Storage and transit time of chemicals in thick unsaturated zones under rangeland and irrigated cropland, High Plains, United States

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In 2000–2002, three rangeland and six irrigated sites were instrumented to assess the storage and transit time of chemicals in thick (15 to 50 m) unsaturated zones (UZ) in the High Plains. These processes are likely to influence relations between land use and groundwater quality, yet they have not been documented systematically in the High Plains. Land use and climate were important controls on the size of subsoil chloride, nitrate, and pesticide compound reservoirs. The reservoirs under irrigated cropland generally were larger than those under rangeland because more chemicals were applied to cropland than to rangeland. In some cases, chloride and nitrate reservoirs under rangeland were larger than those under cropland, presumably because of long-term evaporative concentration near the base of the root zone. Natural salts mobilized by irrigation return flow accounted for as much as 60 and 80% of the nitrate and chloride reservoirs, respectively, under some cropland, as indicated by detailed chemical profiles and isotopic tracers ($^{15}$N, $^{18}$O in nitrate and $^2$H, $^3$H, $^{18}$O in water). Advection chemical transit times in the UZ under cropland ranged from about 50 to 375 years, longer than any of the instrumented fields had been irrigated, yet agrichemicals were detected at the water table at four of the six sites. The data provide evidence for the existence of slow and fast paths for water movement in the UZ, with larger subsoil chemical reservoirs occurring in areas dominated by slow paths. Implications of these findings with respect to water quality in the aquifer are significant because they indicate that the amount of chemical mass reaching the aquifer could increase with time as chemicals that still reside under irrigated fields reach the water table.


1. Introduction

The effect of agriculture on groundwater quality is of interest because of the large scale at which this land use practice occurs, the large agrichemical mass applied to cropland, and the reliance on groundwater as a drinking water supply in many agricultural regions. Groundwater containing agrichemicals also is of concern where it discharges to sensitive surface water bodies such as streams and estuaries. The connection between land use and groundwater quality is difficult to establish in regions with large (>15 m) depths to water because chemical transit times through thick unsaturated zones (UZ) can be on the order of years or decades or much longer [Pratt et al., 1972; Gvirtzman and Magaritz, 1986; Spalding and Kitchen, 1988; Johnston et al., 1998; Stonestrom et al., 2003]. Thus substantial agrichemical mass may be stored in thick UZ in the absence of any apparent groundwater contamination [Pratt et al., 1972; McMahon et al., 1999]. Further complications in understanding links between chemical applications at the land surface and groundwater quality arise because large subsoil reservoirs of soluble salts including nitrate (NO$_3^-$) occur naturally in some arid and semiarid environments [Erickson, 1981; Edmunds and Gaye, 1997; Densmore and Bohlke, 2000; Stonestrom et al., 2003; Walvoord et al., 2003]. These solutes may be readily mobilized when such areas are converted to irrigated cropland.

[1] A better understanding of the relation between land use and groundwater quality can be attained if the amount of chemical mass available for movement to the water table and chemical transit times through the UZ are known. The purpose of this paper is to report on the storage and transit time of chemicals in the thick UZ under rangeland and irrigated cropland in the agriculturally important High Plains region of the western United States. The experimental design used in this study, in which rangeland (control) and irrigated sites were instrumented in the southern, central, and northern High Plains, provided an opportunity...
to examine the effects of land use and climate gradients on the storage and transit time of chemicals in the UZ.

2. Study Area Description

The High Plains aquifer underlies an area of about 450,000 km² in parts of eight western states (Figure 1), and is subdivided into the southern (SHP), central (CHP), and northern High Plains (NHP) aquifers. Large-scale irrigation in the High Plains began in the late 1950s. In 1992, irrigated cropland represented about 12% of the High Plains land area [Qi et al., 2002]. The primary irrigated crops were cotton in the SHP and corn in the CHP and NHP. In 2000, about 30% of the groundwater used for irrigation in the U.S. was pumped from the HP aquifer [Maupin and Barber, 2005]. About 2% of the water pumped from the aquifer was used for drinking [Maupin and Barber, 2005].

Median UZ thicknesses ranged from about 15 to 40 m under rangeland and from 25 to 60 m under irrigated cropland in the three High Plains regions. The UZ in the study area consisted of unconsolidated clay, silt, sand, and gravel with scattered cemented zones consisting of calcium carbonate and sometimes silica. The cemented zones were most common near the land surface and were thickest in the SHP where the caprock caliche forms a prominent layer that is resistant to weathering. Soils in the High Plains generally are developed on windblown loess or sand. Over much of the High Plains, slopes are flat to gentle, and soil texture is sufficiently coarse to allow moderate to high infiltration rates.

The study area has a middle-latitude dry continental climate with abundant sunshine, moderate precipitation, frequent winds, low humidity, and a high rate of evaporation. From north to south, mean annual air temperatures and mean annual precipitation near the study sites ranged from about 10°C to 14°C and from about 500 to 420 mm, respectively (period of record 1971–2000) (High Plains Regional Climate Center, http://www.hprcc.unl.edu/, 2005, hereinafter High Plains Regional Climate Center, 2005; Southern Regional Climate Center, http://www.srcc.lsu.edu/, 2005, hereinafter Southern Regional Climate Center, 2005). Evaporation rates measured from free water surfaces in the High Plains ranged from about 1520 mm yr⁻¹ in the north to 2670 mm yr⁻¹ in the south [Gutentag et al., 1984]. Potential annual recharge under rangeland in the High Plains from 1951 to 1980 was estimated by Dugan and Zelt [2000] to range from less than 6 mm in the western and southern areas to as much as 127 mm in the northeastern area. Recharge in rangeland areas of the High Plains probably is not aerially uniform but rather is focused in dry streambeds, ditches, and shallow depressions in the land surface. Playa basins in the SHP, in particular, are thought to be important locations of focused
<table>
<thead>
<tr>
<th>Site</th>
<th>Land Use</th>
<th>Unsaturated Zone Thickness at Time of Sampling, m</th>
<th>Year Irrigation Began</th>
<th>Years of Irrigation at Time of Sampling</th>
<th>Irrigation Method</th>
<th>Range of Applied Water Amounts, mm yr⁻¹</th>
<th>Year N Applications Began</th>
<th>Year Pesticide Applications Began</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMP</td>
<td>rangeland, Nebraska</td>
<td>28</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GNT</td>
<td>irrigated corn, Nebraska</td>
<td>45</td>
<td>1974</td>
<td>28</td>
<td>sprinkler (1974 to present)</td>
<td>140 to 520</td>
<td>late 1950s</td>
<td>1974</td>
</tr>
<tr>
<td>UMA</td>
<td>irrigated corn, Colorado</td>
<td>47</td>
<td>1956</td>
<td>46</td>
<td>flood (1956–1988); sprinkler (1989 to present)</td>
<td>380 to 700</td>
<td>1986&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1986&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>CNG</td>
<td>rangeland, Kansas</td>
<td>50</td>
<td>-</td>
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<td>-</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CAL121</td>
<td>irrigated corn, Kansas&lt;sup&gt;b&lt;/sup&gt;</td>
<td>45</td>
<td>1956</td>
<td>44</td>
<td>flood (1956–1989); sprinkler (1990 to present)</td>
<td>425 to 850</td>
<td>1956</td>
<td>1960</td>
</tr>
<tr>
<td>CAL122</td>
<td>irrigated corn, Kansas&lt;sup&gt;b&lt;/sup&gt;</td>
<td>45</td>
<td>1955</td>
<td>45</td>
<td>flood (1955–1989); sprinkler (1990 to present)</td>
<td>425 to 760</td>
<td>1955</td>
<td>1958</td>
</tr>
<tr>
<td>MWR</td>
<td>rangeland, Texas</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>JRW</td>
<td>irrigated cotton, Texas</td>
<td>46</td>
<td>1958</td>
<td>43</td>
<td>flood (1958–1961); sprinkler (1962 to present)</td>
<td>255 to 610</td>
<td>late 1960s</td>
<td>early 1960s</td>
</tr>
<tr>
<td>MPL</td>
<td>irrigated cotton, Texas</td>
<td>43</td>
<td>1958</td>
<td>43</td>
<td>flood and sprinkler (1958–1975); sprinkler (1976 to present)</td>
<td>255 to 915</td>
<td>1958</td>
<td>late 1950s or early 1960s</td>
</tr>
</tbody>
</table>

<sup>a</sup>First documented use, but producer believes there was use prior to this year.

<sup>b</sup>Borehole location was directly under flood-irrigated corn from 1955 or 1956 through 1989, but it was 25 m from edge of sprinkler-irrigated corn after 1989. Vegetation at borehole location consisted of nonirrigated wheat and sorghum from 1990 to 1999 and annual grasses in 2000.
3. Sampling and Analysis

The UZ was instrumented and monitored at a total of nine sites, with three sites in each of the three major High Plains regions (Figure 1). Within each region, there were two monitoring sites in irrigated settings and one site in rangeland. All of the irrigated sites had been irrigated for at least 28 years at the time of site installation. Basic site characteristics are listed in Table 1.

3.1. Borehole Drilling and Instrumentation

A single borehole (15 to 20 cm in diameter) was drilled to a depth of about 5 m below the water table at each site using a casing-advance drilling method that returned cuttings to the land surface using compressed air [Hammermeister et al., 1986; McMahon et al., 2003]. Boreholes were drilled in 2000 (CHP), 2001 (SHP), and 2002 (NHP). A 5-cm-diameter monitoring well with a 3-m-long screen, the top of which was placed about 1.5 m below the water table at the time of drilling, was installed in each borehole (Figure 2). A suction lysimeter was used to collect groundwater samples at the SHP rangeland site because of the small saturated thickness at that site. Heat dissipation probes were installed above the water table in each borehole to measure matric potentials.

3.2. Collection and Analysis of Sediment Samples

Sediment cuttings were collected at 30-cm intervals from the land surface to the water table at each site and analyzed for particle size distributions and water-extractable concentrations of chloride (Cl⁻) and NO₃⁻. At each site, 13
to 19 sediment cores were collected in 0.6-m-long aluminum core-barrel liners between the land surface and the water table. Once at the surface, the core liners were capped, wrapped in plastic, and heat-sealed inside foil pouches to minimize loss of moisture from the sediment. Sediment cores were analyzed for particle size distributions, bulk density, water content, Cl\(^{-}\), NO\(_3\); \(^{2}\)H, \(^{3}\)H, and \(^{18}\)O in H\(_2\)O; \(^{15}\)N and \(^{18}\)O in NO\(_3\); and selected corn and cotton pesticides. Comparison of chemical profiles developed from cuttings and core data indicates that little mixing of cuttings from different depths occurred as they were transported up the cased borehole.

Particle-size analyses of sediment cuttings and core materials were done through a combination of sieve and hydrometer analyses. Bulk density and gravimetric and volumetric water contents of core samples were measured using standard methods [Dane and Topp, 2002].

Concentrations of deionized-water-extractable Cl\(^{-}\) and NO\(_3\) were quantified by ion chromatography [McMahon et al., 2003], with detection limits of 0.8 and 0.2 \(\mu g\) \(g\) \(^{-1}\), respectively. Water for \(^{3}\)H analysis was extracted from sediment cores using vacuum distillation and \(^{3}\)H concentrations quantified by electrolytic enrichment and liquid scintillation counting at the USGS Tritium Laboratory in Menlo Park, California [Thatcher et al., 1977]. The 1-sigma precision of the analysis ranged from 0.3 to 2.8 TU and was better for moist cores than for dry cores. Methanol-extractable pesticides were analyzed by various GC/MS and LC/MS methods at the USGS Organic Research Laboratory in Lawrence, Kansas, and the Colorado Department of Agriculture Laboratory in Denver, Colorado [McMahon et al., 2003]. Reporting limits ranged from 0.07 to 0.9 \(\mu g\) \(kg\) \(^{-1}\) depending on the specific compound being analyzed. The stable isotopes of H\(_2\)O were analyzed at the USGS Stable Isotope Laboratory in Menlo Park, California [Coplen et al., 1991; Epstein and Mayeda, 1953], and are reported using the \(\delta\) notation, in per mil relative to VSMOW (Vienna Standard Mean Ocean Water). The 2-sigma precisions of O and H isotope results are 0.2 and 2\(\%\), respectively. The isotopes of water-extractable NO\(_3\) were analyzed at the USGS Stable Isotope Laboratory in Reston, Virginia [Sigman et al., 2001; Cascio et al., 2002; Böhlke et al., 2003], and are reported using the \(\delta\) notation, in per mil relative to air for N and VSMOW for O. The 2-sigma precisions for N and O isotope results are 0.5 and 1.0\(\%\), respectively.

3.3. Collection and Analysis of Water Samples

Water from monitoring wells was collected using a submersible pump made of stainless steel and Teflon parts, and processed for chemical analysis using methods previously described [McMahon et al., 2003]. Well water samples were analyzed for dissolved O\(_2\), major ions, nutrients; \(^{2}\)H, \(^{3}\)H, and \(^{18}\)O in H\(_2\)O; \(^{15}\)N and \(^{18}\)O in NO\(_3\); and selected corn and cotton pesticides. Dissolved O\(_2\) was measured in the field using a portable meter and the modified Winkler method [Hach Company, 1989]. Major ion and nutrient analyses were done at the USGS National Water-Quality Laboratory in Lakewood, Colorado [Fishman, 1993]. Analyses of pesticides were done at the USGS Organic Research Laboratory in Lawrence, Kansas [Kish et al., 2000; Lee et al., 2001] and the National Water-Quality Laboratory [Zaugg et al., 1995]. The isotopes of H\(_2\)O were analyzed at the USGS Stable Isotope Laboratory in Reston, Virginia.

3.4. Heat Dissipation Probes

Heat dissipation probes (HDPs) (Model 229, Campbell Scientific, Inc, Logan, Utah) were used to measure matric potentials in the unsaturated zone. The HDPs were calibrated at the USGS Hydrologic Research Laboratory in Sacramento, California. In the field, the HDPs were embedded in silica flour, wrapped in cheesecloth, and saturated with deionized water before placing them in the borehole. Once the probes were placed in the borehole, the annular space around them was filled with silica flour (about 0.3 m thickness) and capped with bentonite. Wires leading from the HDPs were connected to a data logger at the land surface. Precision of the HDPs was approximately \(\pm\)0.1 m. Total potential, referenced to the water table, was calculated as the sum of matric and gravitational potentials and assumes potentials associated with thermal and solute gradients were small.

4. Results and Discussion

4.1. Water Movement in the Unsaturated Zone

Total potentials below the root zone decreased monotonically with depth at the NHP rangeland site and irrigated sites in the SHP and NHP (Figure 3), indicating the potential for downward water movement in the deep UZ at those sites. Deep total potential profiles similar to these three were measured at the CHP irrigated sites by McMahon et al. [2003]. Profiles under the irrigated fields and NHP rangeland site indicate potential gradients close to 1 (0.83 to 0.97) and

![Figure 3](image-url)
showed little seasonal change, consistent with gravity-driven quasi-steady flow below the root zone. The root zone at the irrigated corn and cotton sites was assumed to extend to a depth of 2 m below land surface (C. Thompson, Kansas State University Extension Service, written communication, 2004; R. L. Baumhardt, Agricultural Research Service, U.S. Department of Agriculture, written communication, 2004). In contrast to the irrigated sites, total potentials increased substantially with depth at the SHP rangeland site (Figure 3), indicating the potential for upward water movement from the water table to the root zone at that site. Sparse HDP data at the CHP rangeland site indicate that the gradient at that site may have been close to zero \[15\] McMahon et al., 2003. The stark contrast in total potential profiles between the NHP and SHP rangeland sites implies that conversion of rangeland to irrigated cropland would have a larger impact on groundwater recharge in the SHP than in the NHP.

\[15\] The absence of HDPs in the upper 2 m at each site prevented the calculation of total potentials in the soil zone, but \(^3\)H profiles provided an alternate measure of water movement from the root zone to the deep UZ. Before the onset of atmospheric testing of nuclear weapons in 1953, the \(^3\)H content of precipitation in the central United States probably ranged from about 3 to 8 TU \[Kaufman and Libby, 1954; Thatcher, 1962\]. As a result of radioactive decay, water in the UZ derived from precipitation that fell before 1953 would have contained no more than about 0.5 TU of \(^3\)H in 2000. Using this concentration to separate prebomb and postbomb \(^3\)H in the UZ, it appears that water originating as post-1952 precipitation was present below the root zone at all of the irrigated sites and the NHP rangeland site, but not at the CHP and SHP rangeland sites (Figure 4). These results are in general agreement with the total potential gradients at those sites. Post-1952 recharge was detected at the water table at four of the six irrigated sites and at the NHP rangeland site, as well as in water from five of the six irrigation wells (Figure 4). At some of the sites, the \(^3\)H content of irrigation water was similar to that of

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**Figure 4.** Profiles of \(^3\)H extracted from unsaturated zone sediment cores and \(^3\)H concentrations in groundwater. Vertical dashed lines represent the estimated maximum concentration of prebomb \(^3\)H in soil water in 2000. Horizontal dashed lines represent water table depths at indicated times. Horizontal bars on data points represent the 1-sigma precision of the analysis.
shallow soil water (GNT), while at other sites the $^3$H content of irrigation water and shallow soil water were quite different (UMA), indicating that recharging water beneath the irrigated fields was a mix of irrigation return flow and modern precipitation. The presence of postbomb $^3$H in groundwater at the SHP cotton sites, despite its general absence in the deep UZ, suggests the presence of fast paths for water movement through the UZ in the vicinity or upgradient from those sites.

4.2. Chemical Storage in the Unsaturated Zone

An inventory of chemical mass stored in the subsoil below a depth of 2 m was calculated separately for Cl$^{-}$ and NO$_3^-$ (using the data in Figures 6 and 7, respectively), as well as for all pesticide compounds (summed as a group), using equation (1):

$$CI = \sum_{-\infty}^{z} C_s \rho dz,$$

where $CI$ is the chemical inventory (M L$^{-2}$), $C_s$ is the concentration in the sediment extract (M M$^{-1}$), $\rho$ is the sediment bulk density (M L$^{-3}$), and $z$ is the depth of the water table at the time of sampling (L).

Subsoil Cl$^{-}$ inventories at the rangeland sites systematically increased from north to south (Table 2 and Figure 6), and they exhibited a positive relation to mean annual air temperature (MAT) (Figure 8). Mean annual wet deposition of atmospheric Cl$^{-}$ near those sites also increased from north to south from 0.35 to 0.53 kg ha$^{-1}$ (National Atmospheric Deposition Program, http://nadp.sws.uiuc.edu/, 2005), respectively. Mean annual precipitation decreased from north to south from about 500 to 420 mm (High Plains Regional Climate Center, 2005; Southern Regional Climate Center, 2005). Although we do not know the details of how those climate parameters varied during the Holocene, the data suggest that climate was an important control on the size of the subsoil Cl$^{-}$ inventories, assuming there were no other geologic sources of Cl$^{-}$ in the UZ. Chloride enrichment near the base of the root zone in arid and semiarid regions is common and is attributed to long-term concentration by evapotranspiration [Scanlon and Goldsmith, 1997; Izbicki et al., 2002; Stonestrom et al., 2002; Walvoord et al., 2003]. The spatial trend in Cl$^{-}$ inventories at the rangeland sites is consistent with the total potential gradients measured at those sites (Figure 3). The upward potential for water movement at the SHP rangeland site during this study indicates that recharge, and thus Cl$^{-}$ flushing from the UZ, was minimal at that site. Recharge was more likely at the NHP rangeland site, as indicated by the

Figure 5. Stable isotope values of water from sediment cores, monitoring wells, and irrigation wells at the unsaturated zone monitoring sites. Line 1 is the global meteoric water line from Craig [1961]. Line 2 is the North Platte, Nebraska, local meteoric water line from Harvey and Welker [2000]. Line 3 is the southern High Plains meteoric water line from Nativ [1988]. The dashed arrows indicate general fractionation trends characteristic of evaporation.

along fractionation trends characteristic of evaporation (Figure 5). Isotopic enrichment of shallow UZ water by evaporation is common in dry environments [Allison and Hughes, 1983; Izbicki et al., 2002]. Water from monitoring and irrigation wells and water extracted from deeper cores at the sites, however, did not exhibit an evaporation signal, indicating that evaporation near the land surface did not substantially alter the isotopic composition of this water before it eventually moved into the deep UZ and aquifer. Mathieu and Bariac [1996] proposed that rapid movement of water below the root zone, possibly by preferential flow, is required to produce isotopically unfractinoned recharge in dry climates. This hypothesis is consistent with the observations of Nativ and Smith [1987] that playa water and groundwater in the SHP were not fractionated isotopically by evaporation. Playas are considered to be areas of focused recharge in the SHP [Wood and Sanford, 1995; Scanlon and Goldsmith, 1997]. Relatively rapid water movement below playas could explain the presence of postbomb $^3$H in groundwater and its absence in the deep UZ under interplaya areas.
downward potential for water movement at that site, which would promote Cl– flushing from the UZ. The Cl– concentration gradient across the water table at the SHP rangeland site could support upward diffusion of Cl– into the UZ; however, the Cl– profile at that site indicates that this process probably contributed only small amounts of Cl– to the UZ. The increase in rangeland Cl– inventories from north to south implies that conversion of rangeland to irrigated cropland could result in larger groundwater Cl– concentrations in the SHP aquifer than in the NHP aquifer if that Cl– was mobilized by irrigation return flow.

[19] The median Cl– inventory under the irrigated fields was about 60% as large as the median Cl– inventory under irrigated alfalfa fields in the Amargosa Desert (Figure 9), and the maximum inventory measured at those sites was about two times larger than the maximum inventory at the HP sites. Stonestrom et al. [2003] indicated that the Cl– inventories under those alfalfa fields contained varying proportions of Cl– from agricultural and natural sources, which may also be the case in the HP.

[20] The MPL cotton site is the only one of the irrigated sites to have had KCl applied to the land surface, according to producer records. This may explain the very large Cl– inventory at that site (Table 2), as well as the cyclic pattern in Cl– concentrations in the depth interval from 0 to about 20 m that also contained postbomb 3H (Figures 4 and 6). The Cl– peak centered at a depth of 25 m at the MPL site appears to have been naturally accumulated Cl– that was mobilized by the leading edge of irrigation return flow, on the basis of its depth relative to the postbomb 3H front and the water table. The amount of Cl– stored in that deep peak represents about 37% of the total subsoil Cl– inventory at the MPL site, with agricultural Cl– apparently accounting for the remaining 63%. Chloride peaks centered at depths of 18 and 44 m at the CAL121 and UMA irrigated corn sites (Figure 6), respectively, also appear to have been mobilized by the leading edge of irrigation return flow, on the basis of their depths relative to the postbomb 3H front and the water table. The amount of Cl– stored in those two peaks represents 50 to 80% of the total subsoil Cl– inventory at

Figure 6. Profiles of Cl– extracted from unsaturated zone sediment cuttings and Cl– concentrations in groundwater. Horizontal dashed lines represent water table depths at indicated times. In groundwater, concentrations plotted on a mass basis were calculated from concentrations measured on a volume basis (in parentheses) and porosity and bulk density data from McMahon et al. [2003].
those sites. The remaining Cl⁻ in those inventories presumably was from irrigation water and precipitation because no Cl⁻ (KCl) was applied to the land surface at those sites, according to producer records. The north-to-south increase in the amount of naturally accumulated Cl⁻ that was mobilized by irrigation return flow at UMA, CAL121, and MPL (from 4542 to 5831 to 9103 kg ha⁻¹) supports the idea that conversion of rangeland to irrigated cropland could result in larger groundwater Cl⁻ concentrations in the SHP aquifer than in the NHP aquifer. Chloride concentrations in groundwater at the irrigated sites did increase from north to south (Figure 6), but relating those concentrations to the chemistry of the overlying UZ is complicated by long chemical transit times through the UZ (discussed later in this report), Cl⁻ contributions to groundwater from upgradient recharge areas, and possible Cl⁻ sources in underlying bedrock [Nativ and Smith, 1987].

In the NHP and SHP, subsoil NO₃⁻ inventories under the irrigated sites were 15 to 26 times larger than the inventories under the rangeland sites, which is consistent with the much larger N application rates at the irrigated sites compared to the rangeland sites (Table 2 and Figure 7). As a result, more NO₃⁻ was likely to be transported to the water table at those irrigated sites than at the rangeland sites. The median cropland NO₃⁻ inventory in the HP was about twice the size of the median inventories under cropland in the Amargosa Desert and in south central Nebraska, but it was half the size of the inventory under dryland corn in southwestern Iowa (Figure 9). The amount of NO₃⁻ stored in the subsoil at the irrigated sites in this study, expressed as a percentage of the total N applied at land surface during their irrigation histories, ranged from about 10 to 30% (Table 2). This range brackets the estimated percentage of N applied to agricultural fields in the U.S. that is lost through leaching (20%) [Howarth et al., 2002]. As was the case with Cl⁻, the subsoil NO₃⁻ inventory at the irrigated sites may not have consisted entirely of applied agricultural N, in which case the percentage of agricultural N leached...
Table 2. Chloride and NO$_3^-$ Inventories Between the Base of the Root Zone and the Water Table and Advective Chemical Transit Times to the Water Table

<table>
<thead>
<tr>
<th>Parameter</th>
<th>IMP</th>
<th>GNT</th>
<th>UMA</th>
<th>CNG</th>
<th>CAL121</th>
<th>CAL122</th>
<th>MWR</th>
<th>JRW</th>
<th>MPL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rangeland, Chase County, Nebraska</td>
<td>2 to 28</td>
<td>2 to 45</td>
<td>2 to 48</td>
<td>2 to 50</td>
<td>2 to 45</td>
<td>2 to 45</td>
<td>2 to 15</td>
<td>2 to 47</td>
<td>2 to 42</td>
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<td>Irrigated Corn, Perkins County, Nebraska</td>
<td>360</td>
<td>1,506</td>
<td>5,645</td>
<td>2,005</td>
<td>11,665</td>
<td>2,726</td>
<td>11,982</td>
<td>10,040</td>
<td>24,456</td>
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<td>70</td>
<td>1,827</td>
<td>1,051</td>
<td>5,400</td>
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<td>1,028</td>
<td>27</td>
<td>620</td>
<td>716</td>
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<td>Rangeland, Morton County, Kansas</td>
<td>6.8$^a$</td>
<td>149$^b$</td>
<td>155$^b$</td>
<td>6.6$^a$</td>
<td>190$^b$</td>
<td>189$^b$</td>
<td>4.2$^a$</td>
<td>169$^b$</td>
<td>120$^b$</td>
</tr>
<tr>
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<td>-</td>
<td>5,960</td>
<td>4,805</td>
<td>-</td>
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<td>8,316</td>
<td>-</td>
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<td>0.31</td>
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<td>0.20</td>
<td>0.12</td>
<td>-</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>Irrigated Cotton, Cochran County, Texas</td>
<td>-</td>
<td>0.31</td>
<td>0.22</td>
<td>-</td>
<td>0.20</td>
<td>0.12</td>
<td>-</td>
<td>0.12</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Chemical Inventory

| Chemical accumulation zone, m below land surface | 2 to 28   | 2 to 45   | 2 to 48   | 2 to 50   | 2 to 45   | 2 to 45   | 2 to 15 | 2 to 47 | 2 to 42 |
| Cl$^-$ inventory (equation (1)), kg ha$^{-1}$    | 360       | 1,506     | 5,645     | 2,005     | 11,665    | 2,726     | 11,982  | 10,040  | 24,456  |
| NO$_3^-$ inventory (equation (1)), kg N ha$^{-1}$| 70        | 1,827     | 1,051     | 5,400     | 1,608     | 1,028     | 27      | 620     | 716     |
| Time-weighted average N application at land surface, kg N ha$^{-1}$ yr$^{-1}$ | 6.8$^a$   | 149$^b$   | 155$^b$   | 6.6$^a$   | 190$^b$   | 189$^b$   | 4.2$^a$ | 169$^b$ | 120$^b$ |
| Total N applied to field, kg N ha$^{-1}$        | -         | 5,960     | 4,805     | -         | 8,170     | 8,316     | -       | 5,070   | 5,040   |
| NO$_3^-$ inventory/N applied                     | -         | 0.31      | 0.22      | -         | 0.20      | 0.12      | -       | 0.12    | 0.14    |

Advective Chemical Transit Time To Water Table

| Water flux (equation (2)), mm yr$^{-1}$ | 70  | 102 | 111   | 5$^c$ | 54  | 39  | 0.2$^a$ | 32  | 17  |
| Depth to water table, m                 | 25  to 28 | 34  to 45 | 33  to 48 | 50  | 27  to 45 | 17  to 45 | 15  | 33  to 47 | 34  to 42 |
| Depth-weighted average volumetric water content | 0.240 | 0.253 | 0.258 | 0.092 | 0.101 | 0.113 | 0.148 | 0.128 | 0.151 |
| Advective chemical transit time (equation (3)), years | 86  to 96 | 84  to 112 | 77  to 112 | 2,000$^c$ | 51  to 84 | 49  to 130 | 10,500$^o$ | 132  to 188 | 302  to 373 |

$^a$Assumed to equal two times the total inorganic N concentration in wet deposition at the nearest National Atmospheric Deposition Program site (http://nadp.sws.uiuc.edu/, 2005). Biological fixation of atmospheric N$_2$ is not included in this estimate, but it could be an important source of soil N at the rangeland sites.

$^b$From producer records.

$^c$Chloride mass balance.
into the subsoil may have been less than 10 to 30. Overestimating the amount of agricultural N leached below the root zone has implications for calculating N mass balances in the root zone and possibly for determining appropriate N application rates at the land surface.

[22] Previous studies identified natural reservoirs of subsoil NO$_3^-$ in some areas of the HP that were larger than the NO$_3^-$ inventories measured under the irrigated sites and reported in Table 2 [Boyce et al., 1976; McMahon et al., 2003; Walvoord et al., 2003]. Nitrate in those reservoirs presumably was produced by oxidation of reduced N in the root zone or subsoil [Boyce et al., 1976], with subsequent concentration of NO$_3^-$ near the base of the root zone by evapotranspiration [Walvoord et al., 2003]. That may have been the case for the CHP rangeland site, which contained a NO$_3^-$ inventory that was about 3 to 9 times larger than the inventories at the irrigated sites (Table 2 and Figure 7). The large variability in the size of the NO$_3^-$ inventories under the three rangeland sites indicates that the aerial distribution of those large natural NO$_3^-$ reservoirs was sporadic. Identifying the factors controlling their distribution is important because of their potential to contaminate groundwater if future land use or climate changes were to increase recharge to the aquifer. The large NO$_3^-$ reservoir described by Boyce et al. [1976] occurred in loess deposits in the NHP and, in our study, there was a significant ($p < 0.001$) positive Spearman correlation between the clay + silt content and NO$_3^-$ concentration in UZ sediments. Thus it appears that lithology is one of possibly several factors that control the distribution of these large NO$_3^-$ reservoirs. This positive correlation could be the result of less water movement for flushing and more reduced N for oxidation in fine-grained sediments compared to coarse-grained sediments. Boyce et al. [1976] also observed that less NO$_3^-$ accumulated under depressions in the land surface than under flat terrain; therefore slope also appears to be a factor controlling NO$_3^-$ accumulation. Plant uptake, which is dependent on plant density and species, also may be important in controlling both the water balance and NO$_3^-$ accumulation in the UZ because prairie vegetation commonly is N limited [Blair et al., 1998]. In addition, climate is an important controlling factor because of its influence on recharge and evapotranspiration.

[23] The downward movement of some NO$_3^-$ peaks at irrigated sites relative to control sites in arid and semiarid regions has been interpreted as mobilization of naturally accumulated NO$_3^-$ by irrigation return flow [Boyce et al., 1976; Stonestrom et al., 2003]. The largest NO$_3^-$ peak at the CAL121 corn site in the CHP moved downward by about 11 m relative to the peak at the CHP rangeland site (CNG) (Figure 10a). Values of $\delta^{15}$N associated with the peak NO$_3^-$ concentrations at both sites were essentially indistinguishable from each other and within the range of values (about 3 to 8%) associated with natural soil N [Heaton, 1986; Kendall and Aravena, 2000]. In contrast, $\delta^{15}$N values for NO$_3^-$ above the peak at the irrigated site ranged from −0.5 to 0.2‰ and are similar to values for N in fertilizer and in nitrogen-fixing plants [Hübner, 1986; Vitoria et al., 2004]. Small NO$_3^-$ peaks below the main peak at CAL121 are thought to be residual from the declining water table on the basis of water level, tritium, and NO$_3^-$ data, and could be from agricultural sources such as manure on the basis of their $\delta^{15}$N values. Thus the $\delta^{15}$N data support the interpretation that the CAL121 NO$_3^-$ peak centered at 14.5 m was naturally accumulated NO$_3^-$ that was mobilized by irrigation return flow. In this case, 57% of the subsoil NO$_3^-$ inventory
at CAL121 consisted of naturally accumulated NO$_3^-$ and the actual percentage of applied agricultural N residing in the subsoil would be reduced from about 20 to 8.

Oxygen isotope data for the large (>5 µg N g$^{-1}$) subsoil NO$_3^-$ peaks at CNG and CAL121, and at the NHP irrigated-corn sites (GNT and UMA), plot above the line representing hypothetical $\delta^{18}$O values for NO$_3^-$ produced by microbial nitrification in the soil zone, assuming the O was derived from a 2:1 proportion of unfractionated H$_2$O-O ($-12.5$ to $-7.5\%_o$) and atmospheric O$_2$-O (-$23.8\%_o$) [Andersson and Hooper, 1983; Hollocher, 1984]. In contrast, oxygen isotope data for NO$_3^-$ from the monitoring wells screened within 3 m of the water table at the rangeland and irrigated sites plot below that line (Figure 11). Relative $^{18}$O enrichment could be expected in the large natural NO$_3^-$ deposits if they were formed under conditions of evaporation, if minor amounts of denitrification were to have occurred in the finer-grained sediments with which they may be associated, or if they contained a small percentage of atmospheric NO$_3^-$ [Amberger and Schmidt, 1987; Michalski et al., 2004]. The NO$_3^-$ peaks at GNT and UMA could contain a small percentage of NO$_3^-$ fertilizer, which can be enriched in $^{18}$O, because it was applied to those fields along with anhydrous ammonia. Anhydrous ammonia was the only form of N applied at CAL121, according to producer records.

The $^{18}$O data imply that large subsoil NO$_3^-$ reservoirs were not the primary source of elevated NO$_3^-$ concentrations in groundwater at the CAL121 and GNT irrigated sites (Figure 11), assuming that all the large NO$_3^-$ reservoirs were similarly enriched in $^{18}$O and that NO$_3^-$ recycling in the subsoil was not important. Nitrate recycling in the soil zone can substantially alter $^{18}$O signals in NO$_3^-$ [Mengis et al., 2001; Michalski et al., 2004]. At those two sites, the $\delta^{15}$N values for NO$_3^-$ in the large subsoil peaks ranged from 5.5 to 7.3%o and in groundwater they ranged from 3.4 to 4.4%o. It is not likely that subsoil NO$_3^-$ would become depleted in $^{15}$N with further transport to the water table; therefore the $\delta^{15}$N data are consistent with the hypothesis that the elevated groundwater NO$_3^-$ concentrations were unrelated to the large subsoil NO$_3^-$ peaks at those two sites. In that case, NO$_3^-$ concentrations in the aquifer could increase with time as the large mass of NO$_3^-$ that still resides under irrigated fields reaches the water table. The groundwater $\delta^{18}$O values could be consistent with a fertilizer source for the NO$_3^-$, possibly with some volatilization or microbial

![Figure 10](image1.png)

**Figure 10.** Profiles of NO$_3^-$ (a) concentration and (b) $\delta^{15}$N values in extracts from unsaturated zone sediment at rangeland (CNG) and irrigated corn (CAL121) sites in the central High Plains.

![Figure 11](image2.png)

**Figure 11.** Values of $\delta^{18}$O[NO$_3^-$] and $\delta^{18}$O[H$_2$O] in extracts from unsaturated zone sediment and in groundwater. The solid line represents hypothetical $\delta^{18}$O values for NO$_3^-$ produced by microbial nitrification in the soil zone, assuming the O was derived from a 2:1 proportion of unfractionated H$_2$O-O and atmospheric O$_2$-O [Andersson and Hooper, 1983; Hollocher, 1984].
reworking of agricultural N in the soil zone causing slightly elevated δ^{15}N values compared to fertilizer [Kreitler, 1979].

[26] The types of pesticide compounds detected in the UZ and groundwater reflect the crops grown at those sites. Common corn herbicides (atrazine, alachlor, metolachlor) and their transformation products were detected at the irrigated corn sites and cotton pesticides commonly used in the past (DDT) and present (malathion, norflurazon, pendimethalin, trifluralin) and their transformation products were detected at the irrigated cotton sites (Table 3). Pesticide inventories in the upper 2 m at most of the irrigated sites were substantially larger than at the rangeland sites (Table 3), with more than 99% of the total pesticide inventory residing under the irrigated fields. Unlike Cl^- and NO_3^-, pesticide detections were confined mostly to the upper 2 m of the UZ. The depth intervals from 0 to 2 m contained about 80 to 100% of the total pesticide inventories at all sites with pesticide detections, except for the irrigated site CAL122. These results are similar to those of Sophoceaous et al. [1990], Bayless [2001], and others [Barbash and Resek, 1996] who found that significant pesticide retention and degradation occurred in the shallow UZ. Despite the apparently efficient retention of pesticide compounds in the top 2 m, several pesticide compounds were detected in groundwater at the irrigated sites (Table 3). Komor and Emerson [1994] observed similar patterns in the Sand Plains of Minnesota, having detected pesticide compounds in groundwater even though detections of the compounds in the overlying 5-m-thick UZ were inconsistent. They concluded that macropore water flow controlled pesticide movement through the UZ at their site. Several other studies have also documented the detection of pesticide compounds in groundwater at depths well below their deepest point of detection in the soil [Barbash and Resek, 1996].

[27] Information on pesticide application rates at the land surface was only available for atrazine at the irrigated-corn sites. Time-weighted average atrazine application rates at those sites ranged from about 1100 to 2100 g ha^{-1} yr^{-1} according to producer records. The summed masses of atrazine, deethylatrazine, and deisopropylatrazine stored in the soil zone at each of the corn sites accounted for about 0.1 to 6% of the atrazine applied to the land surface on a yearly basis. These small amounts of atrazine + metabolites are in general agreement with the amount of atrazine stored in the soil zone at several other sites, including other HP sites [Barbash and Resek, 1996; Juracek and Thurman, 1997; Bayless, 2001], and they indicate that the UZ was not a major storage compartment for atrazine, deethylatrazine, and deisopropylatrazine. Juracek and Thurman [1997] and Bayless [2001] showed that the small amount of atrazine stored in the soil zone under Kansas and Indiana corn fields, respectively, was the result of atrazine transformation to several degradation products.

4.3. Water Flux and Chemical Transit Times in the Unsaturated Zone

[28] Water flux in the UZ was estimated by using tritium data from the irrigated sites and NHP rangeland site (Figure 4) and equation (2):

\[ q = \frac{\theta}{t} \]

where \( q \) is the water flux (L T^{-1}), \( \theta \) is the depth-weighted average volumetric water content (L^3 L^{-3}), \( z_q \) is the depth to either the interface between prebomb and postbomb ^3H or the ^3H center of mass (L), and \( t \) is the time elapsed from 1953 or 1963 to the sampling time (T). The years 1953 and 1963 correspond to the start of atmospheric testing of nuclear weapons and the peak in atmospheric tritium concentrations, respectively. Equation (2) assumes that flow was one-dimensional and vertically downward, that \( \theta \) was at steady state, and that vapor transport was insignificant. Scanlon [1992] calculated a downward vapor flux of about 6 mm yr^{-1} in the UZ of the Chihuahuan Desert, but those sediments were likely to have been drier than the sediments under our irrigated sites, where there was sufficient moisture to support gravity-driven flow below the root zone (Figure 3). The absence of ^3H below the root zone at the CHP and SHP rangeland sites also indicates that vapor transport of ^3H was negligible. Water flux at the CHP and SHP rangeland sites was estimated using the Cl^- mass balance method [McMahon et al., 2003; Watwood et al., 2003], because of the absence of ^3H below the root zone at those sites. The resulting water flux estimates for all sites are listed in Table 2.

[29] Water fluxes at the irrigated sites ranged from 17 to 111 mm yr^{-1} and they ranged from 0.2 to 70 mm yr^{-1} at the rangeland sites (Table 2). The Cl^- based flux at the SHP rangeland site, and possibly at the CHP rangeland site, must have represented past conditions because upward hydraulic gradients existed in the UZ at the SHP site during this study (Figure 3) [McMahon et al., 2003]. The estimated water flux at that site is within the range of Cl^- based fluxes reported for interplaya areas of the SHP [Scanlon and Goldsmith, 1997]. The inverse relation between rangeland water flux and MAT (Figure 8), and the positive relation between rangeland Cl^- inventory and MAT, further illustrate the influence of climate on water fluxes and subsoil chemical inventories in semiarid rangeland settings. Water fluxes at the irrigated sites were, on average, 1.5, 9.3, and 122 times larger than the water fluxes at the NHP, CHP, and SHP rangeland sites, respectively. This north to south proportional increase in water fluxes between cropland and rangeland resulted, in part, from climatic differences between the north and south that promoted more evapotranspiration in the SHP than in the NHP. The proportional increase in water fluxes supports the conclusion that conversion of rangeland to irrigated cropland would have a larger impact on groundwater recharge in the SHP than in the NHP, as previously discussed.

[30] Wherever possible, water fluxes calculated using the ^3H data were compared to water fluxes calculated using the Cl^- peak displacement method [Stonestrom et al., 2003]. Chloride profiles at the UMA and CAL121 irrigated corn sites in the NHP and CHP, respectively, and at the MPL irrigated cotton site in the SHP, contained large Cl^- peaks near the leading edge of the postbomb ^3H front (Figures 4 and 6), indicating that they may have represented naturally accumulated Cl^- that was mobilized by irrigation return flow. The Cl^- peaks at the NHP, CHP, and SHP moved downward by 42, 15, and 18 m, respectively, relative to those under the corresponding rangeland sites. Taking into account the time elapsed since irrigation began at those sites (Table 1) and the depth-weighted average volumetric water content (Table 2), water fluxes at those NHP, CHP, and SHP
### Table 3. Pesticide Compound Inventories in the Unsaturated Zone and Concentrations in Groundwater From Water Table Monitoring Wells

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Northern High Plains</th>
<th>Central High Plains</th>
<th>Southern High Plains</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IMP</td>
<td>GNT</td>
<td>UMA</td>
</tr>
<tr>
<td></td>
<td>Rangeland, Chase County, Nebraska</td>
<td>Irrigated Corn, Perkins County, Nebraska</td>
<td>Irrigated Corn, Yuma County, Colorado</td>
</tr>
<tr>
<td>Number of Samples</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Pesticide compound inventory (equation (1)), g ha⁻¹</td>
<td>0</td>
<td>904</td>
<td>167</td>
</tr>
<tr>
<td>Compounds detected</td>
<td>no detections</td>
<td>acetylchol ESA b</td>
<td>acetochlor OXA d</td>
</tr>
<tr>
<td>Shallow inventory as percentage of total inventory</td>
<td>-</td>
<td>100</td>
<td>84</td>
</tr>
<tr>
<td>Unsaturated Zone (0 – 2 m)</td>
<td>0</td>
<td>29</td>
<td>3</td>
</tr>
<tr>
<td>Compounds detected</td>
<td>deisopropylatrazine</td>
<td>atrazine</td>
<td>atrazine</td>
</tr>
<tr>
<td>Unsaturated Zone (&gt;2 m)</td>
<td>100</td>
<td>81</td>
<td>6</td>
</tr>
<tr>
<td>Compounds detected</td>
<td>-</td>
<td>atrazine</td>
<td>atrazine</td>
</tr>
<tr>
<td>Groundwater</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Compounds detected</td>
<td>No detections</td>
<td>No detections</td>
<td>No detections</td>
</tr>
</tbody>
</table>

| Unsaturated Zone (0 – 2 m) | 0 | 29 | 3 |
| Compounds detected | atrazine | atrazine | atrazine |
| Unsaturated Zone (>2 m) | 100 | 81 | 6 |
| Compounds detected | - | atrazine | atrazine |
| Groundwater | 0 | 0 | 0 |
| Compounds detected | No detections | No detections | No detections |

- Only detected compounds listed.
- ESA, ethane sulfonic acid.
- SAA, sulfynil acetic acid.
- OXA, oxanilic acid.

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sites were estimated to be 236, 34, and 63 mm yr\(^{-1}\) respectively. These values are within a factor of 1.6 to 3.7 of the \(^3\)H-based water fluxes for those sites (Table 2).

[31] Advective chemical transit time through the UZ was calculated using equation (3):

\[
t_c = \frac{L}{q}
\]

where \(t_c\) is the advective chemical transit time (T) and \(z_t\) is the depth to the water table (L). Equation (3) is subject to the same assumptions as equation (2) and it assumes that chemical movement below the root zone was conservative. Chemical transit times through the UZ under irrigated cropland ranged from 49 to 373 years (Table 2). Lateral spreading of water in the UZ would result in even longer transit times. Chemical transit times under irrigated corn (median = 84 years) were significantly shorter (p < 0.01) than the transit times under irrigated cotton (median = 245 years). This difference is largely a reflection of the larger water fluxes under the irrigated corn sites, rather than a thinner UZ (Table 2). Although the chemical transit times are only approximations, they exceeded the irrigation period at all of the study sites (Tables 1 and 2). This conclusion would not change if transit times were calculated using water fluxes determined by the Cl\(^{-}\) peak displacement method discussed earlier. These long transit times imply that chemicals from irrigated agriculture should not have reached the water table at any of these sites. Indeed, this appears to have been the case at the UMA irrigated corn site and the MPL irrigated cotton site, where the elevated concentrations of \(^3\)H, Cl\(^{-}\) (UMA), NO\(_3\), and pesticide compounds in the UZ did not appear to have reached the water table (Figures 4, 6, and 7 and Table 3). Groundwater at the other irrigated sites contained some combination of elevated \(^3\)H, Cl\(^{-}\) (UMA), NO\(_3\), and pesticide compound concentrations. The discordant finding of long chemical transit times under irrigated cropland and the absence of agrochemicals at the water table is not explainable in the simple framework of matrix flow through the UZ.

[32] The hydrologic, chemical, and isotopic data presented thus far support the interpretation that fast and slow paths for chemical transport existed in the UZ. It is well recognized that fast paths may result from focused recharge under depressions in the land surface, macropore flow, or other preferential flow processes [Freeze and Banner, 1970; Beven and Germann, 1982; Glass et al., 1988; Kung, 1990; Prazak et al., 1992; Delin and Landon, 2002], resulting in relatively rapid transport of NO\(_3\) or other chemicals to the water table. Nieber [2001] suggested that the various preferential flow processes exist at different spatial scales and that focused recharge under depressions in the land surface may occur at a scale from about 10\(^{-1}\) to 10\(^{3}\) m. This scale is applicable to UZ thicknesses in the HP and topographic focusing of recharge is consistent with current models for recharge in the SHP [Wood and Sanford, 1995; Scanlon and Goldsmith, 1997]. Slow paths may occur in fine-grained sediments or under flat terrain [Boyce et al., 1976; Scanlon and Goldsmith, 1997], and possibly in other environments, with evapotranspiration further restricting water movement in both settings.

[33] Conceptual models for fast and slow transport of NO\(_3\) to the HP aquifer are presented in Figure 12. We chose to represent NO\(_3\) transport in the models because substantial subsoil NO\(_3\) reservoirs occurred under rangeland and cropland and because NO\(_3\) is perhaps the most common contaminant in HP groundwater [Litke, 2001]. Fast paths under rangeland would result in relatively small subsoil NO\(_3\) inventories and groundwater NO\(_3\) concentrations because periodic flushing would prevent the buildup of large NO\(_3\) concentrations in the UZ and because of small N inputs at the land surface (see IMP, Figure 7). Slow paths under rangeland would result in the accumulation of large subsoil NO\(_3\) reservoirs (see CNG, Figure 7), in part because of evaporative concentration near the base of the root zone over long periods of time [Walvoord et al., 2003]. Slow paths under rangeland would likely result in the smallest groundwater NO\(_3\) concentrations because of a lack of recharge in those settings (see the upward total potential gradient for MWR in Figure 3). Fast paths under irrigated sites apparently were not sampled during this study but they could result in subsoil NO\(_3\) inventories and groundwater NO\(_3\) concentrations of variable size, depending on N application rates. In contrast, slow paths under irrigated cropland, which the UZ data from our irrigated sites may represent, would result in large subsoil NO\(_3\) reservoirs from agricultural and natural sources (see GNT and CAL121, Figure 7) and possibly produce the largest groundwater NO\(_3\) concentrations when those subsoil NO\(_3\) reservoirs eventually reach the water table. The conceptual models presented in Figure 12 are related to the Wood and Sanford [1995] and Scanlon and Goldsmith [1997] models for recharge to the SHP aquifer and to previous models for preferential chemical transport in the UZ [as summarized by Nieber, 2001], but they extend the concepts of Wood and Sanford [1995] and Scanlon and Goldsmith [1997] to other areas of the HP and they extend the preferential transport concepts to thick UZ in the HP.

[34] Areas of the HP containing fast paths for chemical transport to the water table may be a small part of the total HP area. For example, Wood and Sanford [1995] estimated that about 50% of the recharge to the SHP aquifer occurred through playa basin floors that occupied about 6% of the total land area. Presumably, a much larger fraction of the land area was dominated by slow paths. Our study indicates that substantial inventories of Cl\(^{-}\) and NO\(_3\) resided in the subsoil under rangeland and cropland dominated by slow paths throughout the HP. Implications of these findings with respect to water quality in the aquifer are significant because they indicate that the amount of chemical mass reaching the aquifer could increase with time as chemicals under this larger area reach the water table because of ongoing irrigation or because of conversion of rangeland to irrigated cropland. Furthermore, long transit times in the UZ may delay future improvements in water quality from implementation of best management practices.

5. Conclusions

[35] The combined use of lithologic, hydrologic, chemical, and isotopic data in a study designed along land use and climate gradients provided a new level of understanding of processes affecting the storage and transit time of chemicals in thick UZ in different parts of the agriculturally important
High Plains region. Agricultural application of chemicals at the land surface was an important control on the size of subsoil chemical reservoirs, but not the only one. Long-term evaporative concentration of Cl$^-$/C0 and NO$^3$/C0 near the base of the root zone under rangeland also produced large subsoil chemical reservoirs. In some cases, conversion of rangeland to irrigated cropland resulted in the mobilization of naturally accumulated salts by irrigation return flow. Land use changes like these may have a larger effect on water quality in the SHP aquifer than in the NHP aquifer because the size of the natural salt deposits generally increased from north to south.

[36] Advection chemical transit times through the UZ under cropland were on the order of decades to centuries and were longer than the irrigation histories of the study sites. Nevertheless, agrichemicals and tritium were detected in groundwater at four of the six irrigated sites. The hydrologic, chemical, and isotopic data support the interpretation that fast and slow paths for chemical transport existed in the UZ. Fast paths most likely resulted from focused recharge under depressions in the land surface, including playas and ephemeral streams. Slow paths may occur in fine-grained sediments or under flat terrain, with evapotranspiration further restricting water movement in both settings. Implications of these findings with respect to water quality in the aquifer are significant because they indicate that the amount of chemical mass reaching the aquifer could increase with time as chemicals from agricultural and natural sources that still reside under irrigated fields reach the water table. Results from this study show that establishing links between land use and groundwater quality in areas with thick UZ is complicated by the presence of large subsoil chemical reservoirs and long transit times to the water table.

[37] Acknowledgments. This work was funded by the USGS National Water-Quality Assessment (NAWQA) program. Matric-potential data collection in the CHP and SHP was a collaborative effort between the Kansas Geological Survey (CHP), Texas Bureau of Economic Geology (SHP), and the USGS. We thank Jack Barbash, Bridget Scanlon, Marios Sophocleous, David Stonestrom, and anonymous reviewers for the journal for their comments on earlier drafts of this manuscript. The cooperation of landowners, who agreed to the installa-
tion and long-term operation of monitoring equipment on their land and who provided historical information on the agronomic practices used at the sites, is gratefully acknowledged.

References


Andersson, K. K., and A. B. Hooper (1983), \( \text{O}_2 \) and \( \text{H}_2\text{O} \) are each the source of \( \text{NO}_3 \) in \( \text{NO}_3 \) produced from \( \text{NH}_3 \) by *Nitrosonomonas*. \( ^{15} \text{N} \) evidence, *FEBS Lett.*, 164, 236–240.


McMahon, P. B., K. F. Denney, R. L. Michel, M. A. Sophocleous, K. M. Ellett, and D. B. Hurlbut (2003), Water movement through thick unsa-


