil organic nitrogen in the system. Bulges of SO₄ related to

¹Auxiliary materials are available in the HTML. doi:10.1029/2009WR003428.

Table 1. Profile Mean and Peak Concentrations and Inventories for Cl, ClO₄, NO₃-N, and SO₄ Below the Root Zone^a (≥1 m depth)

Setting Region	Profile	Interval (m)	Mean Concentration				Peak Concentration				Peak Depth				Inventory				
			Cl (mg/L)	ClO ₄ (μg/L)	NO ₃ -N (mg/L)	SO ₄ (mg/L)	Cl (mg/L)	ClO ₄ (μg/L)	NO ₃ -N (mg/L)	SO ₄ (mg/L)	Cl (m)	ClO ₄ (m)	NO ₃ -N (m)	SO ₄ (m)	Cl (kg/ha/m)	ClO ₄ (g/ha/m)	NO ₃ -N (kg/ha/m)	SO ₄ (kg/ha/m)	
SHP-N	1 (Pot07-03)	1.0-3.7	110	11	48	1600	170	17	80	2500	2.8	2.8	1.6	3.7	310	30	130	4200	
	2 (Hal08-01)	1.0-6.1	290	21	120	580	1500	120	440	1400	1.1	1.2	1.2	1.1	740	52	340	1300	
	3 (Ter05-03)	1.0-6.5	380	25	120	1000	1600	120	220	5700	1.6	1.6	1.3	1.3	910	65	270	2900	
	4 (Ter08-03)	1.0-4.3	720	28	81	1200	1800	75	210	3500	2.7	3.0	2.7	1.8	2100	82	230	2900	
	5 (Daw08-01)	1.0-6.1	970	32	55	1500	2100	70	93	3700	4.3	4.3	4.9	1.5	2400	81	130	3200	
	6 (Lub08-01)	1.0-14.6	540	13	71	370	1500	24	250	1800	1.8	1.1	1.5	1.3	1300	30	160	840	
	7 (Mar08-01)	1.0-4.9	1500	29	8	1600	2500	45	14	6700	2.7	2.7	3.0	1.2	3500	67	20	3200	
	8 (Mar08-02)	1.0-7.4	1700	30	42	1900	6400	130	180	12,000	1.4	1.4	1.8	1.2	3800	66	86	4100	
	9 (Ter05-04)	1.0-9.5	720	18	52	1100	2400	50	120	4100	2.8	2.8	2.8	1.6	1600	39	110	2400	
	10 (Mar08-03)	1.0-4.3	1900	49	150	2100	2900	78	240	5800	1.2	1.2	2.4	1.2	4400	110	400	4100	
	11 (Gal08-01)	1.0-7.9	650	54	67	1900	1200	94	140	8600	3.7	3.7	3.7	1.2	1300	110	140	3700	
	12 (Ter08-01)	1.0-12.2	940	37	76	1600	1600	63	150	3600	8.5	8.5	7.3	4.0	1200	49	98	2700	
	13 (Ter08-02)	1.0-6.5	670	33	77	680	1700	83	170	2600	5.5	5.5	5.5	4.9	1400	70	160	1500	
Median (S) ^b		720	30	71	1500	1800	75	170	4100	2.7	2.8	2.8	1.3	1600	67	140	2900		
Median (N + S) ^c		720	29	71	1500	1700	75	170	3700	2.7	2.8	2.7	1.3	1400	66	140	2900		
SHP-N	1 (Pot07-03)	3.7-18.0	400	11	9.1	320	1100	26	14	1600	5.6	5.6	4.6	4.6	740	20	16	600	
	2 (Hal08-01)	6.1-26.8	600	16	1.0	520	1100	27	7.3	2400	15.8	15.8	7.3	9.8	860	23	6.0	1500	
	16 ^d (Pot07-04)	1.0-14.6	670	17	12	1300	3000	41	17	19,000	1.6	1.3	4.6	1.3	1000	28	20	2000	
	17 ^e (Daw06-01)	1.0-8.4	2500	63	7.2	5400	4800	110	34	29,000	7.7	8.3	2.2	7.7	3400	83	8.8	6400	
	18 ^f (Lyn06-01)	1.0-29.0	890	21	1.6	1700	2300	47	8.3	6900	4.3	5.5	4.3	8.0	2200	36	4.2	5600	
	19 ^g (And05-02)	1.0-8.5	480	34	8.9	970	1300	62	25	2100	8.3	8.3	2.2	8.3	710	46	9.9	1300	
	Median (S) ^h		890	34	7.2	1700	2300	62	25	6900	7.7	8.3	2.2	8	2200	46	8.8	5600	
	Median (N + S) ^h		780	28	8.1	1500	2700	55	21	13,000	6.0	6.9	3.3	7.9	1600	41	9.4	3800	
	SHP-S	1 (Pot07-03)	3.7-18.0	400	11	9.1	320	1100	26	14	1600	5.6	5.6	4.6	4.6	740	20	16	600
		2 (Hal08-01)	6.1-26.8	600	16	1.0	520	1100	27	7.3	2400	15.8	15.8	7.3	9.8	860	23	6.0	1500
		16 ^d (Pot07-04)	1.0-14.6	670	17	12	1300	3000	41	17	19,000	1.6	1.3	4.6	1.3	1000	28	20	2000
		17 ^e (Daw06-01)	1.0-8.4	2500	63	7.2	5400	4800	110	34	29,000	7.7	8.3	2.2	7.7	3400	83	8.8	6400
		18 ^f (Lyn06-01)	1.0-29.0	890	21	1.6	1700	2300	47	8.3	6900	4.3	5.5	4.3	8.0	2200	36	4.2	5600
19 ^g (And05-02)		1.0-8.5	480	34	8.9	970	1300	62	25	2100	8.3	8.3	2.2	8.3	710	46	9.9	1300	
Median (S) ^h			890	34	7.2	1700	2300	62	25	6900	7.7	8.3	2.2	8	2200	46	8.8	5600	
Median (N + S) ^h			780	28	8.1	1500	2700	55	21	13,000	6.0	6.9	3.3	7.9	1600	41	9.4	3800	

^aRegion, regional location defined by groundwater 500 mg/L TDS contour (Figure 1); Profile, profile number and borehole designation in parentheses (Figure 1); Interval, borehole depth interval (profiles 1 and 2 have shallow zone impacted by irrigation and deeper zones reflecting natural conditions); Mean concentration, depth-weighted mean solute concentration below the root zone (≥1 m depth); Peak concentration, peak solute concentration; Peak depth, depth of peak concentration; Inventory, total solute mass below the root zone (≥1 m depth) normalized by borehole depth interval.

^bProfiles 3-13.

^cProfiles 1-13.

^dScanlon et al. [2008a].

^eScanlon et al. [2008b].

^fProfiles 17-19.

^gProfiles 16-19.

Table 2. Measured Solute Concentrations and Pearson's Correlation (r) Between Chloride and Other Constituents in Irrigation Water Applied at the Profile Locations^a

Profile	Cl (mg/L)	ClO ₄ (μg/L)	NO ₃ -N (mg/L)	SO ₄ (mg/L)	TDS (mg/L)
<i>SHP-N</i>					
1	8.6	0.4	0.1	51	360
2	83	2.2	4.8	54	610
<i>SHP-S</i>					
3	99	6.3	13	220	910
4	210	9.1	11	360	1400
5	350	11	9.3	300	1400
6	140	4.6	7.8	120	800
7	200	4.2	4.9	200	950
8	140	3.1	4.3	130	770
9	270	2.5	2.8	310	1200
10	790	23	15	950	3000
11	210	4.2	16	240	980
12	330	17	19	370	1500
13	150	10	9.9	160	910
	Cl (mg/L)	ClO ₄ (μg/L)	NO ₃ -N (mg/L)	SO ₄ (mg/L)	TDS (mg/L)
Median ^b	210	6.3	9.9	240	980
Median ^c	200	4.6	9.3	220	950
r (Cl) ^c	-	0.86	0.50	0.96	0.98

^aSHP-N and SHP-S, regions defined by groundwater 500 mg/L TDS contour (Figure 1). Profile, profile number (Figure 1).

^bProfiles 3–13.

^cProfiles 1–13.

the natural ecosystem in these profiles have not been displaced as deeply as Cl following increased irrigation percolation rates; therefore, mean concentrations and inventories in the irrigation impacted zones include some SO₄ related to the natural bulges, particularly in profile 1 (Figures 3j and 3o).

3.2. Impacts of Irrigation on Soil Water Quality in the Area of Poor Quality Irrigation Water

[18] Profiles in the SHP-S region have been irrigated with moderate to high salinity water (e.g., Cl: 99–790 mg/L) and NO₃-N (2.8–19 mg/L) (Table 2). Concentrations of ClO₄ and SO₄ in applied irrigation water at the sampled sites generally follow patterns similar to those of the other ions (Table 2 and auxiliary material Figure S1) and are highly correlated with Cl (ClO₄, $r = 0.86$; SO₄, $r = 0.96$). Profiles under irrigated agroecosystems in this region are characterized by large Cl bulges caused by evapotranspirative enrichment in the root zone (Figure 4 and auxiliary material Figures S2–S4). The range in Cl inventories in irrigation bulges (910–4400 kg/ha/m) is similar to that beneath natural ecosystems (710–3400 kg/ha/m) (Table 1). Total profile Cl inventories under irrigated agroecosystems (5000–24,000 kg/ha, auxiliary material Table S2) accumulated over 18–53 years; however, such bulges would require 3700–18,000 years (median 9400 years) to accumulate if Cl in bulk precipitation had been the only input, as in natural ecosystems (Table 3). These Cl inventories are highly correlated with Cl input from irrigation ($r = 0.94$), excluding profiles 7 and 8, which appear to be outliers. The Cl bulges from irrigation have peak concentrations near the root zone (1.2–1.8 m depth) in 4 of the 11 profiles (Table 1, Figure 4q, auxiliary material Figures S2–S4). Although KCl fertilizers can provide an additional source of Cl, as shown by *McMahon*

et al. [2006], landowners in this area did not report use of such fertilizers. Chloride concentration factors estimated from peak Cl concentrations relative to total ($I + P$) Cl input range from 12 to 42, excluding one outlier (110, profile 8) (Table 3). Similar concentration factors were calculated using percolation rates (7.6–38, Table 3). The total range in concentration factors corresponds to irrigation efficiencies of 87–98% (median 95%).

[19] Profiles under irrigated agroecosystems have large ClO₄ bulges, similar to Cl bulges. Peak ClO₄ concentrations are high (median 75 μg/L). Concentrations of ClO₄ and Cl are highly correlated within each profile (median $r = 0.98$) (auxiliary material Table S1), indicating that ClO₄ behaves conservatively. Concentrations of ClO₄ are generally highly correlated with NO₃-N ($r = 0.72 - 0.93$), with the exception of profiles 7, 11, and 12. Because NO₃ is more readily taken up by plants and reduced by microorganisms, high NO₃ concentrations in most profiles should inhibit ClO₄ losses to these processes.

[20] Profiles under irrigated agroecosystems are characterized by large NO₃-N inventories (median 140 kg/ha/m) (Figure 2 and Table 1). Sources of NO₃-N loading in irrigated cropland include fertilizers (median 34 kg/ha/a), irrigation water (median 30 kg/ha/a), and precipitation (~3 kg/ha/a) (Table 3). The median concentration of NO₃-N in irrigation water is 10 mg/L (Table 2). Mineralization and nitrification of soil organic nitrogen can also contribute to NO₃-N in the soil profile, as estimated in a previous study in this region (11–52 kg/ha), with higher values in finer grained soils [*Chua et al.*, 2003]; however, it is difficult to quantify this input.

[21] Average annual input of NO₃-N from irrigation water represents 45% (median) of total NO₃-N input to the system, including precipitation, irrigation, and fertilizers. Inventories of NO₃-N below the root zone (1 m) represent a large percentage of total profile NO₃-N (median 96%, Table 3). These NO₃-N inventories indicate large-scale leaching below the root zone (median 34%) of annual applied NO₃-N over the irrigation period (Table 3). Leaching rates are underestimated for some profiles that did not extend deep enough to sample the entire section impacted by irrigation return flow. However, leaching rates would be overestimated if subsurface mineralization and nitrification of SON contributes to the NO₃-N inventory. In contrast, *McMahon et al.* [2006] reported much lower leaching rates for profiles 14 and 15 (12–14% of applied NO₃-N). Peak NO₃-N concentrations below the root zone range from 14 to 250 mg/L (Table 1). Correlations between NO₃-N and Cl concentrations in different profiles are mostly high (median $r = 0.88$) (auxiliary material Table S1). High NO₃-N levels below the root zone may be related partly to fertilizer application timing such as 50% 3 weeks prior to and 50% 6 weeks after planting reported in studies by *Bronson et al.* [2006]. Recommendations for NO₃-N application rates from local agricultural experimental stations often do not account for NO₃-N input from irrigation water (median 30 kg/ha/a in this study), which is similar in magnitude to that from fertilizers (median 34 kg/ha/a).

[22] The SO₄ distributions in unsaturated zone profiles generally mimic those of Cl (Figure 4 and auxiliary material Figures S2–S4). Variations in SO₄ inventories are attributed to the range in SO₄ concentrations in irrigation water (Table 2). Landowners indicated that they did not apply

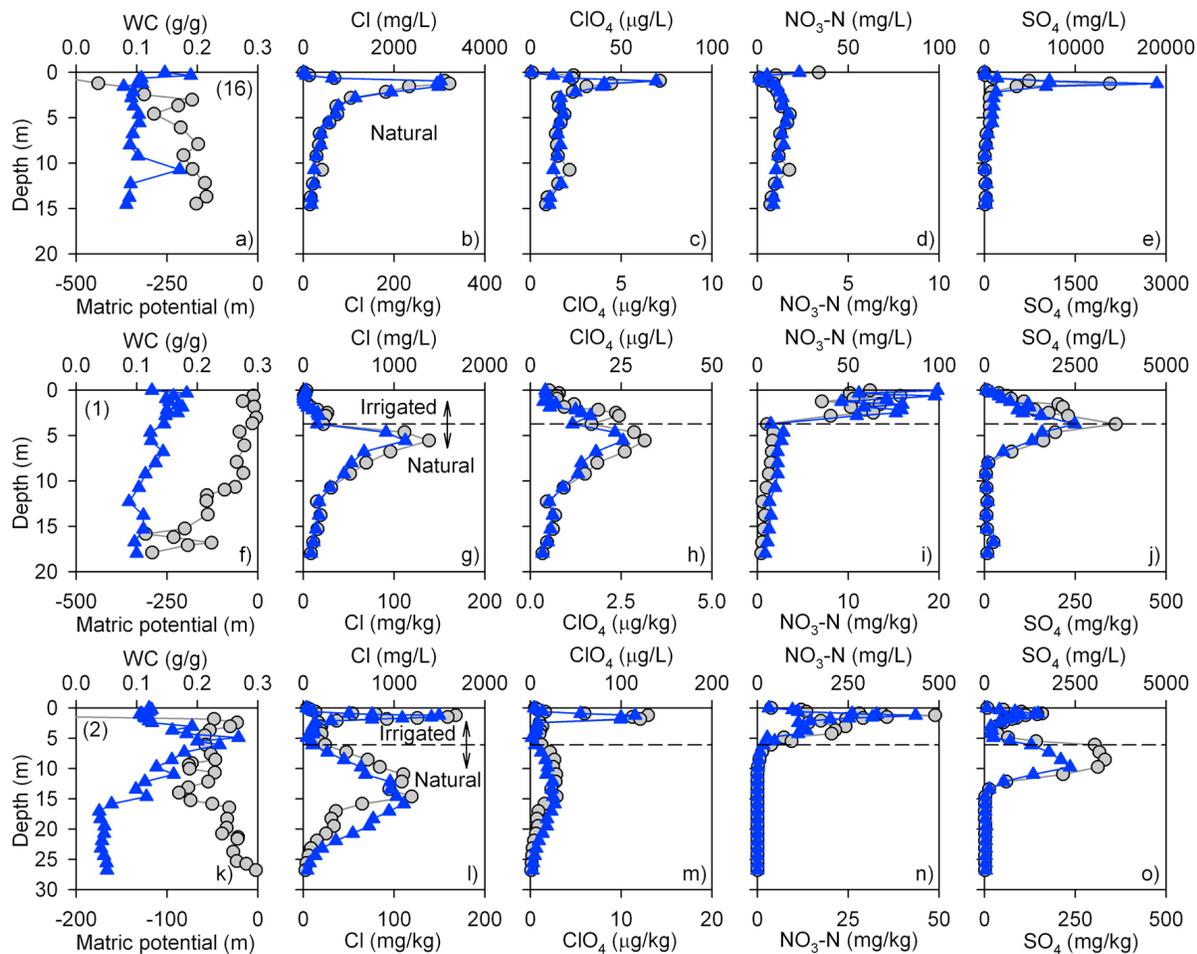


Figure 3. Profiles of water content (WC, blue triangles), matric potential (gray circles), and chloride (Cl), perchlorate (ClO_4), nitrate-N ($\text{NO}_3\text{-N}$), and sulfate (SO_4) concentrations for natural (16) and irrigated (1, 2) setting boreholes located in Pullman clay loam soils in the SHP-N region (Figure 1). Volumetric basis (mg/L or $\mu\text{g/L}$, blue triangles) and mass basis (mg/kg or $\mu\text{g/kg}$, gray circles) concentrations are shown. Horizontal dashed lines shown in profiles 1 and 2 indicate the depth intervals impacted by irrigation.

SO_4 . Peak SO_4 concentrations are high (median 4100 mg/L), and peak depths coincide with or lag behind Cl peak depths by up to 2.7 m , with the exception of profile 12 (4.5 m lag). Although SO_4 cycles can be much more complex than Cl cycles, with additional sources from fertilizers and gypsum and sinks from plant uptake, the general similarity between SO_4 and Cl profiles in irrigated sites indicates that SO_4 is behaving like Cl, with some sorption.

3.3. Potential Impact of Irrigation on Crop Production

[23] Increasing soil water salinity can negatively impact root water uptake in crops by reducing osmotic potential [Ayers et al. 1943; Homae et al., 2002]. Salinity tolerance varies among crops according to physiological factors [Flowers, 2004]. The general lack of salinity problems currently in the SHP is attributed to high salt tolerance of the dominant crop (cotton, electrical conductivity [EC] tolerance: 7.7 dS/m) [Ayers and Westcot, 1976; Ashraf, 2002]. The relationship between EC and Cl in groundwater in the SHP suggests that an EC of 7.7 dS/m corresponds to a Cl concentration of 1300 mg/L . Values of Cl in root-zone pore

water are generally $< 1300 \text{ mg/L}$; however, peak Cl concentrations are near the root in 4 of the 11 profiles in the sandier, southern part of the SHP. The salinity problem may be exacerbated in the future if less salt-tolerant crops are grown, e.g., wheat, EC 6.0 dS/m ; sorghum, EC 4.0 dS/m ; groundnut, EC 3.2 dS/m ; and corn, EC 1.7 dS/m [Ayers and Westcot, 1976]. Expansion of subsurface drip irrigation could also increase soil salinity problems if percolation rates are reduced, resulting in increased salt-concentration factors. Maintenance of drip irrigation systems also increases salt loading because of acids introduced to keep the lines clear.

[24] Increasing ClO_4 concentrations in soil water can result in higher ClO_4 concentrations in crops, which can bioaccumulate in the food chain and increase the ClO_4 exposure pathway to humans. Although cotton was the only crop grown in the sampled sites in the SHP and does not enter the food chain, measured ClO_4 concentrations in cotton leaves (1.1 , 2.6 , and 0.8 mg/kg of dry plant near profiles 2, 5, and 6) indicate that ClO_4 is taken up by crops. The corresponding bioconcentration factors (ratios of plant weight concentration to measured concentration in irrigation water ($\mu\text{g/kg}$)/ $\mu\text{g/L}$) are 500 , 240 , and 170 L/kg , respec-

Table 3. Estimated Solute Loading Rates for Irrigated Agroecosystem Profiles^a

Region	Profile	P (mm/a)	I (mm/a)	t _i (a)	Age _p (a)	Irrigation				SO ₄ (kg/ha/a)	Total NO ₃ -N ^b (kg/ha/a)	NO ₃ -N Inventory		Peak Cl ^c (mg/L)	Annual Cl (mg/L)	P _e ^d (mm/a)	t _{ir} (a)	CF _{Cl}	CF _{Pe}
						Cl (kg/ha/a)	ClO ₄ (g/ha/a)	N (kg/ha/a)	NO ₃ -N (kg/ha/a)			≥1 m (kg/ha)	Profile (%)						
SHP-N	1 (Pot07-03)	485	440	19	670	38	1.8	0.4	230	91	370	66	22	170	4.2	36	520	40	26
	2 (Hal08-01)	480	380	68	2900	320	8.4	18	200	110	1700	88	22	1500	37	22	1000	41	39
	3 (Ter05-03)	480	300	46	3700	300	19	39	660	59	1500	96	55	1600	38	25	280	42	31
SHP-S	4 (Ter08-03)	480	200	47	4800	420	18	22	720	92	740	97	17	1800	62	18	230	29	38
	5 (Daw08-01)	485	320	18	8500	1100	35	30	960	170	670	89	22	2100	140	57	110	15	14
	6 (Lub08-01)	475	380	53	13,000	530	17	30	460	120	2200	90	34	1500	62	55	190	24	16
SHP	7 (Mar08-01)	440	350	23	9400	700	15	17	700	37	77	52	9.0	2500	89	39	140	28	20
	8 (Mar08-02)	440	300	33	18,000	420	9.3	13	390	33	540	95	50	6400	57	48	150	110	15
	9 (Ter05-04)	455	300	45	12,000	810	7.5	8.4	930	56	960	96	38	2400	110	41	180	22	18
	10 (Mar08-03)	450	200	52	10,000	1600	46	30	1900	60	1300	97	41	2900	250	73	68	12	8.9
	11 (Gai08-01)	435	300	30	7600	630	13	48	720	85	930	100	37	1200	82	97	68	15	7.6
	12 (Ter08-01)	480	250	53	9500	830	43	48	930	84	1100	97	24	1600	110	86	33	15	8.5
	13 (Ter08-02)	435	300	53	6200	450	30	30	480	67	890	99	25	1700	61	33	170	28	22
	Median (S) ^e	455	300	46	9400	630	18	30	720	67	930	96	34	1800	82	48	150	23 ^f	16
	Median (N + S) ^g	475	300	46	8500	530	17	30	700	84	930	96	25	1700	62	41	170	26 ^f	18

^aRegion, regional location defined by groundwater 500 mg/L TDS contour (Figure 1); Profile, profile number and borehole designation in parentheses (Figure 1); P, mean annual precipitation (Prism Climate Group, www.prism.oregonstate.edu); I, mean annual irrigation (from landowner and agricultural research station records, auxiliary material); t_i, number of years irrigated [Scanlon et al., 2010]; Age_p, apparent Cl mass balance age assuming precipitation as the only Cl input; Irrigation, mean annual solute mass loading rates from irrigation water based on measured solute concentrations in irrigation water (Table 2) and irrigation amounts (I); Fertilizer NO₃-N, mean annual mass loading rates from fertilizers based on landowner estimates; Total NO₃-N, mean total annual NO₃-N mass loading rate, including precipitation, fertilizer, and irrigation inputs; NO₃-N Inventory ≥ 1 m, inventory below the root zone (≥ 1 m depth); NO₃-N Inventory Profile %, NO₃-N inventory in the entire profile; NO₃-N inventory in the entire profile; NO₃-N Inventory Ann. %, NO₃-N inventory below the root zone as a percentage of total NO₃-N applied to the profile over the irrigation period; Peak Cl, peak Cl concentration in the irrigated profile section; Ann. Cl, volume-weighted mean annual Cl concentration calculated as [(P_eC_f + IxC_f)/(P + I)]; P_e, percolation rate; t_{ir}, time lag for irrigation return flow to reach current water table depth following initial cultivation [Scanlon et al., 2010, equation (5)]; CF_{Cl}, concentration factor based on profile peak Cl concentration relative to annual Cl input in precipitation and irrigation [Peak Cl/Annual Cl]; CF_{Pe}, concentration factor based on percolation rate relative to precipitation and irrigation [(P + I) / P_e].

^bIncludes 3.0 kg/ha/a NO₃-N from precipitation based on data from NADP (~1980-2007).

^cIncludes ~0.30 mg/L Cl from precipitation based on data from NADP (~1980-2007).

^dScanlon et al. [2010], percolation rates based on velocity for profiles 1-9 and Cl mass balance for profiles 10-13.

^eProfiles 3-13.

^fExcludes profile 8.

^gProfiles 1-13.

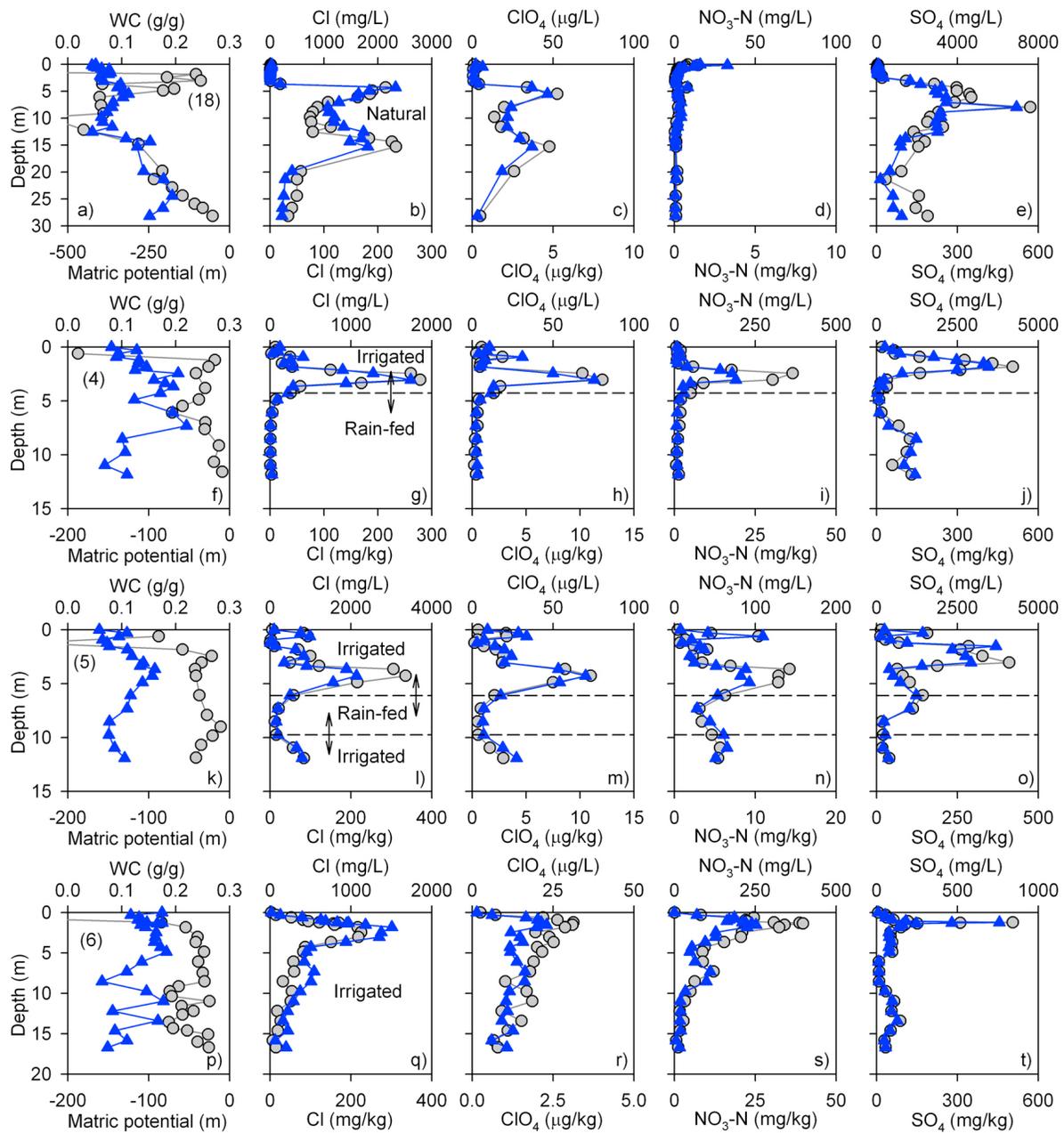


Figure 4. Profiles of water content (WC, blue triangles), matric potential (gray circles), and chloride (Cl), perchlorate (ClO_4), nitrate-N ($\text{NO}_3\text{-N}$), and sulfate (SO_4) concentrations for natural (18) and irrigated (4, 5, and 6) setting boreholes located in the SHP-S region (Figure 1). Volumetric basis (mg/L or $\mu\text{g/L}$, blue triangles) and mass basis (mg/kg or $\mu\text{g/kg}$, gray circles) concentrations are shown. Horizontal dashed lines shown in profiles 4 and 5 indicate the depth intervals impacted by different land uses.

tively. These values are similar to those found in a previous study for wheat stems and heads (215–230 L/kg) and alfalfa (380 L/kg) [Jackson *et al.*, 2005]. Although high correlations between ClO_4 and Cl indicate that ClO_4 is behaving conservatively, these levels of ClO_4 uptake in plants, while important for exposure pathways, should have a negligible impact on subsurface ClO_4 distribution [Tan *et al.*, 2004].

[25] One of the primary issues for crop production is maintaining low salt concentrations in the root zone. Approximately 77% of mean annual precipitation occurs during the growing season in the SHP (May through

October), when ET rates are highest and potential for flushing of accumulated salts is much lower. However, extreme events can flush salts from the root zone, as occurred following September–November 2004 precipitation (380 mm, 320% of 1971–2000 average; Prism Climate Group, www.prism.oregonstate.edu), when peak Cl and NO_3 concentrations were displaced from depths of 1–2 m in profile 15 [Gurdak *et al.*, 2007]. Some of the measured profiles show low Cl concentrations, with a chloride mass balance (CMB) age of ~ 4 years generally coincident with the 2004 event, e.g., profile 5 (350 mg/L, 3.1 m depth,

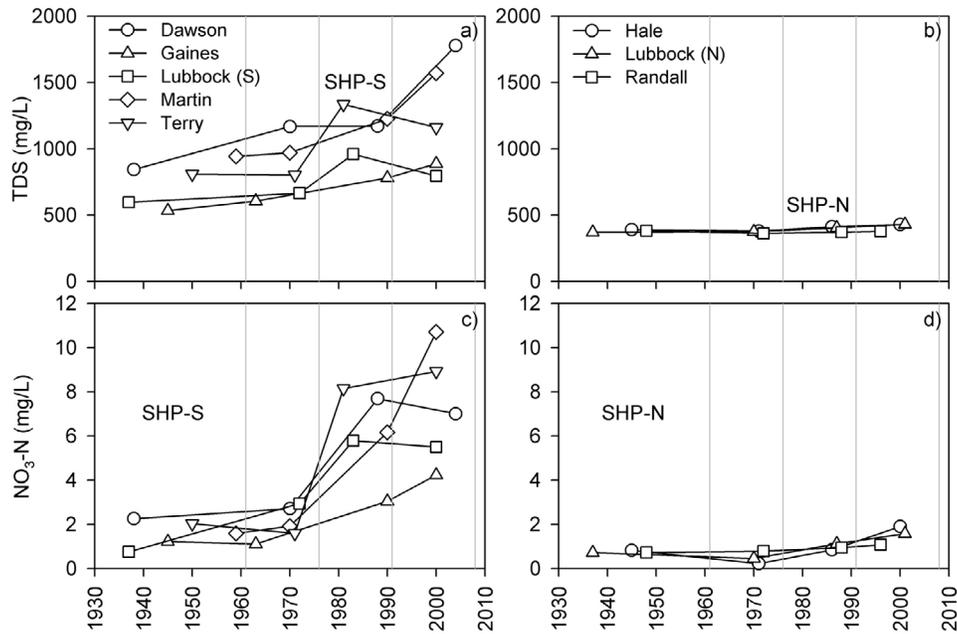


Figure 5. Temporal changes in groundwater: (a) total dissolved solids (TDS) in the SHP-S region, (b) TDS in the SHP-N region, (c) $\text{NO}_3\text{-N}$ in the SHP-S region, and (d) $\text{NO}_3\text{-N}$ in the SHP-N region. Points represent median values of TDS or $\text{NO}_3\text{-N}$ for median sample dates by county areas during the periods ≤ 1960 , 1961–1975, 1976–1990, and 1991–2008 demarked by vertical gray lines. Areas of Lubbock County lie in each region.

3.9 years) and profile 12 (140 mg/L, 3.0 m depth, 2.9 years) (Figure 4l and auxiliary material Figure S4). The increased frequency of such intense precipitation events, as predicted with climate change [Intergovernmental Panel on Climate Change, 2007], could further alleviate salinization in the root zone in the future but not necessarily salinization in deeper soil zones or in groundwater.

3.4. Impact of Irrigation on Groundwater Quality

[26] The large inventories of Cl, ClO_4 , NO_3 , and SO_4 currently accumulating under irrigated agroecosystems could further degrade groundwater if mobilized into the underlying aquifer. Groundwater in the SHP-N region is not considered vulnerable because groundwater quality is high and because of the long time (520–1000 years) for irrigation return flow to reach current water table depths (76–79 m) in this region, given the percolation rates (Table 3) [Scanlon *et al.*, 2010]. With continually declining water tables, it is unclear whether irrigation return flow will reach the water table until irrigation significantly decreases. The lack of recharge away from playas is supported by the absence of large-scale change in median groundwater quality in the SHP-N region (Figures 5b and 5d and auxiliary material Table S3).

[27] In the SHP-S region, groundwater solute hydrographs show large increases in salt concentrations, beginning in the 1960s and increasing through the 1980s and 1990s (Figures 5a and 5c and auxiliary material Table S3). Some areas show continued increases in salt concentrations through the 2000s, whereas others show a leveling off after the 1990s. Median concentrations calculated for county regions increased by ≤ 960 mg/L in TDS, ≤ 240 mg/L in Cl,

≤ 230 mg/L in SO_4 , and ≤ 9.4 mg/L in $\text{NO}_3\text{-N}$ (auxiliary material Table S3).

[28] Although degradation of groundwater quality is evident, the process responsible for mobilizing salts and nutrients into the aquifer is not. The most rapid pathway from land surface to the aquifer is through playas; however, unsaturated pore water beneath playas generally contains low salt concentrations [Wood and Sanford, 1995; Scanlon and Goldsmith, 1997]. Enwright and Hudak [2009] showed that groundwater $\text{NO}_3\text{-N}$ concentrations are lower near playas. Fryar *et al.* [2000] also showed that denitrification occurs beneath playas in the SHP. Gurdak *et al.* [2008] suggested seasonal ponding near leaky irrigation wells as a mechanism for depression-focused preferential flow and enhanced solute migration through the unsaturated zone of the High Plains aquifer. Although this process could contribute chemicals to the underlying aquifer, whether the mass transported by this process would be sufficient to explain the regional distribution of salts and nutrients in the aquifer is unclear.

[29] Inventories of Cl and SO_4 are high enough under natural ecosystems to account for the measured increases in these ions in groundwater since the 1960s. The salts originally in groundwater measured in the 1930s were attributed to upward movement of salts from the underlying Dockum aquifer. A previous study of rain-fed agroecosystems in the SHP-S region indicates that mobilizing the salt accumulation in profile 18 (natural ecosystem) would increase median groundwater concentrations of Cl by an additional 150 mg/L, SO_4 by 480 mg/L, and TDS by 900 mg/L, peaking approximately 100 years after initial cultivation [Scanlon *et al.*, 2009b]. Transport of these salts that accumulated under natural ecosystems by increased percolation under rain-fed agroecosystems should continue under irrigated agroeco-

systems because of the similarity in percolation rates beneath rain-fed and irrigated agroecosystems. The time lag between mobilization at the root zone and peak concentration in groundwater under rain-fed agroecosystems (~100 years) and similarity with irrigated agroecosystems suggests that these natural salts may account for the measured increases in salt concentrations in groundwater since the 1960s. The behavior of ClO_4 is similar to that of Cl , and mobilization and mixing of the inventory for profile 18 using equation (4) results in an increase in groundwater ClO_4 concentration of $14 \mu\text{g/L}$ [Scanlon *et al.*, 2008c]. Although $\text{NO}_3\text{-N}$ concentrations are low under natural ecosystems (median 7.2 mg/L) relative to irrigated agroecosystems (median 71 mg/L , Table 1), concentrations under natural ecosystems are much higher than background levels in the aquifer (~ $0.5 \text{ mg/L NO}_3\text{-N}$); therefore, flushing of this pore water could account for some of the early $\text{NO}_3\text{-N}$ increase in groundwater. In addition, flushing of $\text{NO}_3\text{-N}$ reservoirs created by mineralization and nitrification of SON related to initial cultivation under rain-fed agroecosystems and associated with the shallower portion of the natural salt bulge could increase groundwater $\text{NO}_3\text{-N}$ concentrations by up to 22 mg/L [Scanlon *et al.*, 2008b]. Most profiles under irrigated agroecosystems in this study indicate the unlikelihood that irrigation return flow has reached the aquifer because of long lag times (33–280 years, median 150 years, Table 3) for salts to transport from the root zone to the current water table depths. These time lags may be considered upper bounds because they are based on an initial water content of $0.13 \text{ m}^3/\text{m}^3$ measured in the natural profile (18) and do not take into account any increases in water content that might have occurred under rain-fed management. Groundwater quality is projected to decline much more in the future as the large measured salt and nutrient inventories under irrigated agroecosystems are mobilized into the aquifer, which is consistent with the findings of McMahon *et al.* [2006]. The timing of such increases in groundwater salinity is uncertain because soil water contents below these profiles have not been measured. Percolation/recharge rates estimated in this study are time integrated estimates; however, salt bulges in irrigation profiles suggest that either these rates may have decreased with improved irrigation technologies and/or salt bulges may reflect increases in salinity of irrigation water with declining water tables.

[30] The irrigated profile locations are considered representative of the regional system because the median aquifer saturated thickness (16 m) and TDS concentration (980 mg/L) of irrigation water applied at the profile locations are similar to regional values (16 m, 890 mg/L). If saturated thickness does not change from current values, mobilizing the measured irrigation profile salt inventories would increase groundwater concentrations of Cl by an additional 280 mg/L , ClO_4 by $8.5 \mu\text{g/L}$, $\text{NO}_3\text{-N}$ by 13 mg/L , and SO_4 by 360 mg/L (auxiliary material Table S4). If irrigation continues until aquifer saturated thickness is reduced to an estimated minimum value that can support irrigation (~6 m), mobilizing measured irrigation profile salt inventories would increase groundwater concentrations of Cl by 720 mg/L , ClO_4 by $21 \mu\text{g/L}$, $\text{NO}_3\text{-N}$ by 52 mg/L and SO_4 by 880 mg/L . Using the regional relationship between TDS and the sum of Cl and SO_4 in groundwater, the median TDS under the measured profiles would increase by 2200 mg/L .

3.5. Sustainable Irrigation Management With Respect to Water Quality

[31] A variety of approaches can be adopted to move from current unintended consequences on water quality to more sustainable practices. Basic information, such as irrigation application rates, irrigation water quality, and fertilizer application rates and any other salts applied to the system, needs to be monitored. From a water-quality perspective, it would be advisable to irrigate with more water to reduce salt buildup in the soil profile; however, this approach runs counter to the current water conservative irrigation practices that favor highly efficient irrigation technologies. Results of this study indicate that current irrigation practices are almost too efficient from a water-quality perspective, suggesting that investments in more efficient irrigation systems, such as subsurface drip systems, may be inappropriate. Additional irrigation applications during crop growth may not be as effective as applying irrigation during the nongrowing season to flush salts below the root zone. Intense precipitation events, such as those recorded in 2004, may also serve this purpose. Rotating between irrigated and rain-fed agriculture should improve water quality because salt loading to the system would be greatly reduced. However, the large economic investment associated with irrigation systems generally requires continuous use of such systems to ensure a return on their investment.

[32] Information on water quality, such as that provided by unsaturated zone profiles in this study, would be valuable to irrigators in developing best management practices related to irrigation. Monitoring salt loads to the system and quantifying existing unsaturated zone salt inventories to depths of 10–20 m would increase awareness of producers and agronomists to potential salinity problems. In addition, data on aquifer thickness and projected declines with further irrigation are essential for quantifying the assimilative capacity of the aquifer and potential impacts of salt mobilization into the aquifer.

[33] Nutrient management is much more complicated than salt management because NO_3 is continually added to the system and there are a variety of sources and sinks of NO_3 . Groundwater NO_3 should be considered a fertilizer resource and included in estimates of fertilizer application rates. In this study, $\text{NO}_3\text{-N}$ loads from irrigation water constituted 15–66% (median 45%) of total $\text{NO}_3\text{-N}$ applications in the SHP-S region (Table 3). In addition, estimates of mineralization and nitrification of SON should be included when determining appropriate fertilizer application rates, according to studies such as those conducted by Bronson *et al.* [2006]. Timing of fertilizer applications is critical for minimizing potential leakage. Split fertilizer applications designed to coincide with crop nutrient requirements should reduce NO_3 leaching in the system. Traditional soil testing for fertilizers is restricted to the upper 0.15- to 0.3-m zone; therefore, many agronomists and producers are unaware of the large levels of NO_3 leaching that is occurring below the root zone. Rotating crops with varying rooting depths and growing winter cover crops could also reduce NO_3 leaching in profiles.

4. Conclusions

[34] Stratified chemical inventories in thick unsaturated zones record impacts of past land-use changes on water and

salt balances as a result of predominantly piston-type flow. Quality of irrigation water is one of the dominant controls on variations in salt inventories under irrigated agroecosystems. Salt inventories in the unsaturated zone are low in the SHP-N region, where groundwater salinity is low (median Cl: 21 mg/L), the aquifer is thick (median predevelopment saturated thickness 45 m), and the water table is currently deep (median 63 m). In contrast, salt inventories in the unsaturated zone are much higher in the south, where groundwater salinity is high (median Cl 180 mg/L), the aquifer is thin (median 16 m), and the water table is currently shallow (median 25 m). Inventories of Cl under irrigated agroecosystems are highly correlated with Cl in irrigation water in this region.

[35] Large salt bulges in the SHP-S region with median inventories of Cl (1600 kg/ha/m), ClO₄ (67 g/ha/m), NO₃-N (140 kg/ha/m), and SO₄ (2900 kg/ha/m) beneath irrigated agroecosystems are attributed to evapoconcentration of input water (irrigation and precipitation) by factors of 12 to 42 for Cl and minimal flushing by percolation rates of 18 to 97 mm/a (median 48 mm/a). Crop ET is similar to desalination, removing pure water and concentrating all salts in the limited percolation water below the root zone. Chloride inventories in salt bulges under irrigated cropland are similar in range to those beneath natural ecosystems. Total profile Cl inventories under irrigated agroecosystems (5000–24,000 kg/ha) accumulated over 18–53 years but would require 3700–18,000 years to accumulate under natural ecosystems where precipitation is the only Cl input. Cl and ClO₄ are highly correlated in individual profiles (median $r = 0.98$), indicating essentially conservative behavior of ClO₄. High correlations between ClO₄ and NO₃-N in most profiles ($r = 0.72 - 0.93$) indicate that ClO₄ may be shielded from microbial processes by NO₃-N in the system. Large NO₃-N inventories below the root zone (median 930 kg/ha) in irrigated agroecosystems represent 96% (median) of total profile NO₃-N, indicating leaching of much of the NO₃-N. NO₃-N input from irrigation water (median 30 kg/ha/a) is similar to that from fertilizers (median 34 kg/ha/a) and should be considered in proposed NO₃-N application rates.

[36] Groundwater solute hydrographs show increases since the 1960s in median concentrations for county areas by ≤ 960 mg/L for TDS, ≤ 240 mg/L for Cl, ≤ 230 mg/L for SO₄, and 9.4 mg/L for NO₃-N. The most likely process for mobilizing these salts and nutrients is percolation/recharge beneath rain-fed and irrigated agroecosystems. These increases in salts and nutrients are attributed to flushing of salts and some nutrients that had accumulated under natural ecosystems and additional nutrients related to mineralization and nitrification of SON during initial cultivation. Most profiles under irrigated agroecosystems in this study indicate that it is unlikely that irrigation return flow has reached the aquifer. Transporting measured unsaturated zone inventories that accumulated under irrigated agroecosystems into an estimated minimum saturated aquifer thickness that could support irrigation (6 m) would increase TDS by an additional 2200 mg/L (median), Cl by 720 mg/L, ClO₄ by 21 μ g/L, SO₄ by 880 mg/L, and NO₃-N by 52 mg/L. Concentrations of NO₃-N under all but one irrigated profile site would exceed the MCL of 10 mg/L. Because the SHP aquifer is essentially a closed basin, with the primary discharge mechanism being irrigation pumpage, salts external from groundwater, such as those that accumulated beneath natural

ecosystems, provide a transient pulse into the aquifer. Nitrate is continuously added to the system, and NO₃-N concentrations in groundwater should continuously increase. Salts derived solely from groundwater and recycled through the system by irrigation water would increase groundwater concentrations linearly in proportion to the reduction in saturated thickness and assimilative capacity of the aquifer. Groundwater quality is projected to degrade much more in the future as the measured salt and nutrient inventories under irrigated agroecosystems are mobilized into the aquifer. Irrigation management should consider both water and salt balances for sustainable irrigation practices.

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