University of Nebraska - Lincoln
DigitalCommons@University of Nebraska - Lincoln

Papers in the Earth and Atmospheric Sciences | Earth and Atmospheric Sciences, Department of

1-1-2009

Inventories and Mobilization of Unsaturated Zone Sulfate, Fluoride, and Chloride Related to Land Use Change in Semiarid Regions, Southwestern United States and Australia

Bridget R. Scanlon
University of Texas at Austin

David A. Stonestrom
United States Geological Survey

Robert C. Reedy
University of Texas at Austin

Fred W. Leaney
CSIRO Land and Water, Glen Osmond, South Australia, Australia

John B. Gates
University of Nebraska - Lincoln, jgates2@unl.edu

See next page for additional authors

Follow this and additional works at: http://digitalcommons.unl.edu/geosciencefacpub

Part of the Earth Sciences Commons

Scanlon, Bridget R.; Stonestrom, David A.; Reedy, Robert C.; Leaney, Fred W.; Gates, John B.; and Cresswell, Richard G., "Inventories and Mobilization of Unsaturated Zone Sulfate, Fluoride, and Chloride Related to Land Use Change in Semiarid Regions, Southwestern United States and Australia" (2009). *Papers in the Earth and Atmospheric Sciences.* Paper 171.
http://digitalcommons.unl.edu/geosciencefacpub/171

This Article is brought to you for free and open access by the Earth and Atmospheric Sciences, Department of at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Papers in the Earth and Atmospheric Sciences by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Authors
Bridget R. Scanlon, David A. Stonestrom, Robert C. Reedy, Fred W. Leaney, John B. Gates, and Richard G. Cresswell

This article is available at DigitalCommons@University of Nebraska - Lincoln: http://digitalcommons.unl.edu/geosciencefacpub/171

WATER RESOURCES RESEARCH, VOL. 45, W00A18, doi:10.1029/2008WR006963, 2009

Click Here for Full Article

Inventories and mobilization of unsaturated zone sulfate, fluoride, and chloride related to land use change in semiarid regions, southwestern United States and Australia

Bridget R. Scanlon,[1] David A. Stonestrom,[2] Robert C. Reedy,[1] Fred W. Leaney,[3] John Gates,[1] and Richard G. Cresswell[4]

Received 29 February 2008; revised 31 October 2008; accepted 23 January 2009; published 13 May 2009.

[1] Unsaturated zone salt reservoirs are potentially mobilized by increased groundwater recharge as semiarid lands are cultivated. This study explores the amounts of pore water sulfate and fluoride relative to chloride in unsaturated zone profiles, evaluates their sources, estimates mobilization due to past land use change, and assesses the impacts on groundwater quality. Inventories of water-extractable chloride, sulfate, and fluoride were determined from borehole samples of soils and sediments collected beneath natural ecosystems ($N = 4$), nonirrigated ("rain-fed") croplands ($N = 18$), and irrigated croplands ($N = 6$) in the southwestern United States and in the Murray Basin, Australia. Natural ecosystems contain generally large sulfate inventories (7800–120,000 kg/ha) and lower fluoride inventories (630–3900 kg/ha) relative to chloride inventories (6600–41,000 kg/ha). Order-of-magnitude higher chloride concentrations in precipitation and generally longer accumulation times result in much larger chloride inventories in the Murray Basin than in the southwestern United States. Atmospheric deposition during the current dry interglacial climatic regime accounts for most of the measured sulfate in both U.S. and Australian regions. Fluoride inventories are greater than can be accounted for by atmospheric deposition in most cases, suggesting that fluoride may accumulate across glacial/interglacial climatic cycles. Chemical modeling indicates that fluorite controls fluoride mobility and suggests that water-extractable fluoride may include some fluoride from mineral dissolution. Increased groundwater drainage/recharge following land use change readily mobilized chloride. Sulfate displacement fronts matched or lagged chloride fronts by up to 4 m. In contrast, fluoride mobilization was minimal in all regions. Understanding linkages between salt inventories, increased recharge, and groundwater quality is important for quantifying impacts of anthropogenic activities on groundwater quality and is required for remediating salinity problems.

Citation: Scanlon, B. R., D. A. Stonestrom, R. C. Reedy, F. W. Leaney, J. Gates, and R. G. Cresswell (2009), Inventories and mobilization of unsaturated zone sulfate, fluoride, and chloride related to land use change in semiarid regions, southwestern United States and Australia, *Water Resour. Res.*, *45*, W00A18, doi:10.1029/2008WR006963.

1. Introduction

[2] Water availability, including water quantity and quality, is a critical issue in many semiarid regions. Many studies have shown that long-term drying under natural ecosystems has resulted in the build up of a reservoir of chloride in soils by evapotranspirative enrichment of infiltrated rainfall and associated dryfall in semiarid regions in the southwestern United States and Australia, mostly over the past 10,000 to 30,000 years [*Scanlon et al.*, 2007a]. Reservoirs of nitrate have also built up in many of the regions in the southwestern United States and in Africa from atmospheric deposition and from nitrogen fixation [*Walvoord et al.*, 2003; *Deans et al.*, 2005]. Land use change, specifically conversion from natural ecosystems to rain-fed (nonirrigated) agricultural ecosystems, has increased groundwater quantity through enhanced recharge. Documented changes in recharge include increases from ~0 to a median of 24 mm/a in the U.S. Southern High Plains [*Scanlon et al.*, 2007b], from ≤0.1 mm/a to >50 mm/a in the Australian Murray Basin [*Allison et al.*, 1990], and from regional estimates of 2 mm/a to 25 mm/a in Niger, Africa [*Favreau et al.*, 2009]. Increased recharge beneath rain-fed agriculture mobilizes chloride that previously had accumulated in the unsaturated zone, increasing chloride concentrations in underlying aquifers in these regions [*Scanlon et al.*, 2007a]. Increased recharge also raises water tables toward the land surface where groundwater can directly evaporate and salinize soils, causing dryland salinity. The cost of increased water quantity from enhanced recharge can

[1]Bureau of Economic Geology, Jackson School of Geosciences, University of Texas at Austin, Austin, Texas, USA.
[2]U.S. Geological Survey, Menlo Park, California, USA.
[3]CSIRO Land and Water, Glen Osmond, South Australia, Australia.
[4]CSIRO Land and Water, Indooroopilly, Queensland, Australia.

Copyright 2009 by the American Geophysical Union.
0043-1397/09/2008WR006963$09.00

be degraded soil water and groundwater quality from salts [*Scanlon et al.*, 2007a].

[3] Many previous studies have examined chloride because it is conservative and serves as a tracer of water movement. The chloride cycle is relatively simple. Chloride from atmospheric deposition (including dryfall) moves into the soil with infiltrating precipitation. Evapotranspiration causes chloride to build up in the soil because chloride is not taken up by plants and is nonvolatile. Chloride is extremely soluble and is rarely found in the solid phase. Chloride moves conservatively in liquid water throughout the hydrologic cycle. Nitrate has also been examined extensively in the southwestern United States and in Africa because it is an essential plant nutrient and a widespread contaminant of water resources [*Walvoord et al.*, 2003; *Deans et al.*, 2005; *Scanlon et al.*, 2008]. Sulfate, another major anion in atmospheric deposition, has been little studied even though it, like chloride, can have large-scale impacts on water quality. The sulfate cycle is more complex than the chloride cycle, because sulfate, like nitrate, has multiple sources and sinks, including biochemical reactions that alter valence states. High concentrations of sulfate can contribute to soil salinity and limit plant water uptake. Mobilization of sulfate to groundwater can negatively affect the quality of groundwater for human consumption and productivity of irrigated cropland.

[4] Fluoride is of great interest in semiarid regions, where high levels are common in groundwater. A micronutrient for mammals, fluoride has a narrow therapeutic range. In humans, values $<\sim 0.5$ mg/L are associated with dental caries, whereas values $\geq 1.5-4$ mg/L are associated with dental and skeletal fluorosis. The maximum contaminant level (MCL) established by the U.S. Environmental Protection Agency (EPA) is 4 mg/L. The corresponding maximum level set by the World Health Organization is 1.5 mg/L [*World Health Organization*, 2004]. A recent National Research Council panel recommended that the MCL for fluoride be lowered in the United States [*National Research Council*, 2006]. Water supplies (mostly groundwater) with concentrations of fluoride exceeding 1.5 mg/L affect $\sim$200 million people globally, including 70 million in India and 45 million in China [*Edmunds and Smedley*, 2005; *Amini et al.*, 2008]. Although fluoride is not known to be a plant nutrient, it is taken up by plants and can become toxic at high concentrations. High fluoride concentrations in irrigation water (e.g., 40 mg/L) have been found to reduce crop yields [*Muller et al.*, 1998]. Despite the importance of sulfate and fluoride to water quality, little is known about their sources, unsaturated zone inventories, or potential mobilization to underlying aquifers.

[5] Mobilization of salts can have large-scale impacts on groundwater quality. Anions are generally excluded from negatively charged mineral surfaces. While chloride is highly conservative and generally not subject to processes that retard its movement, sulfate and fluoride are potentially affected by chemical and biochemical reactions. In addition to mineral precipitation and dissolution, sulfate and fluoride are subject to reactions such as adsorption-desorption, ion exchange, and surface complexation, which are often collectively termed "sorption" because they are difficult to distinguish [e.g., *Fluhler et al.*, 1982; *Alloway*, 2005]. The solubility of salts considered in this study varies greatly, with halite (NaCl) being most soluble ($K_{sp} \approx 10^{1.6}$) [*Lide*, 1991], followed by gypsum ($CaSO_4 \cdot 2H_2O$; $K_{sp} \approx 10^{-4.6}$). [*Hem*, 1985] and fluorite (CaF_2; $K_{sp} \approx 10^{-10.58}$) [*Hem*, 1985]. Fluorite precipitation was found to control fluoride concentrations in Nigerian soils of northwest Africa [*Barbiero et al.*, 1995]. Low fluorite solubility results in saturation at $\sim$3 mg F/L in the presence of 10^{-3} mol Ca/L (40 mg Ca/L) [*Hem*, 1985]. *Clifford* [1999] determined the relative sorptivity of anions for activated alumina (pH 5.5–8.5), which serves as an analog for soils, to be

$$OH^- > H_2AsO_4^- > F^- > SO_4^{2-} \gg HCO_3^- > Cl^- > NO_3^- > Br^-$$

The high sorptivity of fluoride and sulfate relative to chloride can greatly reduce their mobilization through unsaturated media.

[6] Given the paucity of prior work on sulfate and fluoride and the complexities affecting their transport, a reconnaissance survey was indicated. The objectives of this study were thus to address the following questions: How much chloride, sulfate, and fluoride are stored in the unsaturated zone beneath natural ecosystems? What is the source of these anions (e.g., atmospheric, anthropogenic, lithogenic)? What is the relative mobility of the different anions (chloride, sulfate, and fluoride)? What impact does salt mobilization have on groundwater quality?

[7] These questions are addressed using data from soil cores from three different regions: (1) the Southern High Plains (SHP) of Texas, (2) the Amargosa Desert (AD) of Nevada, and (3) the Murray Basin (MB) of New South Wales and South Australia (Figure 1). Quantifying inventories of chloride, sulfate, and fluoride in unsaturated media is needed for predicting potential loading to underlying aquifers. If sulfate and fluoride are derived from atmospheric deposition, similar to chloride, then subsurface profiles of these salts should provide archives of long-term preindustrial atmospheric deposition. Anthropogenic activities add salt to the system through irrigation, fertilizer, and pesticide applications. The relative mobility of the different ions under increased recharge caused by land use change impacts the vulnerability of underlying aquifers to contamination.

2. Materials and Methods

2.1. Site Characteristics and History

[8] The Southern High Plains (75,000 km^2) region is located in Texas and New Mexico (Figure 1). General site characteristics and history are described by *Scanlon et al.* [2005, 2007b]. Mean annual precipitation ranges from 376 mm in the south (Midland, 1931–2005) to 501 mm in the north (Amarillo, 1947–2005). Clay content in surface soils (upper 1.5–2.0 m) ranges from 1 to 68% (mean 28%) on the basis of the SSURGO database [*U.S. Department of Agriculture*, 1995]. Mean clay content generally decreases from $\sim$36% in the northern 40% of the Southern High Plains to $\sim$23% in the south 60%. Native vegetation originally consisted of shortgrass prairie. Cultivation began in the late 1800s and early 1900s. Land use includes natural grasslands (33%) and shrublands (12%) used for grazing, rain-fed agriculture (42%) dominated by cotton production, irrigated agriculture (11%), and other (2%) (Figure 1) (1992 National

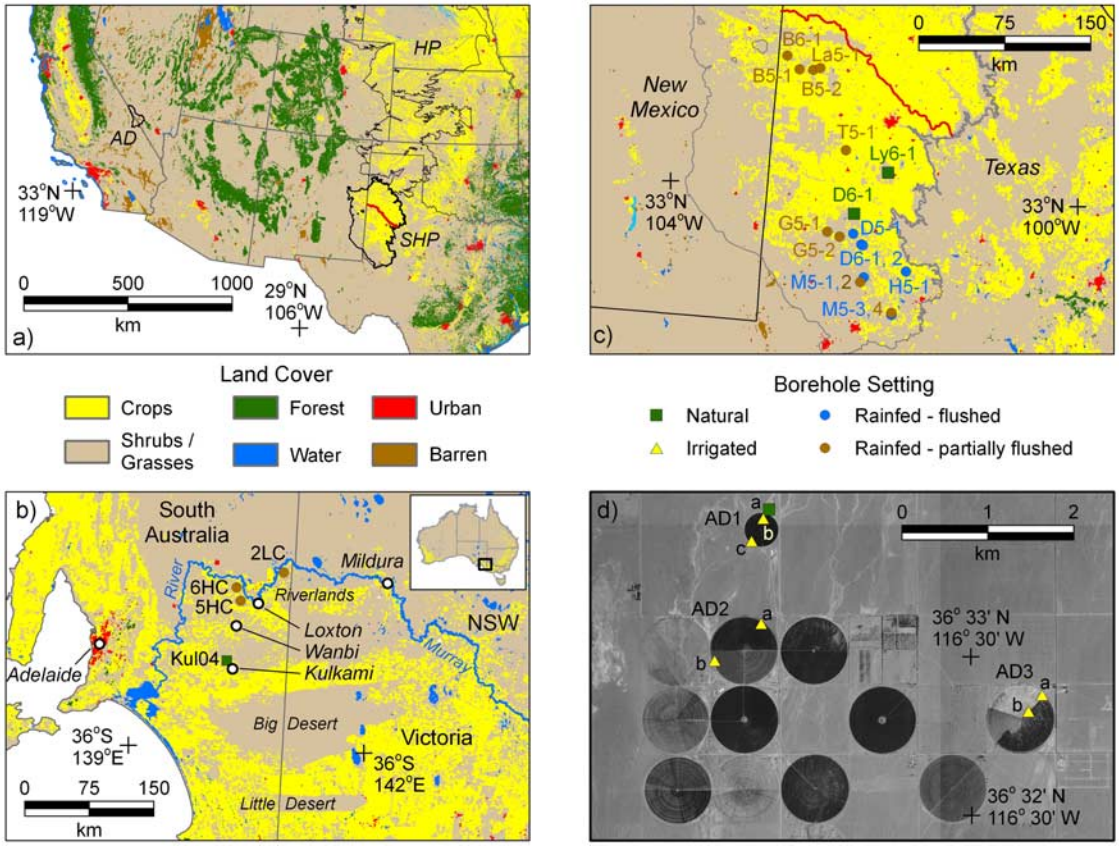

Figure 1. Generalized land use for (a) southwestern United States and (b) Murray Basin and detailed maps of (c) the Southern High Plains and (d) the Amargosa Desert regions. The High Plains (HP), Southern High Plains (SHP), and Amargosa Desert (AD) are delineated in the southwestern United States. Southern High Plains borehole designations are abbreviated to the least number of unambiguous characters (see Table 1 for unabbreviated borehole designations). The red line within the Texas portion of the Southern High Plains delimits the northern high-quality and the southern low-quality groundwater regions. The Murray Basin Riverlands sites are located in the northeast mallee area (boreholes 2LC, 5HC, and 6HC) and in the Kulkami site (Kul04). Generalized U.S. land cover is based on National Land Cover Data, 1992 [*Vogelmann et al.*, 2001]. Land use categories represent classification combinations: grassland (grassland/herbaceous), forest (deciduous, evergreen, and mixed forest), and crops (pasture/hay, row crops, small grains, and fallow). Generalized Australia land cover is based on Australian Collaborative Land Use Mapping Program data from the Australian Government Bureau of Rural Sciences (http://adl.brs.gov.au) using similar classification combinations.

Land Cover Data) [*Vogelmann et al.*, 2001]. The thickness of the unsaturated zone ranges from 0 to 134 m (median 37 m).

[9] The Amargosa Desert region (~3300 km^2 in area) is in the Mojave Desert, Nevada (Figure 1). Mean annual precipitation is 113 mm (1966–2001; Amargosa Farms). Aridic soils are developing on eolian-modified alluvial sands and gravels. Land cover includes mostly native vegetation (primarily creosote bush, *Larrea tridentata*, and saltbush, *Atriplex contertifolia*) and ≤3% irrigated agriculture (mostly alfalfa, various species). Irrigation applications range from 2.0 to 2.7 m/a at the sites studied. The thickness of the unsaturated zone is ~35 m in the area under cultivation, and exceeds 150 m elsewhere in the basin [*Kilroy*, 1991].

[10] The Murray Basin study region extends from the Big/Little Desert area to the Riverlands area, near the Murray River (Figure 1). Mean annual precipitation is ~500 mm/a in the Big Desert, ~370 mm/a in Kulkami, and ~260 mm/a in the Riverlands area [*Blackburn and McLeod*, 1983]. Soil texture ranges from deep sandy soils in dunes to more clayey soils in interdune areas in the Big and Little Deserts [*Leaney et al.*, 2003]. The Riverlands area consists of predominantly sandy loams with clays restricted to the floodplains of the Murray River [*Cook et al.*, 2004]. Native vegetation includes eucalyptus mallee vegetation that was replaced by crops and pasture in many regions from the early 1900s. The unsaturated zone thickness ranges from 0 to 70 m.

2.2. Chemical Measurements

[11] Detailed descriptions of methods for sample collection can be found in work by *Walker et al.* [1991], *Stonestrom et al.* [2003], *Cook et al.* [2004], and *Scanlon et al.* [2005, 2007b]. Boreholes in all regions were drilled without drilling fluid (Table 1). Soil cores from the Southern High Plains (2 natural, 15 rain-fed agriculture), the Amar-

gosa Desert (1 natural, 6 irrigated agriculture), and the Murray Basin (1 natural, 3 rain-fed agriculture) were analyzed in the laboratory for water-extractable concentrations of chloride, bromide, sulfate, and fluoride generally following procedures described by *Rhoades* [1982]. Double deionized water was added to the soils in a ~1:1 or 2:1 weight ratio, and samples were either shaken periodically for 24 h (Amargosa Desert sites) or shaken continuously in a reciprocal shaker for 4 h (Southern High Plains and Murray Basin sites). The samples were then centrifuged at 7000 rpm for 20 min and the supernatant was filtered to 0.2 μm. Soil samples from the Amargosa Desert region were previously analyzed for chloride and sulfate [*Stonestrom et al.*, 2003]; water extracts from the previous study were stored in poly sealed glass bottles at 20°C and were reanalyzed for chloride and sulfate and were also analyzed for bromide and fluoride. The chloride and sulfate data from the two sets of analyses are highly correlated (r^2 = 0.99 for both). The average absolute difference between analyses for chloride across 3.5 orders of magnitude is 5% and for sulfate across almost 3 orders of magnitude is 3% (auxiliary material, Figure S1).[1] In the Murray Basin, soil samples from a natural site at Kulkami (Kul04) were previously analyzed for chloride and sulfate [*Walker et al.*, 1991]. Soil samples from the Riverlands area were previously analyzed for chloride (5:1 dilution, reciprocal shaker for 3 h) [*Cook et al.*, 2004] and were reextracted and analyzed for chloride, bromide, sulfate, and fluoride in this study. Chloride concentrations from the two sets of analyses are highly correlated (r^2 = 0.95) and the average absolute difference between analyses is 14% (auxiliary material, Figure S2).

[12] Water-extractable concentrations of ions were measured in this study to evaluate potential mobilization resulting from increased water flux following land use change. Concentrations of ions in supernatant liquid were determined by ion chromatography (Dionex ICS 2000). Samples were oven dried at 105°C for 24 h to determine soil water content. Water-extractable ion concentrations are expressed on a mass basis as mg of ion per kg of dry soil (supernatant concentration times extraction ratio (g water/g soil) and divided by water density). Ion concentrations are also expressed as mg ion per L of pore water (mg/kg divided by gravimetric water content and multiplied by water density). Because of potential water loss during sample collection and processing, ionic concentrations on a mass basis (mg ion/kg dry soil) are considered more robust than ionic concentrations on a pore water volume basis (mg ion/L soil water). Salt inventories (kg/ha) were calculated by multiplying depth-weighted salt concentrations (mg/kg) by interval thickness (m), soil bulk density (kg/m^3), and unit conversion factor 10^4 (m^2/ha). Correlation coefficient (r) values were calculated on the basis of log-transformed mg/kg or kg/ha values.

[13] Mineral equilibrium controls on chloride, fluoride, and sulfur compounds were evaluated using the chemical equilibrium model PHREEQC (auxiliary material). Extraction water represents pore water, diluted, and possibly altered by induced desorption and mineral dissolution (auxiliary material, Tables S1–S5). To evaluate reproducibility of the entire extraction and analysis procedure, soil samples from the natural profiles in the Southern High Plains were reextracted and analyzed. Average absolute differences between analyses were 6% for chloride, 9% for sulfate, and 6% for fluoride (auxiliary material, Figure S3).

[14] Chloride and sulfate concentrations in precipitation (wet fallout) for the southwestern U.S. regions were obtained from the National Atmospheric Deposition Program (NADP) (http://nadp.sws.uiuc.edu/). In addition, precipitation samples collected in 2001 and 2002 from three NADP stations in or near the Southern High Plains were analyzed for chloride, sulfate, and fluoride in this study (auxiliary material, Tables S6a–S6c). Bulk precipitation samples (wet and dry fallout) collected at the Amargosa Desert from 1998 to 2001 were previously analyzed for chloride and sulfate and were analyzed for chloride, sulfate, and fluoride in this study (Table 2 and Table S7). Bulk precipitation samples at Loxton (Riverlands site) and Wanbi (Kulkami site) in the Murray Basin for 1 year from 1974 to 1975 were previously analyzed for chloride and sulfate [*Blackburn and McLeod*, 1983] (Figure 1 and Table 2). Bulk precipitation samples were also collected at a number of sites in Australia for 1 year from 2007 to 2008 and were analyzed for chloride, sulfate, and fluoride for this study. The Mildura site is closest to the Murray Basin region (Tables 2 and S8). In addition to salt inputs from precipitation, fertilizers and irrigation water provide additional inputs to cropland that were previously evaluated for the Amargosa Desert region [*Stonestrom et al.*, 2003].

[15] Sulfur isotopes were measured at the University of Ottawa on water extracts of selected samples from two profiles in the Southern High Plains to evaluate likely sulfate sources. Barium sulfate (precipitated from salt solutions by adding $BaCl_2$) was mixed with a tungsten oxide catalyst and flash combusted at 1800°C in a Costech Elemental Analyzer, producing cleaned SO_2 gas in a helium stream that flowed directly into a DeltaPlusXP Isotope Ratio Mass Spectrometer (ThermoFinnigan, Germany) [*Grassineau et al.*, 2001]. The data are reported relative to Canon Diablo Troilite with analytical precision of ~±0.2‰. Oxygen isotopes in sulfate were also measured at the University of Calgary and are reported relative to IAEA standards (NBS 127, IAEA SO5, and IAEA SO6).

2.3. Chloride Accumulation Times and Estimated Water Fluxes

[16] The time (t, years) required to accumulate chloride in profiles beneath native vegetation was estimated by dividing the cumulative mass of chloride in the profile by chloride input from bulk precipitation (P):

$$t = \frac{\sum Cl_{uz}\rho_b dz}{PCl_p} \tag{1}$$

where Cl_{uz} and Cl_p are chloride concentrations in unsaturated zone pore water (mg/kg) and in bulk precipitation (wet and dry fallout, mg/L), respectively, ρ_b is soil dry bulk density (kg/m^3), dz is depth interval, and P is precipitation (mm/a). This chloride accumulation time is used to estimate atmospheric deposition rates of sulfate and fluoride from subsurface salt inventories.

[1]Auxiliary materials are available in the HTML. doi:10.1029/2008WR006963.

Table 1. Borehole Depth and Water-Extractable Concentration Data for Chloride, Sulfate, and Fluoride[a]

Setting Area	Borehole	Total Depth (m)	Chloride Flush Depth (m)	Sulfate Flush Depth (m)	Total Depth Interval									Flushed Depth Interval (≥1 m)								
					Cl mg/kg	Cl mg/L	Cl kg/ha	SO_4 mg/kg	SO_4 mg/L	SO_4 kg/ha	F mg/kg	F mg/L	F kg/ha	Cl mg/kg	Cl mg/L	Cl kg/ha	SO_4 mg/kg	SO_4 mg/L	SO_4 kg/ha	F mg/kg	F mg/L	F kg/ha
										Natural												
SHP	Daw06-01	8.3	-	-	200	2,300	27,000	580	7,700	77,000	7.5	87	990	-	-	-	-	-	-	-	-	-
SHP	Lyn06-01	29.0	-	-	91	860	41,000	270	2,500	120,000	8.5	80	3,900	-	-	-	-	-	-	-	-	-
AD	AD1a	14.2	-	-	29	660	6,600	63	1,300	14,000	2.8	63	630	-	-	-	-	-	-	-	-	-
MB	Kul04	6.8	-	-	280	6,400	31,000	72	1,600	7,800	-	-	-	-	-	-	-	-	-	-	-	-
										Rain Fed												
SHP	Daw05-01	4.0	>4.0	>4.0	0.5	4.8	32	17	150	1,100	6.0	51	390	0.51	4.4	25	21	190	1,000	7.4	61	360
SHP	Daw06-02	9.2	>9.2	>9.2	0.4	3.7	55	24	210	3,500	7.1	68	1,000	0.38	3.5	50	26	230	3,400	7.2	66	950
SHP	Daw06-03	7.9	>7.9	>7.9	0.8	9.4	100	15	150	1,900	5.1	54	650	0.79	8.4	88	17	170	1,900	5.7	59	630
SHP	How05-01	6.2	>6.2	4.0	0.7	5.3	64	41	300	4,000	8.7	66	860	0.69	5.3	57	23	180	1,600	10	76	840
SHP	Mar05-01	7.5	>7.5	>7.5	0.5	3.8	58	10	79	1,200	8.5	68	1,000	0.52	4.1	55	12	88	1,200	9.6	75	1,000
SHP	Mar05-03	6.5	>6.5	>6.5	0.6	4.3	60	10	71	1,100	5.1	35	530	0.62	4.7	55	12	79	1,000	5.5	37	490
SHP	Bai05-01	11.4	7.7	3.4	26	280	4,700	270	2,600	49,000	8.3	77	1,500	1.0	5.3	110	19	170	930	10	92	1,200
SHP	Bai05-02	6.0	2.8	2.2	37	350	3,600	230	1,800	22,000	8.9	72	880	2.4	19	83	28	220	1,100	10	82	350
SHP	Bai06-01	4.7	2.5	2.5	12	90	880	460	3,300	34,000	5.4	44	400	1.8	16	54	44	410	2,000	6.3	56	190
SHP	Gai05-01	5.0	1.6	1.6	76	460	6,000	300	1,800	24,000	7.2	50	570	5.4	41	78	32	270	960	9.8	74	140
SHP	Gai05-02	10.7	8.9	6.5	19	110	3,200	460	5,000	79,000	7.1	75	1,200	0.82	8.2	110	30	360	3,500	8.4	93	1,100
SHP	Lam05-01	8.5	3.4	2.8	75	740	10,000	250	2,200	34,000	6.1	50	830	3.3	20	160	40	330	2,000	8.7	63	430
SHP	Mar05-02	8.9	2.2	2.2	48	550	6,800	120	1,400	17,000	4.5	50	650	3.8	34	94	29	320	1,200	5.1	52	120
SHP	Mar05-04	4.5	3.4	4.5	8.0	80	580	38	390	2,700	5.4	56	390	2.5	21	110	38	390	2,700	6.0	63	260
SHP	Ter05-01	7.1	5.9	3.4	4.0	38	450	180	1,400	20,000	9.5	76	1,100	1.4	10	110	48	380	2,900	11	83	910
MB	2LC	17.0	-	-	1,000	11,000	270,000	650	7,000	170,000	1.0	10	270	-	-	-	-	-	-	-	-	-
MB	5HC	13.0	3.8	3.8	1,300	12,000	270,000	590	5,100	120,000	5.8	69	1,200	91	1,200	4,400	53	640	2,400	9.1	120	440
MB	6HC	17.0	7.8	7.8	590	6,100	160,000	290	2,800	77,000	4.5	51	1,200	10	150	1,100	3.3	160	130	5.2	68	580
										Irrigated												
AD	AD1b	12.0	5.9	5.9	87	770	17,000	150	1,100	28,000	3.4	37	660	13	110	1,100	130	1,100	8,900	5.3	51	430
AD	AD1c	14.4	11.1	11.1	20	97	4,500	29	210	6,600	3.4	37	760	2.9	26	500	19	180	3,200	3.6	36	550
AD	AD2a	9.8	6.4	6.4	3.6	35	560	22	220	3,500	4.3	48	670	1.4	24	130	10	190	940	4.1	58	380
AD	AD2b	9.7	>9.7	>9.7	7.9	84	1,200	51	510	7,900	5.0	63	780	8.0	87	1,100	51	520	7,300	4.6	60	640
AD	AD3a	14.5	9.9	9.9	23	150	5,300	71	540	17,000	2.0	25	470	4.9	52	690	41	380	5,900	2.0	24	290
AD	AD3b	16.0	>16.0	>16.0	3.9	38	1,000	70	580	18,000	3.4	28	880	3.8	37	910	11	91	2,500	3.6	29	860

[a]Boreholes are located in the southern High Plains (SHP), Amargosa Desert (AD), and Murray Basin (MB) study areas. SHP boreholes "xxx05-xx" were sampled in May–June 2005, and boreholes "xxx06-xx" were sampled in February 2006 except Lyn06-01 (sampled July 2006). AD boreholes were sampled in February 2001. MB boreholes were sampled in early 2003 except Kul04 (sampled August 1987). Total depth interval values represent the entire sampled profile. Flushed depth intervals represent the portion of the borehole that has been flushed with respect to either chloride or sulfate resulting from conversion from natural to agricultural land use. Flushed depth interval fluoride values are calculated for the chloride-flushed intervals. Values with units of mg/kg and mg/L represent averages, and values in kg/ha represent inventories for the specified depth interval. Concentration and inventory values are depth-weighted on the basis of sample depth intervals and are rounded to two significant digits after calculation. Profiles AD1a, AD1b, and AD1c are equivalent to AFCA1, AFCA2, and AFCA3; profiles AD2a and AD2b are equivalent to AFCA4 and AFCA5; profiles AD3a and AD3b are equivalent to AFPL1 and AFPL2, respectively, in the work by *Stonestrom et al.* [2003].

Table 2. Precipitation or Irrigation Amount and Chloride, Sulfate, and Fluoride Concentrations in Precipitation Measured in the Study Areas[a]

Study Area	Location	Date	Amount (mm)	Cl (mg/L)	SO_4 (mg/L)	F (μg/L)	Cl (kg/ha/a)	SO_4 (kg/ha/a)	F (g/ha/a)
SHP	MNWR	1985–2007	189–1123 (433)	0.06–0.19 (0.12)	0.78–1.67 (1.22)	3.54–4.21[b] (3.86)[b]	0.23–0.83 (0.57)	2.18–9.86 (6.03)	16.6–19.0[b] (17.8)[b]
AD	Amargosa Farms	1998–2001	82–234 (145)	0.42–0.81 (0.49)	1.02–2.25 (1.52)	5.80–20.7 (12.1)	0.48–0.99 (0.77)	1.62–3.26 (2.40)	13.6–21.3 (17.1)
		1971–2000	113	0.49[c]	1.52[c]	12.1[c]	0.55[d]	1.72[d]	13.7[d]
		1974	2000–2700[e]	6.6	26	-	132–178	520–702	-
		2001	2000–2700[e]	6.9	26	230	138–186	520–702	4600–6210
MB	Riverlands	1974–1975	260	3.3	1.71	-	8.6	4.1	-
	Kulkami	1974–1975	370	3.8	1.20	-	14	4.4	-
	Mildura	2007–2008	143	4.13	1.48	17.0	5.91	2.11	24.3

[a]Values represent annual precipitation-weighted ranges (separated by en dashes), period of record precipitation-weighted averages (in parentheses), or single reported measurements.
[b]Fluoride concentrations and deposition rates for 2001 and 2002 (auxiliary material, Table S6a).
[c]Concentrations for 1998–2001 (auxiliary material, Table S7).
[d]Estimated deposition rates using precipitation-weighted average 1998–2001 concentrations.
[e]Irrigation amounts at Amargosa Desert (AD) site.

[17] Previous studies have estimated drainage rates below the root zone or recharge to groundwater using either the chloride front displacement (CFD) method [*Walker et al.*, 1991] or the chloride mass balance (CMB) method [*Allison and Hughes*, 1983]. Correspondence between drainage/recharge rates from these two methods indicates piston-type flow and complete displacement of chloride through the unsaturated zone. Drainage (D) or recharge (R) rates based on the CFD method are estimated by multiplying the apparent displacement velocity of the chloride front (equivalent to the top of the chloride bulge) (v_{cf}) by the average volumetric water content in the flushed (wetted, w) zone ($\bar{\theta}_w$) [*Walker et al.*, 1991]:

$$D = R = v_{cf}\,\bar{\theta}_w = \frac{(z_2 - z_1)}{(t_2 - t_1)}\,\bar{\theta}_w \tag{2}$$

where the depth of the chloride front under native vegetation is z_1 and under cropland is z_2 and the time interval ($t_2 - t_1$) represents the time since cultivation began.

[18] According to the CMB method, chloride input (precipitation, P, multiplied by chloride concentration in bulk precipitation, Cl_p) equals chloride output (drainage or recharge rate, D or R, multiplied by chloride concentration in unsaturated zone pore water, Cl_{uz}):

$$P\mathrm{Cl}_p = D\mathrm{Cl}_{uz} \quad \text{or} \quad R\mathrm{Cl}_{uz}, \qquad D = R = \frac{P \times \mathrm{Cl}_p}{\mathrm{Cl}_{uz}} \tag{3}$$

If chloride is added to the system in irrigation water or fertilizer, the extra water and solute are accounted for as additional terms in the numerator of equation (3) [*Stonestrom et al.*, 2003].

2.4. Estimating Potential Impact of Salt Mobilization on Groundwater Quality

[19] Movement of salt inventories into the underlying aquifer should degrade groundwater quality; however, the effect should be transient as the salt moves through the system. Maximum impacts of flushing salts on groundwater quality (e.g., Cl_{gw}) can be evaluated by moving the entire inventory of salt (e.g., Cl_{inv}) from the unsaturated zone into a specified saturated thickness of aquifer (the mixing zone, z_{mix}) with porosity n:

$$\frac{\mathrm{Cl}_{inv}}{n}\,\frac{1}{z_{mix}} = \mathrm{Cl}_{gw} \tag{4}$$

If a chloride inventory of 1000 kg/ha is transferred into a 15 m thick aquifer mixing zone with a porosity of 0.3 m^3/m^3, the resultant groundwater chloride concentration would be 22 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)).

[20] An analytical approach was developed by *Cook et al.* [1993] to estimate the time lag and groundwater concentrations from mobilizing salts and water into a prespecified mixing zone in an aquifer [*Leaney et al.*, 2003]. The unsaturated zone salt profiles in this model are represented by a step increase in concentration with low concentrations

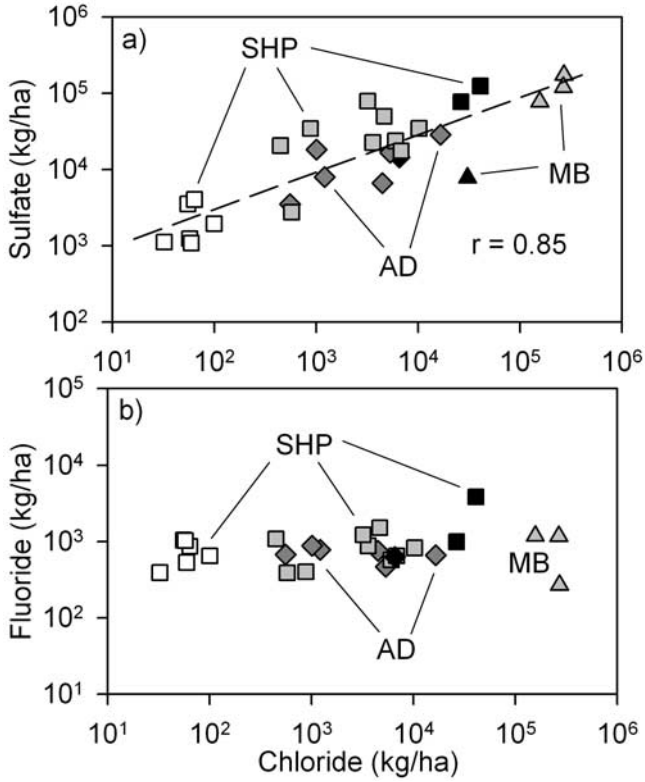

Figure 2. Inventories of (a) sulfate versus chloride and (b) fluoride versus chloride for sampled boreholes beneath natural ecosystems (solid black symbols), rain-fed agriculture (solid light gray and open symbols), and irrigated agriculture (solid dark gray symbols). Solid light gray symbols represent partially flushed profiles. Open symbols represent completely flushed profiles. Southern High Plains (SHP), squares; Amargosa Desert (AD), diamonds; Murray Basin (MB), triangles; r is the correlation coefficient.

near the land surface representing the flushed zone underlain by high concentrations representing precultivation solutes, typical of profiles in the Murray Basin. The analysis was modified to account for bulge-shaped profiles typical of the southwestern United States by including low concentrations at the base of the profile and specifying the thickness and concentrations associated with the bulge. Details of the modified analysis are given in the auxiliary material.

3. Results and Discussion

[21] The results from all profiles can be found in Table 1 and in Figures S4–S7 in the auxiliary material.

3.1. Unsaturated Zone Salt Reservoirs Beneath Natural Ecosystems

[22] Profiles beneath natural ecosystems have large, but variable, chloride and sulfate inventories and generally much lower fluoride inventories (Figure 2 and Table 1). Total chloride inventories range from 6600 to 41,000 kg/ha. In the Murray Basin region, the chloride inventory in the Kulkami profile (KUL04: 31,000 kg/ha) is generally at the low end of the range of inventories in other profiles in the Kulkami area (7 profiles: 57,000–140,000 kg/ha [*Jolly et al.*, 1990]). These other profiles are not detailed in this paper because sulfate was not measured and samples were not available for reextraction. The low chloride inventory in the Amargosa Desert region (AD1a: 6600 kg/ha) reflects a shorter accumulation time of ~12,000 years relative to accumulation times of 17,000 and 29,000 years in the Southern High Plains profiles (Table 3) [*Stonestrom et al.*, 2003]. Chloride inventories are normalized by profile depth to account for variations in profile depth. Normalized chloride inventories are highest in the Murray Basin region (Kul04, 4500 kg/ha/m) and lowest in the Amargosa Desert region (460 kg/ha/m) (auxiliary material, Figure S8).

[23] Vertical chloride profiles are also variable among regions. Profiles in the southwestern United States are generally bulge shaped, typified by profile AD1a in the Amargosa Desert, with a peak concentration of 2900 mg/L near the base of the root zone (1.6 m depth, Figure 3d). One of the Southern High Plains profiles (Lyn06-01) is double peaked (2300 mg/L, 4.3 m; 1800, 15.3 m, Figure 3a), whereas the other profile (Daw06-01) may not have extended deep enough to show the base of the bulge (8.3 m) (Figure 4a). Chloride profiles in the Murray Basin differ from those in the southwestern United States in that concentrations generally increase to a maximum and remain high with depth [*Jolly et al.*, 1989; *Walker et al.*, 1991]. The Kul04 profile in this study shows only increasing concentrations throughout the profile (peak 13,000 mg/L) and may not have extended deep enough for concentrations to plateau (Figure 3g). In contrast, many of the other natural profiles in the Kulkami area have peak concentrations of 11,000–16,000 mg/L at depths of 3.3–10.3 m, below which concentrations remained high to the base of the profiles (Figure 5). The different shapes of the chloride profiles are attributed to variable water fluxes resulting from distinct paleoclimate histories; in the southwestern United States, downward water flux occurred during late Pleistocene pluvials or earlier (~10,000–30,000 years ago) followed by upward water flux during most of the Holocene [*Scanlon et al.*, 2003], whereas in the Murray Basin, low downward water fluxes and semiarid conditions prevailed for up to ~30,000 years [*Cook et al.*, 2004].

[24] Total sulfate inventories range from 7800 to 120,000 kg/ha and are correlated with chloride inventories ($r = 0.85$, Figure 2a). Sulfate inventories are generally similar to chloride inventories on a molar basis, with sulfate/chloride ratios of 0.8 to 1.1, with the exception of the Murray Basin profile (Kul04), where the sulfate inventory is one tenth the chloride inventory. Sulfate inventories normalized by profile depth range from 1000 to 9300 kg/ha/m; lowest in Murray Basin and highest in the Southern High Plains (auxiliary material, Figure S4). The shapes of sulfate profiles (Figures 3b, 3e, and 3h) are generally similar to those of chloride profiles (Figures 3a, 3d, and 3g). Peak sulfate concentrations range from 1000 to 6600 mg/L at depths of 4.5 to 8.0 m.

[25] Total fluoride inventories range from 630 to 3900 kg/ha and are not correlated with chloride inventories (Figure 2b and Table 1). Fluoride inventories are much lower than chloride inventories on a molar basis, with fluoride/chloride ratios of 0.1 to 0.2. Fluoride inventories normalized by profile depths range from 44 to 130 kg/ha/m

Table 3. Annual Precipitation, Chloride in Precipitation, Chloride Mass Balance Age, Measured Profile Inventories of Sulfate and Fluoride, and Estimated and Measured Sulfate and Fluoride Concentrations in Precipitation[a]

Study Area	Location	P (mm/a)	Cl_p (mg/L)	CMB Age (years)	SO_4 Inventory (kg/ha)	Estimated SO_{4p} (mg/L)	Measured SO_{4p} (mg/L)	F Inventory (kg/ha)	Estimated F_p (μg/L)	Measured F_p (μg/L)
SHP	Daw06-01	444	0.34	17,000	77,000	1.58[b]	0.78–1.67	1000	13.2	3.54–4.21
SHP	Lyn06-01	514	0.27	29,000	124,000	0.83	0.78–1.67	3900	26.2	3.54–4.21
AD	AD1a	113	0.49	12,000	14,000	1.03	1.02–2.25	630	46.5	5.80–20.7
MB	Kul04	370	3.8	2,000	7,800	1.05	1.20	NA		
MB	2LC	260	3.3	28,000	172,000	2.36	1.71	270	3.71	17

[a] P is precipitation, Cl_p is chloride in precipitation, CMB is chloride mass balance, SO_{4p} is sulfate concentration in precipitation, and F_p is fluoride concentration in precipitation. Estimated concentrations in (bulk) precipitation are calculated from the inventory divided by the CMB age and by 0.01 for units conversion. Measured chloride, sulfate, and fluoride concentrations for the SHP area are for wet deposition only, while remaining sites include both wet and dry (bulk) precipitation. NA means not available.

[b] Upper 5.9 m with corresponding CMB age of 11,000 years.

(auxiliary material, Figure S4). Fluoride profiles are generally bulge shaped with a narrow range in peak concentrations from 196 to 205 mg/L at depths of 1.1 to 3.7 m (Figures 3c and 3f). Fluoride bulges tend to be more spread out than chloride or sulfate bulges (Figure 3).

3.2. Sources of Salts

3.2.1. Chloride Sources and Accumulation Times

[26] Previous studies have shown that chloride accumulations in unsaturated zones of semiarid regions result from evapotranspirative concentration of chloride from bulk precipitation (precipitation and dry fallout) [*Phillips*, 1994; *Cook et al.*, 2001]. Ratios of chloride to bromide in the high chloride zones of profiles beneath natural ecosystems range from 120 to 260 in the Southern High Plains, 90 to 300 in the Amargosa Desert, and 190 to 280 in the Murray Basin, and are generally consistent with an atmospheric deposition source [*Davis et al.*, 1998].

[27] In the Southern High Plains region, the time required to accumulate chloride beneath natural ecosystems is 17,000 and 29,000 years (equation (1) and Table 3). The double-peaked chloride profile in Lyn06-01 (Figure 3a) includes a shallow bulge representing ~10,000 years of accumulation to 10.7 m depth, which generally corresponds to the transition from Pleistocene to Holocene conditions in semiarid regions throughout the southwestern United States [*Phillips*, 1994; *Scanlon et al.*, 2003]. The deeper peak indicates that late Pleistocene climatic conditions were insufficiently wet to flush preexisting chloride from the unsaturated zone.

[28] In the Amargosa Desert region, the accumulation time for the AD1a chloride profile under the natural ecosystem (Figure 3d) is ~12,000 years, generally coincident with the Pleistocene-Holocene transition [*Stonestrom et al.*, 2003]. Irrigation applications (2.0–2.7 m/a) are the primary chloride source in profiles beneath irrigated fields (132–186 kg/ha/a) relative to much smaller input from precipitation (0.55 kg/ha/a) (Table 2). Liquid fertilizer applied to field 2 in 1991 corresponds to coincident peaks in chloride, sulfate, and nitrate at the base of the AD2a profile (Figure 6) [*Stonestrom et al.*, 2003; *Scanlon et al.*, 2005].

[29] In the Murray Basin region, extremely high chloride concentrations in profiles beneath natural ecosystems are attributed to high chloride concentrations in bulk precipitation, which are about an order of magnitude higher than in the southwestern United States (Table 2) [*Simpson and Herczeg*, 1994]. Approximately half of the chloride in atmospheric deposition in the Murray Basin is attributed to resuspended continental dust [*Simpson and Herczeg*, 1994]. The time required to accumulate chloride in the Kul04 profile is ~2000 years on the basis of precipitation and chloride in precipitation (Tables 2 and 3); however, this profile does not extend deep enough to sample the full extent of the chloride accumulation (Figure 3g). In contrast, the chloride accumulation time in the 2LC profile is 28,000 years on the basis of precipitation and chloride in precipitation in Riverlands (Tables 2 and 3). Previous studies suggest that semiarid conditions have persisted over the last 30,000 years in Murray Basin [*Herczeg et al.*, 2001]. Chloride concentrations in bulk precipitation from 1974 to

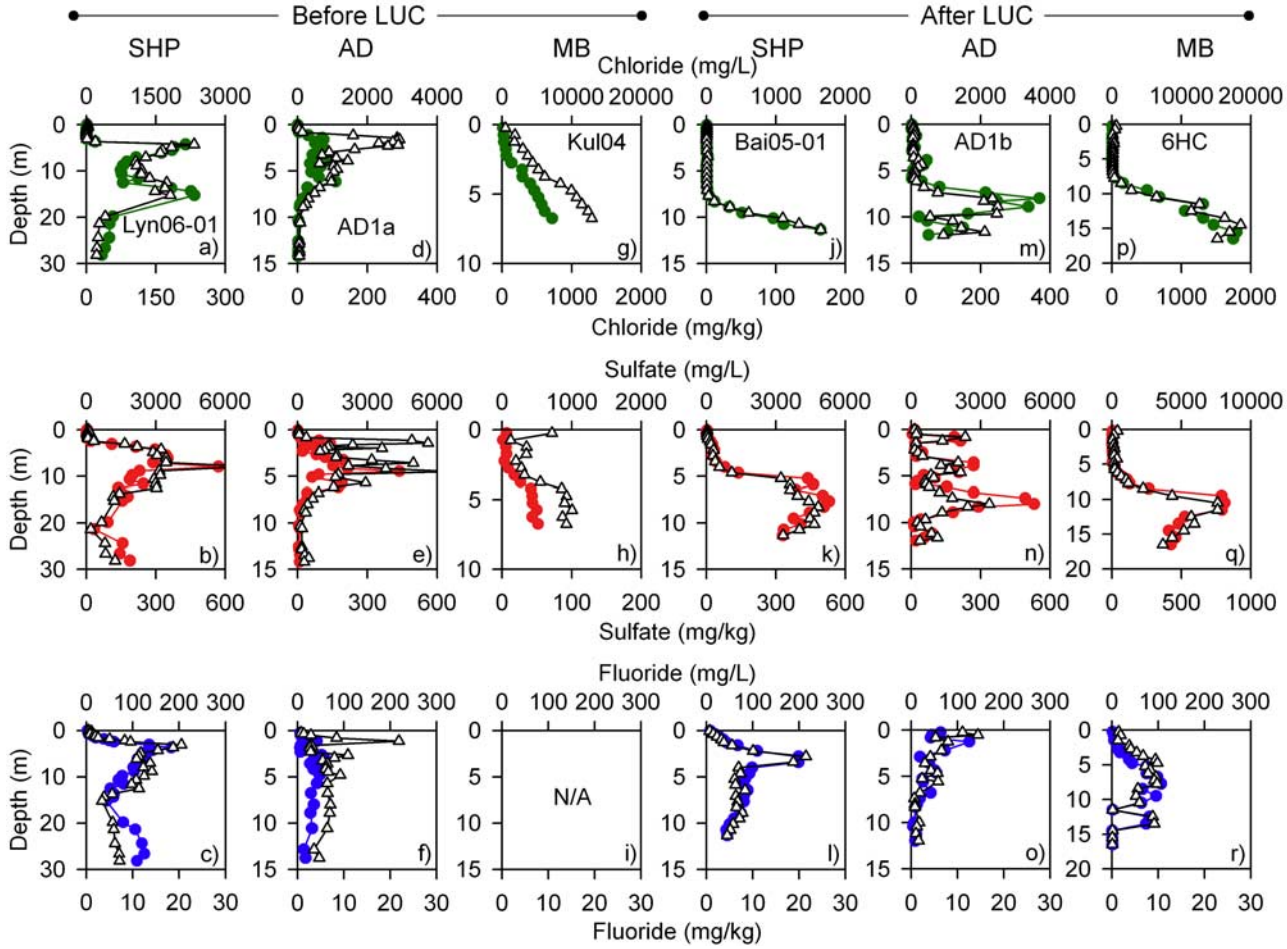

Figure 3. Representative chloride, sulfate, and fluoride profiles in (a–i) natural ecosystems and (j–l, p–r) rain-fed and (m–o) irrigated agricultural ecosystems. Values are shown for mg/L (triangles) and mg/kg (circles). LUC, land use change; SHP, Southern High Plains; AD, Amargosa Desert; MB, Murray Basin.

1975 (3.3–3.8 mg/L) are similar to those from the Mildura station sampled in 2007–2008 (mean 4.1 mg/L) (Table 2).

3.2.2. Sulfate Sources

[30] Sulfate can be derived from atmospheric deposition sources (wet and dry fallout), anthropogenic sources (industrial fallout, fertilizer, or irrigation water), and sedimentary lithogenic sources (gypsum, anhydrite, pyrite). Naturally occurring atmospheric sulfate is derived from marine sources (from sea spray and oxidation of biogenic sulfur-containing volatiles, particularly dimethyl sulfide), volcanic sources (from post emission oxidation of SO_2 and H_2S), and terrestrial aquatic sources (from oxidation of H_2S emitted by anaerobic wetlands) [*Chivas et al.*, 1991].

[31] Total inventories of sulfate and chloride are highly correlated (r = 0.85) in profiles beneath natural ecosystems (Figure 2a). Inventories of sulfate can be used with chloride accumulation times to estimate long-term sulfate deposition rates, assuming all sulfate is derived from atmospheric deposition and that there are no sinks for sulfate.

[32] In the Southern High Plains, very high sulfate concentrations toward the base of one of the natural profiles (Daw06-01; peak 47,300 mg/L; 7.7 m depth, Figure 4) is attributed to dissolution of gypsum, which was visually identified in the sediments at this depth. High correlations (r = 0.93, 0.85) between sulfate and chloride concentrations in the shallower reaches of this profile (Daw06-01, <5.9 m depth) and throughout the Lyn06-01 natural profile, respectively, suggest that sulfate was mostly derived from atmospheric deposition. Estimated sulfate in precipitation from the sulfate inventory is 1.58 mg/L for Daw06-01 and 0.83 mg/L for Lyn06-01 (Table 3). These estimated con-

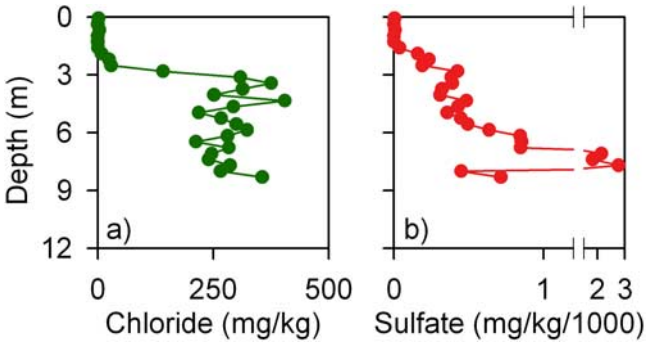

Figure 4. Profiles of chloride and sulfate at a natural site in the Southern High Plains (borehole Daw06-01) showing atmospheric sulfate (≤5.9 m) and lithogenic sulfate (>5.9 m).

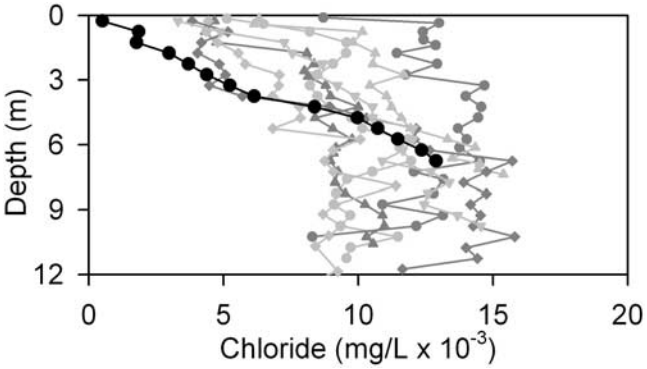

Figure 5. Chloride profile for the Kul04 borehole (black curve) compared with seven other chloride profiles under natural ecosystems (Kul20–Kul26) in the Kulkami region [*Jolly et al.*, 1990].

centrations in precipitation overlap the current sulfate wet deposition rates from the NADP Muleshoe Station (0.78 to 1.67 mg/L, Tables 2 and 3). Sulfate data from Greenland ice cores indicate that recent wet deposition increased by a factor of two and dry deposition by a factor of five compared with preindustrial rates in northerly latitudes [*Fischer et al.*, 1998]. The salt bulges in the Southern High Plains, and other arid sites are mostly preindustrial sulfate, providing a window into long-term atmospheric sulfate deposition rates in semiarid temperate latitudes.

[33] Sulfur and oxygen isotopes can be used to help evaluate sulfate sources and transformations [*Krouse and Mayer*, 2000]. For example, sulfate derived from deep brines and Paleozoic evaporite-rich confining units underlying the Southern High Plains are isotopically much heavier than sulfate derived from atmospheric deposition [*Nativ and Smith*, 1987; *Wood and Jones*, 1990]. Values of sulfate δ^{34}S and δ^{18}O measured in the Daw06-01 and Gai05-02 profiles ranged from 9.7 to 11.3‰ and from 4.6 to 7.5‰, respectively, fairly close to sulfate in geographically relevant (and relatively pristine) atmospheric deposition (Figure 7 and Table S9). The isotopic compositions of sulfate in the gypsum-containing sediments at depth are similar to those elsewhere in the profile, suggesting a common, originally atmospheric source.

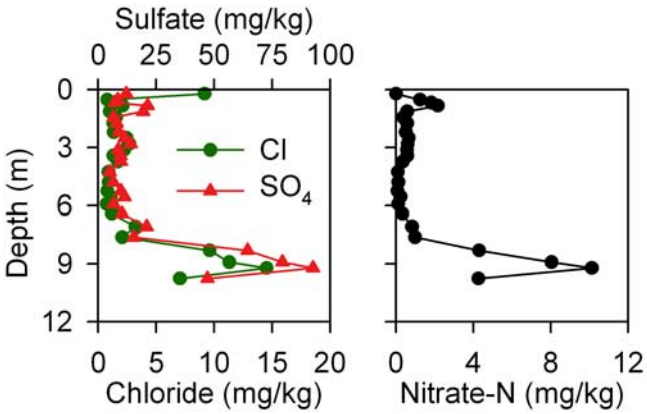

Figure 6. Profiles showing mobilization of chloride, sulfate, and nitrate in borehole AD2a at the Amargosa Desert site.

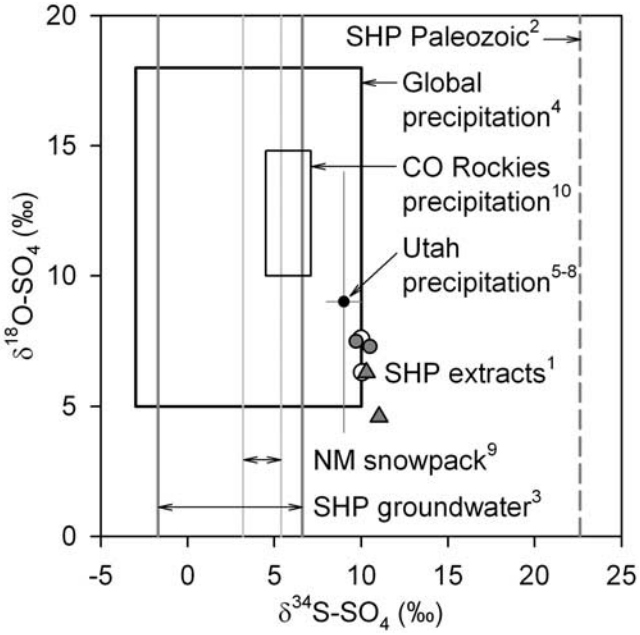

Figure 7. Sulfur and oxygen isotopes of sulfate for shallow (open symbols) and deep (solid gray symbols) unsaturated zone samples from Daw06-01 (circles) and Gai05-02 (triangles) profiles in the Southern High Plains (data in auxiliary material, Table S9). Superscripts refer to the following work: 1, this study; 2, *Wood and Jones* [1990]; 3, *Nativ* [1988]; 4, *Krouse and Mayer* [2000]; 5, *Grey and Jensen* [1972]; 6, *Gat and Gonfiantini* [1981]; 7, *Holt et al.* [1982]; 8, *Novak et al.* [2007]; 9, *Mast et al.* [2001]; 10, M. A. Mast, unpublished data, 1993–1999. Colorado Rockies, rain plus snow, 1993–1999, N = 15.

[34] In the Amargosa Desert, the natural profile (AD1a) is characterized by high correlation between sulfate and chloride (r = 0.88). The sulfate inventory results in estimated sulfate concentrations in precipitation of 1.0 mg/L, which is at the low end of the range of measured sulfate concentrations in bulk precipitation (wet and dry fallout; 1.02–2.25 mg/L), suggesting that here too atmospheric deposition was the dominant source (Tables 2 and 3).

[35] In the Murray Basin, previous studies attributed groundwater sulfate to atmospheric deposition and mineralization of organic sulfur in the soil on the basis of higher sulfate/chloride ratios relative to seawater (>0.14) and S and O isotopes of sulfate [*Dogramaci et al.*, 2001]. The unsaturated zone profiles that represent the natural system in this study show high correlations between sulfate and chloride (Kul04: r = 0.91, 2LC: r = 0.92). The much higher sulfate inventory in the 2LC profile (170,000 kg/ha) relative to the Kul04 profile (7800 kg/ha) is attributed to longer accumulation time (28,000 years) in clayey soils in the 2LC profile relative to the accumulation time (2000 years) in the sandier Kul04 profile (Tables 1 and 3). The estimated annual sulfate concentrations in precipitation are 1.05 and 2.36 mg/L on the basis of sulfate inventories and chloride accumulation times (Table 3). These concentrations are similar to measurements of wet and dry deposition (sulfate: 1.20 and 1.71 mg/L) (Table 3).

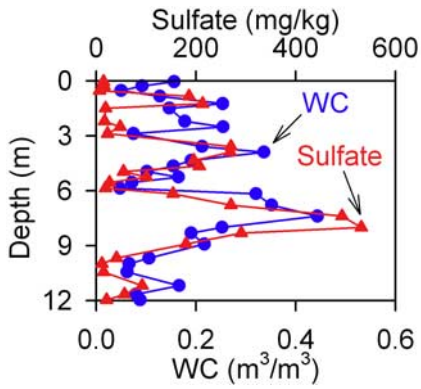

Figure 8. Sulfate concentration and water content (WC) profiles for borehole AD1b (irrigated agriculture) at the Amargosa Desert site showing correlation between peaks.

[36] Beneath cropland in all study regions, sulfate concentrations are generally higher than those estimated from current atmospheric deposition in the chloride flushed section of the profiles. These higher sulfate concentrations could reflect incomplete flushing of precultivation sulfate and/or input of sulfate from irrigation water and/or fertilizers. In the Southern High Plains, the dominant fertilizer is urea-ammonium nitrate [*Bronson et al.*, 2006]. Because sulfate generally is not added to soils in this region, high residual sulfate concentrations in the chloride flushed sections of these profiles (mean 12–48 mg/kg for 15 profiles) are attributed to incomplete flushing of precultivation sulfate (Table 1).

[37] Irrigated cropland in the Amargosa Desert region is characterized by preirrigation sulfate near the base of profiles in field 1 (Figure 3n). High residual sulfate in the chloride flushed section of this field is attributed to incomplete flushing of preirrigation sulfate in finer textured soils, as shown by high correlation (r = 0.81, $\geq$ 1 m depth) between sulfate and water content in profile AD1b (Figure 8). Preirrigation sulfate and chloride reservoirs have been displaced from profiles in irrigated fields 2 and 3. Sulfate and chloride concentrations in profiles in field 2 are highly correlated (r = 0.85 and 0.97). The high concentrations correspond to nitrate peaks at depth that are attributed to application of concentrated fertilizer when the field was returned to production in 1992 [*Stonestrom et al.*, 2003]. Peaks in chloride and sulfate occur at the same depths along with nitrate peaks (Figure 6). In field 3, high sulfate (up to 980 and 10,200 mg/L, AD3a, AD3b) in the shallow subsurface ($\leq$2.5 m) is related to gypsum addition at rates of 300–500 kg/ha/a (auxiliary material, Figure S7). The profile near the center of field 3 (AD3b) had uniformly low solutes at greater depths, indicating complete flushing to at least 16 m. In contrast, the profile near the edge of field 3 (AD3a) had coincident deep peaks of chloride, sulfate, and nitrate at a depth of $\sim$11 m, just above a cemented layer, suggesting lateral flow along this low-permeability layer [*Stonestrom et al.*, 2003].

3.2.3. Fluoride Sources

[38] Potential sources for fluoride include atmospheric deposition, mineral weathering, pesticides, and impurities in fertilizers (particularly phosphate fertilizers). Fluoride in atmospheric deposition is derived from sea spray, terrestrial dust, and volcanic sources. Fluorite (CaF_2) and apatite [$Ca_5(PO_4)_3$(OH, F, Cl)] are common accessory minerals in the source rocks of sediments. In the Southern High Plains region, the two natural fluoride profiles are generally bulge shaped, with peak concentrations in a narrow range from 16.1 to 18.3 mg/kg (3.1 to 3.7 m depth). Fluoride concentrations in precipitation from the Muleshoe NADP station in the Southern High Plains range from 3.5 to 4.2 μg/L on the basis of samples from 2001 and 2002 (auxiliary material, Table S6a). If the fluoride beneath natural ecosystems in the Southern High Plains was derived entirely from atmospheric deposition, the calculated fluoride concentrations in bulk precipitation would range from 13.2 to 26.2 μg/L (Table 3). Current measured fluoride concentrations in precipitation are about a factor of 3 to 7 times less than that required to account for the measured fluoride inventory during the most recent cycle of chloride accumulation.

[39] Similarly, in the Amargosa Desert region, the measured range of fluoride concentration in bulk precipitation (5.80–20.7 μg/L, Table 2) is much less than the fluoride concentration estimated from the fluoride inventory in the profile (46.5 μg/L, Table 3). These results suggest that atmospheric deposition is insufficient to account for the measured subsurface fluoride accumulation during the time represented by chloride accumulation. PHREEQC results indicate that extracts were supersaturated with respect to sesquioxides, phyllosilicates, and fluorite (auxiliary material, Tables S2–S5). This suggests atmospherically derived fluoride accumulates in the profile as secondary fluorite and by exchanging with surface-exposed hydroxyl units (e.g., on phyllosilicates) during chloride accumulation. The imbalance between atmospheric deposition and inventory further suggests that incoming fluoride from past climatic cycles has remained in the profile during pluvial periods.

[40] In the Murray Basin, there is no information on fluoride concentrations in the Kulkami natural profile. The cropland profile (2LC) provides a surrogate, although for a more finely textured soil. The estimated fluoride concentration in precipitation at this site is 3.7 μg/L (Table 3). Fluoride concentrations in bulk precipitation at the Mildura station are much higher (2007–2008: 17 μg/L) (Table 2). This limited comparison indicates that there is sufficient fluoride in atmospheric deposition to account for fluoride in the subsurface at this site.

3.3. Mobilization of Salts

3.3.1. Chloride Mobilization

[41] Chloride is the most mobile of the ions evaluated in this study (auxiliary material). Chloride concentrations in each of the regions are much lower than the solubility limit of halite (NaCl); therefore, there is no halite solid phase to consider.

[42] In the Southern High Plains, under rain-fed agriculture, chloride is flushed throughout the entire profile depth in 6 profiles (4.0–9.2 m deep) and partially flushed in the remaining 9 profiles (4.5–11.4 m deep), with sharp chloride fronts at the base of these profiles (Table 1 and Figures 3j and S5). Average chloride concentrations in the flushed portion of profiles are extremely low (3.5 to 41 mg/L). In the partially flushed profiles, correspondence between chloride mass balance (CMB) ages at the base of the flushed zone (43 to 82 years) and timing of land use change, as

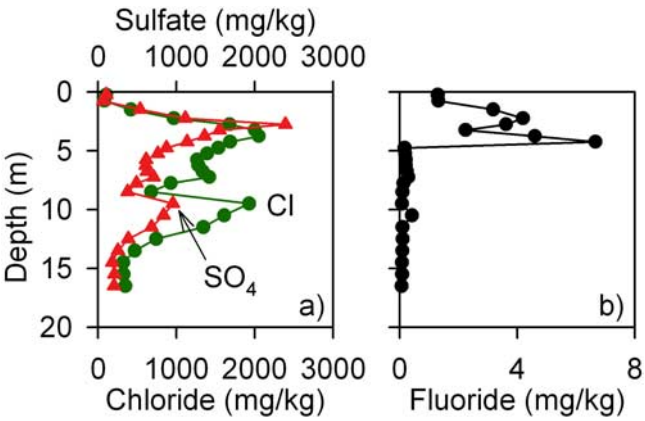

Figure 9. (a) Chloride and sulfate (b) and fluoride concentration profiles for borehole 2LC (rain-fed agriculture) in the Murray Basin Riverlands area.

determined from air photos and landowner accounts [*Scanlon et al.*, 2007b], shows that preexisting chloride bulges were displaced completely from this zone, indicating piston-type displacement. Water fluxes estimated using the CMB approach for the flushed zones range from 5 to 92 mm/a beneath rain-fed crops (median 24 mm/a, 5% of mean annual precipitation) [*Scanlon et al.*, 2007b].

[43] In the Amargosa Desert, subroot zone chloride concentrations beneath irrigated agriculture are generally low throughout the ~6 to >16 m flushed zone (mean 24 to 110 mg/L, Table 1). Water fluxes estimated by chloride front displacement (CFD) are generally similar to those estimated by chloride mass balance (field 1, CFD: 190–300 mm/a versus CMB: 100–230 mm/a; field 2 CFD: 130–170 mm/a versus CMB: 230–530 mm/a), suggesting predominantly piston-type displacement of preexisting chloride from the flushed zone [*Stonestrom et al.*, 2003].

[44] In the Murray Basin, chloride is not mobilized beneath rain-fed agriculture in low-permeability soils (profile 2LC, Table 1 and Figure 9), indicating low water fluxes beneath the root zone. In profile 2LC, chloride increases to a peak of 16,600 mg/L at 4.3 m depth and remains high throughout the profile to 17 m depth, typical of profiles under natural ecosystems [*Jolly et al.*, 1989; *Leaney et al.*, 2003]. In contrast, profiles in higher-permeability sandy soils have lower chloride concentrations to depths of 3.8 to 7.8 m, with maximum concentrations in the flushed zone of 370 to 2100 mg/L (40 to 140 mg/kg) (e.g., Figure 3p). The higher residual chloride concentrations in these profiles relative to profiles in the southwestern United States cannot be directly attributed to higher current chloride inputs from atmospheric deposition or fertilization. The extremely high chloride concentrations beneath natural ecosystems (e.g., Kul04, Figure 3g) may require multiple pore volumes to flush the chloride to levels that are found in the flushed zones of the Southern High Plains and Amargosa Desert. The high residual chloride concentrations (Table 1) may indicate some degree of preferential flow, where the initial wetting front bypasses parts of the soil matrix.

3.3.2. Sulfate Mobilization

[45] Mobilization of sulfate under cultivation-induced drainage/recharge is more highly variable than that of chloride. Reduced mobilization of sulfate relative to chloride may be related to plant uptake, gypsum or anhydrite precipitation and dissolution, or sorption. Cycling of sulfur through organic matter can delay and diminish downward sulfate movement. The lower solubility of gypsum ($K_{sp} \approx 10^{-4.6}$) [*Hem*, 1985] relative to halite ($K_{sp} \approx 10^{1.6}$) [*Lide*, 1991] can result in reduced mobilization of sulfate relative to chloride; however, simulated pore waters tended to be undersaturated with respect to gypsum and anhydrite (auxiliary material, Tables S4 and S5). Sulfate sorbs more strongly than chloride to mineral surfaces [*Clifford*, 1999]. Sulfate sorption can occur onto hydrous Al and Fe oxide surfaces by electrostatic attraction or by replacement of OH^- ions [*Van Stempvoort et al.*, 1990]. Sorption of sulfate to hydrous Fe oxides is greatest under acidic conditions but extends into slightly alkaline conditions [*Dzombak and Morel*, 1990].

[46] In the Southern High Plains, although preexisting chloride is completely displaced from the chloride flushed zone, sulfate is incompletely displaced from these zones. Flushed zones of sulfate were identified by comparing cropland profiles with profiles beneath natural ecosystems and, in some profiles, on the basis of relative increases in sulfate at depth. Three of the nine profiles have coincident chloride and sulfate fronts, whereas sulfate fronts lag chloride fronts in the other five profiles by up to 4 m (e.g., Figures 3j and 3k and Table 1). The sulfate front is slightly deeper than the chloride front in one profile. Mean residual sulfate concentrations in the flushed section of the profiles range from 79 to 410 mg/L.

[47] In the Amargosa Desert, high sulfate concentrations toward the base of profiles in field 1 reflect preirrigation sulfate (Figure 3n) that was mobilized with chloride (Figure 3m). Profile AD1b shows sulfate increasing at 6.2 m to a peak at 8.0 m, similar to chloride. Concentrations of chloride and sulfate are much lower in the AD1c profile (auxiliary material, Figure S7) in the same field, where the sulfate peak lags the deep chloride peak by 1.6 m. Residual sulfate concentrations in the chloride flushed zone of both profiles are much higher than residual chloride concentrations (on both relative and absolute bases), with sulfate peaks of 2000–2100 mg/L at 3.6–4.7 m depth (AD1b, Figure 3n) and 310–550 mg/L at 5.0–9.2 m depth (AD1c). The large spikes in residual sulfate may be controlled by fine-grained soil layers, as suggested by the high correlation (r = 0.81, ≥1 m depth) between sulfate and water content in profile AD1b (Figure 8). Redox conditions in these clayey layers may also impact sulfate mobilization. In the older irrigated fields (fields 2 and 3, Figure 1) preirrigation chloride and sulfate bulges have been more or less completely displaced from the profiles. Spikes in sulfate and chloride in profiles in field 2 are coincident and are attributed to variations in irrigation that, prior to 1992, was applied by manually moved wheel line sprinklers.

[48] In the Murray Basin, concentrations of sulfate and chloride are highly correlated in cropland profiles (5HC: r = 0.96; 6HC: r = 0.90). Peaks of chloride and sulfate coincide at depths of 5.8 and 8.8 m in profile 5HC (auxiliary material, Figure S6). However, the sulfate peak in profile 6HC lags the chloride peak by ~3 m (Figures 3p and 3q). Residual sulfate concentrations (mean 160 and 640 mg/L)

are similar to residual chloride concentrations (mean 150 and 1200 mg/L, Table 1).

3.3.3. Fluoride Mobilization

[49] Fluoride was little mobilized by increased drainage/recharge under cropland over the multiple decades since land use changed. Fluoride inventories beneath natural ecosystems and croplands are similar in each region (Figure 2b). In the Southern High Plains, the partly and completely flushed chloride profiles also have similar total fluoride inventories (Figure 2b and Table 1). In the Amargosa Desert, irrigated profiles have fluoride inventories similar to those beneath the natural ecosystem. In the Murray Basin, although fluoride was not measured in the profile beneath the natural ecosystem in the Kulkami region, the low-permeability cropland profile in the Riverlands site (2LC) has generally chloride patterns similar to those beneath natural ecosystems. The fluoride inventory in profile 2LC is similar to inventories beneath rain-fed agriculture (Figure 2b). Peak fluoride concentrations and peak depths beneath cropland are similar to those beneath natural ecosystems, consistent with little mobilization of fluoride (Figure 3).

3.4. Potential Impact of Unsaturated Zone Salt Reservoirs on Future Groundwater Quality

[50] Groundwater does not appear to be vulnerable to contamination by fluoride from flushing of surface or near surface sediments in the studied regions at least on decadal time scales, as shown by the comparison of unsaturated zone profiles under natural and cropland conditions (Figure 3). Because fluoride is largely immobilized beneath the root zone, perhaps even accumulating across glacial/interglacial climatic cycles, the potential for groundwater contamination by fluoride following land use change appears to be small. The general lack of fluoride mobility is particularly important because fluoride is applied to cultivated fields through impurities in phosphate fertilizers. *Fluhler et al.* [1982] similarly concluded that point sources of fluoride, such as smelters, did not pose an imminent threat to underlying aquifers. In contrast, groundwater is vulnerable to contamination from chloride and sulfate that are flushed from near surface sediments by land use changes. The impact of mobilizing chloride and sulfate into underlying aquifers is expected to be transient as salts are flushed through the system. Potential impacts on groundwater vary according to water table depth, salt inventory, relative mobility of salts in the unsaturated zone, postcultivation drainage/recharge rates, preexisting groundwater quality, and thickness of aquifer in which mixing occurs. There is a trade off between water table depth and aquifer vulnerability. Although increasing water table depths result in longer times for flushed salts to reach the aquifer, salt inventories generally increase with increased unsaturated zone thickness.

3.4.1. Groundwater in the Southern High Plains

[51] The Ogallala aquifer in the Southern High Plains has generally poor quality water in the south region (median values: TDS = 893 mg/L, chloride = 180 mg/L, sulfate = 70 mg/L, fluoride = 3.3 mg/L) and generally high quality in the north region (median values: TDS = 388 mg/L, chloride = 21 mg/L, sulfate = 33 mg/L, fluoride = 2.3 mg/L) (Figure 1, red line separating N and S parts of Southern High Plains). The percentage of wells that exceed the EPA MCLs is much greater in the south (chloride = 37%; sulfate = 43%; fluoride = 37%) than in the north (chloride = 0.1%; sulfate = 0.4%; fluoride = 5%). A total of 85% of wells exceed the WHO recommended fluoride limit of 1.5 mg/L in both the north and south regions. Variations in water quality are related to water table depth (median, $S = 25$ m; $N = 63$ m) and aquifer saturated thickness (median $S = 15$ m; $N = 21$ m). The shallower water table depth in the south results in greater aquifer vulnerability to contamination from surface sources, and the reduced aquifer thickness in the south results in less water to dilute incoming contaminants.

[52] The impact of mobilizing salts by increasing recharge beneath cropland areas was evaluated using the modified *Cook et al.* [1993] model (auxiliary material) using parameters to approximate the Lyn06-01 chloride and sulfate profiles (Table 4). The model indicates that groundwater chloride concentrations would increase from 180 to a peak of 330 mg/L after ~100 years (Figure 10a). A similar analysis was conducted for sulfate. Assuming all sulfate is completely mobilized, groundwater concentrations would increase from 220 to a peak of 700 mg/L after ~100 years. Using the regional relationship between total dissolved solids (TDS) and chloride plus sulfate in groundwater from wells, groundwater TDS would increase from 900 to 1800 mg/L.

3.4.2. Groundwater in the Amargosa Desert

[53] Information on groundwater chemistry near the water table in the Amargosa Desert is limited. Irrigation wells for the cultivated fields currently have high-quality groundwater, but are screened tens of meters below the water table. An irrigation well first sampled in 1974 had virtually identical chemistry in 2001 and 2002 [*Stonestrom et al.*, 2003], indicating that irrigation return flow had not measurably perturbed the production zone of this aquifer (Table 2). This is consistent with unsaturated zone profile data because potential impacts in the Amargosa Desert are small. An upper bound on groundwater salinity was estimated by mobilizing the entire unsaturated zone salt inventory (without pore water) into aquifer mixing zones ranging from 15 to 50 m on the basis of the screened intervals of irrigation wells. Chloride concentrations increase from 9 to 53–155 mg/L and sulfate concentrations from 33 to 129–353 mg/L. The irrigation rates at this site (2.0–2.7 m/a) are much higher than typical values in the Southern High Plains (0.3–0.9 m/a) [*McMahon et al.*, 2006], and prevent irrigation supplied salts from accumulating in the soil zone, minimizing the potential for soil salinization. Given the high irrigation rates and high quality of groundwater used for irrigation, measurable impacts on groundwater quality will most likely take centuries.

3.4.3. Groundwater in the Murray Basin

[54] Groundwater quality varies regionally in the unconfined Murray Group aquifer of the Murray Basin [*Dogramaci et al.*, 2001]. Groundwater is extremely saline in the Riverlands area near the Murray River in the north, with typical chloride concentrations of ~7000–13,000 mg/L and sulfate concentrations of ~600–1400 mg/L [*Dogramaci et al.*, 2001] (Table 4). Estimated precultivation unsaturated zone chloride concentrations in profiles in the Riverlands area range from ~10,000 to 20,000 mg/L [*Cook et al.*, 2004]. Although sulfate concentrations were not measured in natural unsaturated zone profiles in this region, sulfate concentrations are estimated to be ~10% of chloride

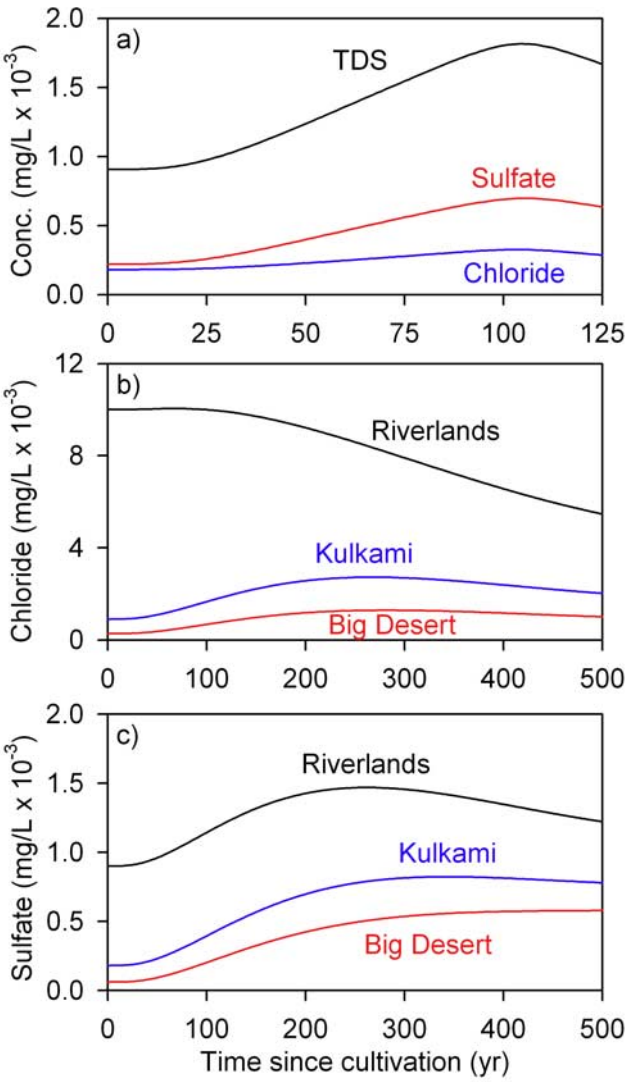

Figure 10. Estimated impacts on groundwater of flushing unsaturated zone (a) chloride and sulfate under the Southern High Plains region and (b) chloride and (c) sulfate under three regions in the Murray Basin study area. Total dissolved solids (TDS) shown in Figure 10a are based on a regional groundwater relationship between TDS and the sum of chloride plus sulfate concentrations [TDS = 1.46(Cl + SO_4) + 321].

concentrations on the basis of data from the Kulkami site (Kul04). Mobilizing the salt inventory for this region to groundwater using the analytical approach of *Leaney et al.* [2003] (Table 4) would decrease the initial groundwater chloride values (~10,000 mg/L), starting after 100 years and dropping to about half (~5000 mg/L) after ~500 years. Even these long-term concentrations are extremely high (Figure 10b). Groundwater sulfate would increase from 900 to a peak of 1500 mg/L after ~270 years, assuming sulfate moves with chloride (Figure 10c). Groundwater quality is higher in the Kulkami area [*Dogramaci et al.*, 2001]. Mobilizing the salts measured in the Kul04 profile would increase chloride from 900 to a peak of 2700 mg/L after ~270 years and sulfate from 180 to a peak of 800 mg/L after ~350 years. The highest groundwater quality is in the 10,000 km^2 area of paleogroundwater under the Big and Little Deserts. This area of fresher groundwater represents ~40% of the groundwater in the mallee region of the Murray Basin and was recharged during a wetter period >20,000 years ago [*Leaney et al.*, 2003]. Previous studies evaluated the impact of mobilizing salts into groundwater in this area [*Leaney et al.*, 2003]. Unsaturated zone chloride concentrations under native vegetation are lower (~6000 mg/L) because of higher precipitation (~500 mm/a). Displacing unsaturated zone chloride (6000 mg/L) into groundwater in the Big Desert would increase groundwater chloride from 270 mg/L to a peak of 1300 mg/L after 290 years (Figure 10b), and sulfate would continually increase from 60 to 600 mg/L over ~500 years (Figure 10c). The proportional effect of salt mobilization is much greater in the Big Desert than in the Riverlands area because groundwater chloride in the Big Desert is typically ~3% of that at the Riverlands area, whereas chloride concentrations in soil water are high at both sites, differing by only 40%. Thus, the percentage increase in groundwater chloride due to land use change is much greater in the Big Desert than in the Riverlands area. Furthermore, although similar rates of deep drainage have been used when modeling salinization rates at each of the three sites in the Murray Basin, higher rainfall in the Big Desert (~500 mm/a) is likely to result in higher drainage rates and hence faster rates of groundwater salinization.

4. Future Work

[55] This reconnaissance examined inventories of two relatively important but undocumented solutes, sulfate and fluoride, in semiarid unsaturated zones relative to inventories of chloride. The study evaluated sources of these solutes, their mobilization due to land use changes, and their subsequent potential impacts on water quality of underlying aquifers. The study was limited to evaluation of water-extractable salt concentrations. While this approach has been used in the past, chemical modeling results suggest that fluoride concentrations reflect some degree of

Table 4. Analytical Model Parameters to Estimate Regional Impacts of Unsaturated Zone Flushing on Groundwater Quality[a]

Parameter	Units	Riverlands	Kulkami	Big Desert	SHP
Drainage, *D*	mm/a	9.3	9.3	9.3	24
D uncertainty	mm/a	2.5	2.5	2.5	2.5
Pre Cl	mg/L	15,000	12,000	6,000	1,500
Pre SO_4	mg/L	4,500	3,000	1,800	3,000
Post Cl	mg/L	200	200	200	10
Post SO_4	mg/L	600	600	600	150
Deep Cl	mg/L	-	-	-	250
Deep SO_4	mg/L	-	-	-	800
Pre WC	m^3/m^3	0.06	0.06	0.06	0.14
Post WC	m^3/m^3	0.12	0.12	0.12	0.21
DTW	m	30	30	30	30
Porosity	m^3/m^3	0.3	0.3	0.3	0.3
GW Cl	mg/L	10,000	900	270	180
GW SO_4	mg/L	900	180	60	220

[a]Three Murray Basin region study areas (Riverlands, Kulkami, and Big Desert) are based on the Kul04 profile, and the Southern High Plains (SHP) region is based on the Lyn06-01 profile. Pre, precultivation; post, postcultivation; deep, below bulge (SHP model only); WC, water content; DTW, depth to water; GW, groundwater.

mineral dissolution during the water extraction process. Because even a small quantity of dissolution can make a large difference in solution chemistry, further evaluation of the relation of water-extractable solutes to pore water solutes is needed. Understanding mobilization can also be improved by batch and column experiments that examine solid phase structure and composition. Mineral surface characterization (before and after mobilization) would shed light on secondary mineralization versus sorption mechanisms of solute retention.

[56] Systematic collection of atmospheric deposition data that includes both wetfall and dryfall components is acutely needed. The U.S. NADP program is limited to wet deposition and could be expanded to include dry deposition. Information on atmospheric deposition in Australia is restricted to the 1974–1975 data from *Blackburn and McLeod* [1983] and the more recent 2007–2008 data. Long-term records of atmospheric deposition would provide more reliable estimates for assessing their effect on subsurface salt distribution. There are few data on natural rates of fluoride deposition beyond those presented in this study. In addition to information on current atmospheric deposition, proxy data on preindustrial atmospheric deposition are needed to assess long-term inputs to the subsurface.

[57] Unsaturated zone studies in semiarid regions have focused primarily on chloride as a proxy for water movement; however, such studies could be expanded to include other solutes in addition to sulfate and fluoride. Ionic and trace element ratios and isotopic signatures can all be used to help identify sources. Information on salt inventories as a function of climate, vegetation, and soil type can be used to assess controls on subsurface salt distribution and mobilization. Information on irrigated sites is restricted to the Amargosa Desert and High Plains regions [e.g., *Stonestrom et al.*, 2003; *McMahon et al.*, 2006]. Additional studies that include different irrigation techniques and variable irrigation water quality, including currently emerging highly efficient sprinkler and subsurface drip designs, are needed to evaluate future impacts of irrigation on soil water and groundwater quality. Data on salt distribution and mobilization relative to soil type and climate are required to evaluate hydraulic controls on solute transport. Finally, the current empirical and analytical approaches to evaluating impacts of salt mobilization on groundwater quality could be supplemented by conducting numerical flow and transport modeling in connection with stratified groundwater sampling to evaluate mixing zones.

5. Conclusions

[58] 1. Large inventories of chloride (6600–41,000 kg/ha) and sulfate (7800–120,000 kg/ha) and much lower inventories of fluoride (630–3900 kg/ha) are found in semiarid unsaturated zones beneath natural ecosystems at sites in the southwestern United States and in the Murray Basin, Australia.

[59] 2. The source of chloride is atmospheric deposition, which is almost an order of magnitude higher in the Murray Basin than in the southwestern United States. Much of the sulfate could also be derived from atmospheric deposition on the basis of high correlations between sulfate and chloride in many profiles and estimated deposition rates similar or less than current levels of sulfate in bulk precipitation. Local zones of very high sulfate (47,000 mg/L) in the Southern High Plains are attributed to dissolution of gypsum, which was found in the sediments. Fluoride in atmospheric deposition is 3 to 7 times less than estimates from unsaturated zone profile inventories in the Amargosa Desert and Southern High Plains, suggesting that incoming fluoride from past climatic cycles has remained in the profiles during pluvial periods. In contrast, estimates of fluoride in precipitation in the Murray Basin are greater than those based on subsurface fluoride inventories; however, the profile data are limited.

[60] 3. Chloride is most readily mobilized by increased drainage caused by land use change from natural ecosystems to cropland ecosystems. Chloride is completely mobilized in profiles in the southwestern United States by increased drainage beneath rain-fed and irrigated agriculture. Incomplete displacement of chloride in the Murray Basin may be attributed to very high initial chloride concentrations and/or preferential flow.

[61] 4. Some sulfate moves with chloride as shown by coincident solute fronts and peaks beneath cropland; however, sulfate fronts lag chloride fronts in many profiles by up to 4 m. High residual sulfate in many profiles under rain-fed or irrigated cropland is attributed to incomplete mobilization of precultivation sulfate related to retardation of sulfate and/or additional sources of sulfate besides atmospheric deposition, such as fertilizers or gypsum dissolution.

[62] 5. Fluoride is not mobilized by increased drainage beneath cropland areas, as shown by similarity in fluoride inventories beneath natural and cropland systems in each of the study regions. Fluoride appears to accumulate in the unsaturated zone across climatic cycles of pluvial and interpluvial periods.

[63] 6. Salt mobilization in the Southern High Plains could increase groundwater chloride from 180 to a peak of 330 mg/L and sulfate from 220 to a peak of 700 mg/L. Groundwater at the Amargosa Desert site would require centuries to degrade because of the high quality of the irrigation water and the large irrigation rates that result in minimal salt buildup in the soil. The impact of salt mobilization on groundwater quality in the Murray Basin varies mostly with the preexisting groundwater quality. Mobilizing salts into poor water quality in the Murray Riverlands area would decrease chloride concentrations from 10,000 to 5000 mg/L. In the Kulkami region, groundwater chloride would increase from 900 to 2700 mg/L and sulfate from 180 to 800 mg/L. The highest-quality water is in the Big and Little Deserts; however, the precultivation salt inventory is lower in this region also because of higher rainfall. Mobilizing salts in this area would increase chloride 270 to 1300 mg/L and sulfate from 60 to 600 mg/L. It will be most critical to minimize salt movement into these high-quality aquifers in the future.

[64] **Acknowledgments.** We are grateful to the USEPA, the Texas Commission on Environmental Quality, and the University of Texas at Austin Jackson School of Geosciences for financial support for this study, as well as the USGS National Research Program, Groundwater Resources Program and Toxic Substances Hydrology Program. D. Kirk Nordstrom (USGS), James J. Thordsen (USGS), and Editor Thomas Torgersen (University of Connecticut) provided helpful suggestions on early drafts of the report. Addition review comments that greatly improved the final manuscript were provided by Guillaume Favreau (IRD, France), Editor James R. Hunt (University of California, Berkeley), and two anonymous

reviewers. We thank the land owners for providing access to their properties for sampling and we are very grateful to groundwater conservation district managers Jason Coleman, Harvey Everhardt, Ken Carver, and Mike McGregor for their assistance in locating suitable sampling locations.

References

Allison, G. B., and M. W. Hughes (1983), The use of natural tracers as indicators of soil-water movement in a temperate semi-arid region, *J. Hydrol.*, *60*, 157–173, doi:10.1016/0022-1694(83)90019-7.

Allison, G. B., P. G. Cook, S. R. Barnett, G. R. Walker, I. D. Jolly, and M. W. Hughes (1990), Land clearance and river salinisation in the western Murray Basin, Australia, *J. Hydrol.*, *119*, 1–20, doi:10.1016/0022-1694(90)90030-2.

Alloway, B. J. (2005), Bioavailability of elements in soil, in *Essentials of Medical Geology*, edited by O. Selinus et al., pp. 347–372, Elsevier, Amsterdam.

Amini, M., K. Mueller, K. C. Abbaspour, T. Rosenberg, M. Afyuni, K. N. Moller, M. Sarr, and C. A. Johnson (2008), Statistical modeling of global geogenic fluoride contamination in groundwaters, *Environ. Sci. Technol.*, *42*(10), 3662–3668, doi:10.1021/es071958y.

Barbiero, L., V. Valles, and A. Regeard (1995), Fluorite precipitation and geochemical control of calcium in alkali soils of Niger. Consequences for a quantitative estimation of the geochemical evolution of soil solution, *C. R. Acad. Sci., IIA, C. R. Geosci.*, *321*, 1147–1154.

Blackburn, G., and S. McLeod (1983), Salinity of atmospheric precipitation in the Murray-Darling drainage division, Australia, *Aust. J. Soil Res.*, *21*, 411–434, doi:10.1071/SR9830411.

Bronson, K. F., J. D. Booker, J. P. Bordovsky, J. W. Keeling, T. A. Wheeler, R. K. Boman, M. N. Parajulee, E. Segarra, and R. L. Nichols (2006), Site-specific irrigation and nitrogen management for cotton production in the Southern High Plains, *Agron. J.*, *98*, 212–219, doi:10.2134/agronj2005.0149.

Chivas, A. R., A. S. Andrew, W. B. Lyons, M. I. Bird, and T. H. Donnelly (1991), Isotopic constraints on the origin of salts in Australian playas. 1 Sulfur, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *84*, 309–332, doi:10.1016/0031-0182(91)90051-R.

Clifford, D. (1999), Ion exchange and inorganic adsorption, in *Water Quality and Treatment*, edited by A. Letterman, pp. 9, 13, Am. Water Works Assoc., McGraw-Hill, New York.

Cook, P. G., A. L. Telfer, and G. R. Walker (1993), Potential for salinization of the ground water beneath mallee areas of the Murray Basin, *CGS Rep. 42*, Flinders Univ., Adelaide, South Aust., Australia.

Cook, P. G., F. W. Leaney, and I. D. Jolly (2001), Groundwater recharge in the mallee region and salinity implications for the Murray River—A review, *Tech. Rep. 45/01*, 133 pp., CSIRO Land and Water, Adelaide, South Aust., Australia.

Cook, P. G., F. W. Leaney, and M. Miles (2004), Groundwater recharge in the north-east mallee region, South Australia, *Tech. Rep. 25/04*, 80 pp., CSIRO Land and Water, Adelaide, South Aust., Australia.

Davis, S. N., D. O. Whittemore, and J. Fabryka-Martin (1998), Uses of chloride/bromide ratios in studies of potable water, *Ground Water*, *36*, 338–350, doi:10.1111/j.1745-6584.1998.tb01099.x.

Deans, J. D., W. M. Edmunds, D. K. Lindley, C. B. Gaye, B. Dreyfus, J. J. Nizinski, M. Neyra, K. Ingleby, and R. C. Munro (2005), Nitrogen in interstitial waters in the Sahel; Natural baseline, pollutant or resource?, *Plant Soil*, *271*, 47–62, doi:10.1007/s11104-004-1994-5.

Dogramaci, S. S., A. L. Herczeg, S. L. Schiff, and Y. Bone (2001), Controls on δ^{34}S and δ^{18}O of dissolved sulfate in aquifers of the Murray Basin, Australia and their use as indicators of flow processes, *Appl. Geochem.*, *16*, 475–488, doi:10.1016/S0883-2927(00)00052-4.

Dzombak, D. A., and F. M. M. Morel (1990), *Surface Complexation Modeling: Hydrous Ferric Oxide*, 39 pp., John Wiley, New York.

Edmunds, M., and P. L. Smedley (2005), Fluoride in natural waters, in *Essentials of Medical Geology*, edited by O. Selinus et al., pp. 310–329, Elsevier, Amsterdam.

Favreau, G., B. Cappelaere, S. Massuel, M. Leblanc, M. Boucher, N. Boulain, and C. Leduc (2009), Land clearing, climate variability and water resources increase in semiarid southwest Niger: A review, *Water Resour. Res.*, *45*, W00A16, doi:10.1029/2007WR006785.

Fischer, H., D. Wagenbach, and J. Kipfstuhl (1998), Sulfate and nitrate firn concentrations on the Greenland ice sheet: 2. Temporal anthropogenic deposition changes, *J. Geophys. Res.*, *103*, 21,935–21,942.

Fluhler, H., J. Polomski, and P. Blaser (1982), Retention and movement of fluoride in soils, *J. Environ. Qual.*, *11*, 461–468.

Gat, J. R., and R. Gonfiantini (1981), *Stable Isotope Hydrology: Deuterium and Oxygen-18 in the Water Cycle*, *IAEA Tech. Rep. Ser.*, vol. 210, 33 pp., Int. At. Energy Agency, Vienna.

Grassineau, N. V., D. P. Mattey, and D. Lowry (2001), Sulfur isotope analysis of sulfide and sulfate minerals by continuous flow-isotope ratio mass spectrometry, *Anal. Chem.*, *73*, 220–225, doi:10.1021/ac000550f.

Grey, D. C., and M. L. Jensen (1972), Bacteriogenic sulfur in air pollution, *Science*, *177*, 1099–1100, doi:10.1126/science.177.4054.1099.

Hem, J. D. (1985), Study and interpretation of the chemical characteristics of natural water, *U.S. Geol. Surv. Water Supply Pap.*, *2254*, 263 pp.

Herczeg, A. L., S. S. Dogramaci, and F. W. J. Leaney (2001), Origin of dissolved salts in a large, semi-arid groundwater system: Murray Basin, Australia, *Mar. Freshwater Res.*, *52*, 41–52, doi:10.1071/MF00040.

Holt, B. D., R. Kumar, and P. T. Cunningham (1982), Primary sulfates in atmospheric sulfates: Estimation by oxygen isotope ratio measurements, *Science*, *217*, 51–53, doi:10.1126/science.217.4554.51.

Jolly, I. D., P. G. Cook, G. B. Allison, and M. W. Hughes (1989), Simultaneous water and solute movement through unsaturated soil following an increase in recharge, *J. Hydrol.*, *111*, 391–396, doi:10.1016/0022-1694(89)90270-9.

Jolly, I. D., M. Trenordan, A. N. Holub, P. G. Cook, and J. C. Dighton (1990), Recharge studies in the western Murray Basin. 4. Results of a drilling program at Kulkami, *Tech. Memo. 90/3*, Div. of Water Resour., CSIRO, Floreat Park, West. Aust., Australia.

Kilroy, K. C. (1991), Ground-water conditions in the Amargosa Desert, Nevada-California, 1952–87, *U.S. Geol. Surv. Water Resour. Invest. Rep.*, 89-4101, 91 pp.

Krouse, H. R., and B. Mayer (2000), Sulphur and oxygen isotopes in sulphate, in *Environmental Tracers in Subsurface Hydrology*, edited by P. Cook and A. L. Herzeg, pp. 195–232, Kluwer Acad., Boston, Mass.

Leaney, F. W., A. L. Herczeg, and G. R. Walker (2003), Salinization of a fresh palaeo-ground water resource by enhanced recharge, *Ground Water*, *41,* 84–92, doi:10.1111/j.1745-6584.2003.tb02571.x.

Lide, D. R. (1991), *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, Fla.

Mast, M. A., J. T. Turk, G. P. Ingersoll, D. W. Clow, and C. L. Kester (2001), Use of stable sulfur isotopes to identify sources of sulfate in Rocky Mountain snowpacks, *Atmos. Environ.*, *35*, 3303–3313, doi:10.1016/S1352-2310(00)00507-0.

McMahon, P. B., K. F. Dennehy, B. W. Bruce, J. K. Böhlke, R. L. Michel, J. J. Gurdak, and D. B. Hurlbut (2006), Storage and transit time of chemicals in thick unsaturated zones under rangeland and irrigated cropland, High Plains, United States, *Water Resour. Res.*, *42*, W03413, doi:10.1029/2005WR004417.

Muller, W. J., R. G. M. Heath, and M. H. Villet (1998), Finding the optimum: Fluoridation of potable water in South Africa, *Water SA*, *24*, 21–27.

National Research Council (2006), *Fluoride in Drinking Water: A Scientific Review of EPA's Standards*, 508 pp., Natl. Acad., Washington, D. C.

Nativ, R. (1988), Hydrogeology and hydrogeochemistry of the Ogallala Aquifer, Southern High Plains, Texas Panhandle and eastern New Mexico, *Rep. Invest. 177*, 64 pp., Tex. Bur. of Econ. Geol., Austin, Tex.

Nativ, R., and D. A. Smith (1987), Hydrogeology and geochemistry of the Ogallala aquifer, Southern High Plains, *J. Hydrol.*, *91*, 217–253, doi:10.1016/0022-1694(87)90206-X.

Novak, M., M. J. Mitchell, I. Jackova, F. Buzek, J. Schweigstillova, L. Erbanova, R. Prikryl, and D. Fottova (2007), Processes affecting oxygen isotope ratios of atmospheric and ecosystem sulfate in two contrasting forest catchments in central Europe, *Environ. Sci. Technol.*, *41*, 703–709, doi::10.1021/es0610028.

Phillips, F. M. (1994), Environmental tracers for water movement in desert soils of the American Southwest, *Soil Sci. Soc. Am. J.*, *58*, 14–24.

Rhoades, J. D. (1982), Soluble salts, in *Methods of Soil Analysis, Part 2*, *Soil Sci. Soc. Am. Book Ser.*, vol. 5, 2nd ed., edited by A. L. Page, R. H. Miller, and D .R. Keeney, pp. 167–180, Soil Sc. Soc. of Am., Madison, Wis.

Scanlon, B. R., K. Keese, R. C. Reedy, J. Simunek, and B. J. Andraski (2003), Variations in flow and transport in thick desert vadose zones in response to paleoclimatic forcing (0–90 kyr): Field measurements, modeling, and uncertainties, *Water Resour. Res.*, *39*(7), 1179, doi:10.1029/2002WR001604.

Scanlon, B. R., R. C. Reedy, D. A. Stonestrom, D. E. Prudic, and K. F. Dennehy (2005), Impact of land use and land cover change on groundwater recharge and quality in the southwestern USA, *Global Change Biol.*, *11*, 1577–1593, doi:10.1111/j.1365-2486.2005.01026.x.

Scanlon, B. R., I. Jolly, M. Sophocleous, and L. Zhang (2007a), Global impacts of conversions from natural to agricultural ecosystems on water resources: Quantity versus quality, *Water Resour. Res.*, *43*, W03437, doi:10.1029/2006WR005486.

Scanlon, B. R., R. C. Reedy, and J. A. Tachovsky (2007b), Semiarid unsaturated zone chloride profiles: Archives of past land use change impacts on water resources in the southern High Plains, United States, *Water Resour. Res.*, *43*, W06423, doi:10.1029/2006WR005769.

Scanlon, B. R., R. C. Reedy, and K. F. Bronson (2008), Impacts of land use change on nitrogen cycling archived in semiarid unsaturated zone nitrate profiles, Southern High Plains, Texas, USA, *Environ. Sci. Technol.*, *42*(20), 7566–7572, doi:10.1021/es800792w.

Simpson, H. J., and A. L. Herczeg (1994), Delivery of marine chloride in precipitation and removal by rivers in the Murray-Darling Basin, Australia, *J. Hydrol.*, *154*, 323–350, doi:10.1016/0022-1694(94)90224-0.

Stonestrom, D., D. E. Prudic, R. J. Laczniak, K. C. Akstin, R. A. Boyd, and K. K. Henkelman (2003), Estimates of deep percolation beneath native vegetation, irrigated fields, and the Amargosa-River channel, Amargosa Desert, Nye County, Nevada, *U.S. Geol. Surv. Open File Rep., 03-104*.

U.S. Department of Agriculture (1995), Soil Survey Geographic Data Base, SSURGO, *Misc. Pub. 1527*, Nat. Resour. Conserv. Serv., Washington, D. C.

Van Stempvoort, D. R., E. J. Reardon, and P. Fritz (1990), Fractionation of sulfur and oxygen isotopes in sulfate by soil sorption, *Geochim. Cosmochim. Acta*, *54*, 2817–2826, doi:10.1016/0016-7037(90)90016-E.

Vogelmann, J. E., S. M. Howard, L. Yang, C. R. Larson, B. K. Wylie, and N. van Driel (2001), Completion of the 1990s National Land Cover Data Set for the conterminous United States from Landsat thematic mapper data and ancillary data sources, *Photogramm. Eng. Remote Sens.*, *67*, 650–662.

Walker, G. R., I. D. Jolly, and P. G. Cook (1991), A new chloride leaching approach to the estimation of diffuse recharge following a change in land use, *J. Hydrol.*, *128*, 49–67.

Walvoord, M. A., F. M. Phillips, D. A. Stonestrom, R. D. Evans, P. C. Hartsough, B. D. Newman, and R. G. Striegl (2003), A reservoir of nitrate beneath desert soils, *Science*, *302*, 1021–1024, doi:10.1126/science.1086435.

Wood, W. W., and B. F. Jones (1990), Origin of solutes in saline lakes and springs on the Southern High Plains of Texas and New Mexico, in *Geologic Framework and Regional Hydrology: Upper Cenozoic Blackwater Draw and Ogallala Formations, Great Plains*, edited by T. C. Gustavson, pp. 193–208, Bur. of Econ. Geol., Univ. of Tex. at Austin, Austin, Tex.

World Health Organization (2004), *Guidelines for Drinking-Water Quality*, 3rd ed., 536 pp., Geneva, Switzerland.

R. G. Cresswell, CSIRO Land and Water, 120 Meiers Road, Indooroopilly, Qld 4068, Australia.

J. Gates, R. C. Reedy, and B. R. Scanlon, Bureau of Economic Geology, Jackson School of Geosciences, University of Texas at Austin, Pickle Research Campus, Building 130, 10100 Burnet Road, Austin, TX 78758, USA. (bridget.scanlon@beg.utexas.edu)

F. W. Leaney, CSIRO Land and Water, Glen Osmond, SA 5064, Australia.

D. A. Stonestrom, U.S. Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025, USA.