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Impacts of Land Use Change on Nitrogen Cycling Archived in Semiarid Unsaturated Zone Nitrate Profiles, Southern High Plains, Texas

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Nitrate (NO_3) profiles in semiarid unsaturated zones archive land use change (LUC) impacts on nitrogen (N) cycling with implications for agricultural N management and groundwater quality. This study quantified LUC impacts on NO_3 inventories and fluxes by measuring NO_3 profiles beneath natural and rainfed (nonirrigated) agricultural ecosystems in the southern High Plains (SHP). Inventories of NO_3—N under natural ecosystems in the SHP normalized by profile depth are extremely low (2−10 kg NO_3—N/ha/m), in contrast to those in many semiarid regions in the southwestern U.S. Many profiles beneath cropland (9 of 19 profiles) have inventories at depth that range from 28−580 kg NO_3—N/ha/m (median 135 kg/ha/m) that correspond to initial cultivation, dated using soil water Cl. These inventories represent 74% (median) of the total inventories in these profiles. This NO_3 most likely originated from cultivation causing mineralization and nitrification of soil organic nitrogen (SON) in old soil water (precultivation) and is attributed to enhanced microbial activity caused by increased soil wetness beneath cropland (median matric potential −42 m) relative to that beneath natural ecosystems (median −211 m). The SON source is supported by isotopes of NO_3 (δ^{15}N: +5.3 to +11.6; δ^{18}O: +3.6 to +12.1). Limited data in South Australia suggest similar processes beneath cropland. Mobilization of the total inventories in these profiles caused by increased drainage/recharge related to cultivation in the SHP could increase current NO_3—N levels in the underlying Ogallala aquifer by an additional 2−26 mg/L (median 17 mg/L).

1. Introduction

How can LUC impact nitrogen cycling and ultimately affect groundwater quality? Many studies have shown that changes from natural ecosystems to agricultural ecosystems decreased soil organic N (SON), which is highly correlated with reductions in soil organic carbon (SOC) (e.g., $r^2 = 0.7$ (*1*)). Cultivation in prairie soils in western Canada caused large losses in ON (31−56%) and OC (41−53%) (*2*). Reductions in SON and SOC are attributed to decreased plant organic matter inputs and increased outputs through erosion, crop harvests, and decomposition of organic matter (*3*). Cultivation breaks up the aggregate structure of soil, which influences soil wetness and oxygenation and increases conversion of SON to NO_3 and SOC to the greenhouse gas, CO_2 (*3*). Experimental results indicate that net N conversion to NO_3 is linearly related to soil wetness (matric potential between −400 and −1 m) (*4*). Conversion of SON to NO_3 is a two step process involving mineralization (ammonification) which converts SON to NH_4 and nitrification which converts NH_4 through NO_2 to NO_3. Therefore, cultivation can result in creation of NO_3 reservoirs. Oxidation of SON during initial cultivation and swamp reclamation based on groundwater $\delta^{15}N_{NO_3}$ of +4.7 to +11.4‰ resulted in contamination of the Coastal Plain aquifer in Israel (*5*). In semiarid regions, increased drainage below the root zone and groundwater recharge generally occur when natural grassland and shrubland ecosystems are converted to rainfed (nonirrigated) agricultural ecosystems (*6*). Increased drainage also increases soil wetness which can enhance microbially mediated mineralization and nitrification, and create NO_3 reservoirs. Mineralization and nitrification of SON are also found in many agricultural areas today and are used as a source of NO_3 for crops (*7*).

In addition to creation of NO_3 reservoirs, LUC can also mobilize these NO_3 reservoirs, including any that existed prior to cultivation. Increased drainage/recharge beneath rainfed cropland in semiarid regions can displace NO_3 reservoirs into underlying aquifers. Irrigation also increases drainage/recharge from excess irrigation applications and results in mobilization of NO_3 reservoirs. Examples of NO_3 reservoirs that existed prior to LUC include NO_3 accumulations from atmospheric deposition and evapotranspirative concentration in the southwestern U.S. (*8*) and from N fixation by leguminous natural vegetation, as evidenced by high NO_3/Cl ratios relative to those in precipitation in Senegal (*9*). Changes in land use from natural ecosystems to cropland are also associated with additional inputs of N from inorganic and organic fertilizers (*10*), from N fixation by leguminous crops (*9*), and from NO_3 in irrigation water (*11*).

Studies that evaluate impacts of LUC on biogeochemical cycles are generally limited by the absence of monitoring data prior to cultivation, which occurred over decades to about a century ago in many regions. However, thick unsaturated zones in semiarid regions provide a historical record of system response to LUC that includes precultivation periods. Kinniburgh (*12*) used the phrase: "The unsaturated zone, key to the past, guide to the future." Soil physics and environmental tracer profiles provide a guide to past impacts of LUC on water and nutrient cycling and a key to the future by predicting groundwater concentrations of different elements from mobilization within the unsaturated zone. Pressure data and water content data in the unsaturated zone provide information on LUC impacts on water movement. Soil−water Cl concentrations provide a conservative tracer that essentially tracks water movement and can be used to date soil water and LUC (*13*). Typical Cl bulges in natural semiarid regions can be used to track conditions prior to cultivation, and the top of the Cl bulge generally represents the transition from natural to cropland conditions (*14*). Comparison of NO_3 and Cl data can be used to evaluate nonconservative processes (e.g., additional sources or sinks for NO_3).

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The objectives of this study were (1) to evaluate impacts of LUC on unsaturated zone NO_3 reservoirs in a semiarid region, including possible creation and mobilization of NO_3 reservoirs, and (2) to assess the implications for groundwater quality. To achieve these objectives, NO_3 reservoirs beneath natural and agricultural ecosystems in the southern High Plains were quantified, processes related to the distribution of NO_3 reservoirs were evaluated, and impacts of mobilizing these NO_3 reservoirs on groundwater quality were estimated. This study represents an expansion of previous work that focused on impacts of LUC on the water cycle (*11, 13*). Novel aspects of this study include the large number of unsaturated zone profiles in different land use settings (natural ecosystems, five profiles; rainfed agricultural ecosystems, 19 profiles); understanding of flow and transport processes in the unsaturated zone provided by data on soil water content, matric potential, and Cl concentrations; and availability of long-term records of groundwater NO_3 concentrations from the Texas Water Development Board database (www.twdb.state.tx.us). The results of this study should provide valuable information to agricultural communities and groundwater resource specialists to optimize N management for enhancing soil fertility and sustainability and minimizing future loading to underlying aquifers.

2. Materials and Methods

The study area in the SHP (75 000 km^2) in Texas is underlain by the Ogallala or High Plains aquifer, the largest aquifer in the U.S. Sediments in the unsaturated zone include clays, silts, sands, and gravels of eolian and alluvial origin. The clay content in the upper 1.5–2 m soil zone ranges from 1 to 68% (mean 28%) in the SHP and decreases from north to south (*15*). Land use in the SHP consists of 53% cropland and fallow, 45% grassland/shrubland, and 2% other (Figure 1). Cotton is the dominant crop in the region. Approximately 11% of the SHP (21% of cropland) is irrigated (*16*).

Previous studies in the SHP showed that groundwater recharge beneath natural ecosystems is restricted to ephemeral lakes, termed playas (*17*). Unsaturated flow in interplaya areas is characterized by net upward flow (no drainage/recharge) and accumulation of Cl with a bulge shape, peaking near the root zone, as a result of evapotranspirative enrichment of infiltrating precipitation during the past 10 000–15 000 years since the Pleistocene time (*13*). The time (t, year) required to accumulate chloride is as follows:

$$t = \int_0^z \rho_b \mathrm{Cl}_{uz} dz/(P \times \mathrm{Cl}_p) \quad (1)$$

where ρ_b is bulk density, Cl_{uz} is Cl concentration in the unsaturated zone (mg/kg of dry soil), dz is depth interval, P is mean annual precipitation, and Cl_p is Cl concentration in the precipitation. LUC from natural ecosystems to rainfed agricultural ecosystems increased drainage below the root zone and ultimately groundwater recharge (*11, 13*). Drainage (D) or recharge (R) rates were calculated using the chloride mass balance (CMB) approach by dividing Cl input by Cl concentrations in the unsaturated zone (Cl_{uz}):

$$D = R = \frac{P \times \mathrm{Cl}_p}{\mathrm{Cl}_{uz}} \quad (2)$$

Potassium chloride fertilizer was not applied at any of the cropland sites in this study. Results from 19 profiles beneath rainfed cropland throughout the SHP showed that drainage/recharge increased from 0 mm/year under natural ecosystems in interplaya settings to 24 mm/year (median) under cropland, which represents $\sim$ 5% of mean annual precipitation (*13*). About half of the profiles (10 of 19) had low Cl concentrations throughout the profile with young pore water ages ($\leq$15–62 years, estimated using the CMB method), corresponding to postcultivation, and high downward water fluxes (6–92 mm/year; median 42 mm/year) (*13*). These profiles are referred to as flushed because the precultivation Cl bulge has been completely displaced through the sampled profile. Although a Cl bulge could exist below the sampled depth, this is unlikely because 9 of the 10 "flushed" profiles are found in the southeastern SHP where the water table has risen several meters in the past few decades, indicating that the wetting front has reached the water table (*13*). High tritium levels in groundwater in this region also indicate recent recharge (*18*). The other nine partially flushed profiles have high Cl concentrations toward the base of the profiles (peaks 238–2103 mg/L), reflecting the transition from natural ecosystems (high Cl) at the base to cropland (low Cl) conditions at shallower depths.

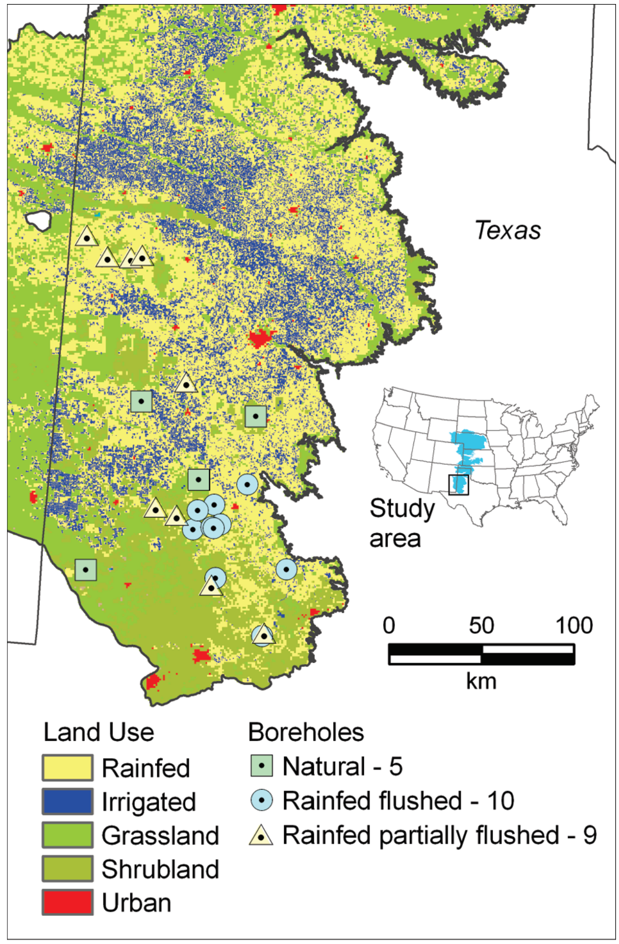

FIGURE 1. Location of sampled boreholes in natural ecosystems (five boreholes) and in rainfed agricultural ecosystems (10 profiles with young soil water, Cl completely flushed and nine profiles with old water at the base, Cl partially flushed). Inset shows location of southern High Plains in the U.S. Generalized land cover is based on National Land Cover Data (NLCD), 1992. Agricultural categories (rainfed and irrigated) represent a combination of NLCD classifications (row crops, 38%, small grains, 12%; pasture/hay, 2%; fallow and orchards, 1%). Irrigation coverage is based on ref *16*.

The same boreholes that were used to evaluate impacts of LUC on the water cycle were also used to evaluate impacts of LUC on NO_3 inventories and fluxes in this study. Most of the methods used in this study are described in ref *13*. A brief description is included in this section. Boreholes were drilled to depths of 2.9–29 m (Figure 1). Core samples were used for laboratory measurement of water content and matric potential. Concentrations of Cl, NO_2, and NO_3 were determined by adding double deionized water to the sediment

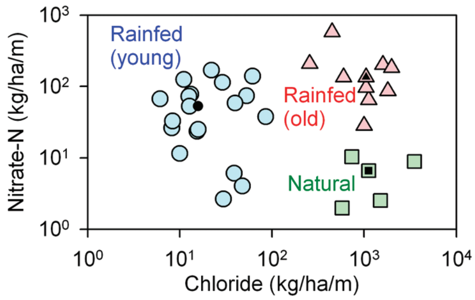

FIGURE 2. Relationship between NO_3—N inventory and Cl inventory in natural ecosystems, and young (postcultivation) and old (precultivation) soil water in rainfed agricultural ecosystems normalized by profile depths. Solid symbols represent median values.

sample in a 1:1 to 2:1 ratio by weight, shaking for 4 h, centrifuging the supernatant, and filtering through 0.2 μm filters. Ion concentrations were analyzed by ion chromatography (Dionex ICS 2000; detection limit 0.01 mg/L). Ion concentrations are expressed on a mass basis as mg ion per kg of dry soil (= supernatant concentration multiplied by extraction ratio, g water/g soil and divided by water density) and as mg ion per L of soil pore water (= mg/kg divided by gravimetric water content and multiplied by water density). Concentrations on a mass basis are useful for interprofile comparisons and to reduce variations from differences in soil water contents due to textural variability. Inventories of ions (kg/ha) were calculated by multiplying depth-weighted salt concentrations (mg/kg) by the interval thickness (m), soil bulk density (kg/m^3), and 10^4 (m^2/ha) for units conversion. Stable isotopes of nitrogen ($\delta^{15}N_{NO_3}$) and oxygen ($\delta^{18}O_{NO_3}$) in NO_3 were analyzed in 10 soil water extracts from six boreholes to determine whether variable sources of NO_3 could be distinguished. The isotopes were analyzed by the bacterial N_2O method at the U.S. Geological Survey Stable Isotope Laboratory in Reston VA (*19*).

3. Results and Discussion

Inventories of NO_3 and Cl, normalized by profile depth, vary by land use: low NO_3 and high Cl beneath natural ecosystems, moderate to high NO_3 and low Cl in young soil water beneath cropland, and high NO_3 and moderate to high Cl in old soil water beneath cropland (Figure 2). All inventories have been normalized by profile depth. All cropland sites are rainfed (nonirrigated).

3.1. Nitrate Profiles beneath Natural Ecosystems. Inventories of NO_3 in five profiles beneath natural ecosystems (grasslands and shrublands) provide information on background levels of NO_3 in the system prior to cultivation. Inventories of NO_3—N are all low (2−10 kg N/ha/m, median 7 kg N/ha/m, ≥1 m depth) and profile concentration means range from 2 to 9 mg NO_3—N/L (median: 7 mg/L) (Table 1, Figures 2, 3c, and Supporting Information Figure S1a). The NO_3/Cl molar concentration ratios in soil water (0.001−1.6) are lower than the [NO_3 + NH_4]/Cl molar ratios in precipitation (3.8−18.2, median 10.9; 1985−2006) from the National Atmospheric Deposition Program (NADP) site at Muleshoe, indicating that no additional source of NO_3 is required to explain the measured NO_3 in these profiles. In contrast to the low NO_3—N inventories in these profiles, Cl inventories are high (580−3500 kg Cl/ha/m, median 1120 kg/ha/m) (Figure 2). Typical Cl profiles are bulge shaped (Figure 3b) and represent accumulation times of 3000−29 000 years, as a result of long-term drying over these times (*13*). Most profiles did not extend deep enough to sample the entire Cl bulge, with the exception of the Lyn06−01 profile. The soils have low water contents and low matric potentials, indicating dry conditions (Figure 3a, Table 1).

3.2. Nitrate Inventories in Young Soil Water Representing Rainfed Agriculture (Postcultivation). Concentrations of NO_3 in soil water, which infiltrated after the land was converted to cropland (postcultivation or young soil water; >15 to >89 years ago in different profiles (Table 1)), provide information on NO_3 levels associated with agriculture. A total of 10 of the 19 profiles had the precultivation Cl bulge completely flushed through the sampled profile and young soil water throughout, whereas the remaining nine profiles had young soil water restricted to the upper 1.6−8.9 m zone underlain by old (precultivation) water with high Cl concentrations representing the top of the Cl bulge. Inventories of NO_3—N in this young soil water range from 3 to 169 kg/ha/m (median 53 kg/ha/m) (Table 1). Many of the profiles (seven profiles) have low NO_3—N concentrations below the root zone (1 m) with peak concentrations from 8 to 26 mg/L (Table 1). The remaining 12 profiles have higher NO_3—N concentrations with distinct peaks from 38 to 287 mg/L with peak depths from 1.0 to 4.6 m (Figure 3i and o).

Potential sources of NO_3 in these young soil waters include atmospheric deposition, fertilizers, biological fixation, and mineralization, and nitrification of soil organic nitrogen (SON). The dominant fertilizers applied in the SHP are ammonium based. Although pesticides and herbicides could be used to track a fertilizer source, previous studies of soils under two irrigated fields in the SHP indicate that pesticides and herbicides are retained or degraded in the upper 2 m of the soil zone (*10*). SON does not represent an original source and could ultimately be derived from atmospheric deposition, biological fixation, and/or fertilizers. Molar ratios of NO_3/Cl in soil water are up to 59 (Table 1) and exceed molar ratios found in precipitation (3.8−18.2) in many profiles indicating an additional source of NO_3 to the system, most likely fertilizer. Isotopic values in young soil water range from +4.7 to +8.8‰ for $\delta^{15}N_{NO_3}$ and from +7.1 to +9.1‰ for $\delta^{18}O_{NO_3}$ (Supporting Information, Figure S2 and Table S1). These $\delta^{15}N_{NO_3}$ values are slightly higher than typical NO_3 fertilizers and may be attributed to volatilization of ^{15}N depleted ammonia during or after application of ammonium-based fertilizers and are within the range of $\delta^{15}N_{NO_3}$ values found in soil water in alluvial fans in Texas that were attributed to ammonia volatilization ($\delta^{15}N_{NO_3}$ 2−14; mean 9) (*20*). The $\delta^{15}N_{NO_3}$ values are also consistent with nitrification of reduced SON in the soil zone from other studies ($\delta^{15}N_{NO_3}$: +4 to +8‰ (*21, 22*)). The $\delta^{18}O_{NO_3}$ values are typical of those expected from microbial nitrification of reduced N in ammonium-based fertilizers or of SON in the soil zone assuming the O was derived from a 2:1 proportion of unfractionated H_2O−O and atmospheric O_2−O (+23.8‰) (*23*). Estimates of $\delta^{18}O_{H_2O}$ from precipitation (−22.7 to +4.9‰; median −6.2‰) or groundwater (−9.1 to −4.2‰; median −6.2‰) in the SHP (*18*) would result in $\delta^{18}O_{NO_3}$ of −7.1 to +11.1‰ (median +3.8‰). The $\delta^{18}O_{H_2O}$ values may also be more enriched in the unsaturated zone as a result of evaporation. Therefore, the isotopes cannot distinguish between mineralization/nitrification of SON and nitrification of ammonium-based fertilizers.

Fertilizer application rates are generally based on expected crop yield. Typical yields for rainfed cotton lint are 150 to 300 kg N/ha and recommended N fertilizer application rates for these yields range from 15−30 kg *N*/ha (*24*). Nitrogen application rates reported by land owners for the sampled sites range from 10−30 kg N/ha. Inputs from atmospheric deposition are much lower (0.3−1.8 kg NO_3—N/ha; 0.1−2.8 kg NH_4—N/ha). Estimates of field-measured net mineralization rates (subtracting inputs from irrigation water and harvests) from previous experiments in the SHP range from 12−51 kg N/ha per growing season in this region and are generally higher in more clayey soils (*7*). The original source of the mineralized N could be fertilizer N, biological fixation,

TABLE 1. Soil Physics (Matric Potential and Water Content) and Concentrations and Inventories of Nitrate and Chloride in Sampled Boreholes[a]

		Historical DTW						concentration			inventory		peak	
setting borehole	depth (m)	date	m	DTW 2000 (m)	MP (−m)	WC (g/g)	CMB age (year)	N/Cl (mol/mol)	Cl (mg/L)	N (mg/L)	Cl (kg/ha(−m))	N (kg/ha(−m))	N (mg/L)	depth (m)
natural ecosystems														
And05−02	8.3	1958	26	28	145	0.08	4183	0.002−1.6	477	9.1	5381 (736)	76 (10)	25	2.2
Daw06−01	8.3	1938	31	30	144	0.09	17291	0.002−0.38	2,514	7.2	25643 (3505)	65 (8.9)	34	2.2
Daw03−12	4.7	1938	27	28	278	0.07	3029	0.003−1.4	1,072	6.1	4012 (1120)	24 (6.6)	29	1.1
Lyn06−01	29.0	1979	26	27	283	0.12	29100	0.001−1.1	889	1.6	41046 (1507)	69 (2.5)	8.3	4.3
Ter06−03	24.0	1969	31	23			10780				13200 (577)	45 (2.0)	36	2.7
Median					211	0.08	10780	0.002−1.3	980	6.6	13200 (1120)	65 (6.6)	29	2.2
rainfed agriculture, chloride partially flushed—old water (precultivation)														
Bai05−01	11.4	1979	32	28	63	0.09	3614	0.05−0.53	785	45	3753 (1119)	219 (65)	62	10.1
Bai05−02	6.0	1979	45	52	18	0.13	2914	0.04−0.11	557	15	3047 (1000)	86 (28)	36	6.2
Bai06−01	4.7	1963	23	21	39	0.14	712	2.0−4.5	210	268	820 (448)	1057 (578)	303	3.7
Gai05−01	5.0	1938	13	9	16	0.17	4150	0.09−0.14	377	32	5508 (1807)	265 (87)	52	4.0
Gai05−02	10.7	1938	30	21	2.5	0.17	2206	0.16−1.1	550	79	2430 (1594)	309 (203)	111	9.5
Lam05−01	8.5	1979	38	36	52	0.11	7600	0.006−1.0	1,220	90	8904 (1981)	824 (183)	168	5.3
Mar05−02	8.9	1947	23	34	59	0.09	4370	0.08−7.2	755	67	6731 (1052)	619 (97)	156	2.8
Mar05−04	4.5	1953	31	32	42	0.10	378	0.24−0.81	385	80	455 (597)	103 (135)	88	4.0
Ter05−01	7.1	1969	35	28	78	0.11	300	1.5−2.4	155	120	235 (257)	191 (209)	145	7.1
Median					42	0.11	2914	0.09−1.0	557	79	3047 (1052)	265 (135)	111	5.3
rainfed agriculture, chloride partially flushed—young water (postcultivation)														
Bai05−01	7.7	1979	32	28	13	0.12	82	0.79−16	5.3	12	108 (15)	165 (24)	51	3.4
Bai05−02	2.8	1979	45	52	6.3	0.13	64	0.16−4.0	19	3.0	83 (39)	13 (6.1)	9.4	1.0
Bai06−01	2.5	1963	23	21	26	0.11	43	2.0−15	16	63	54 (29)	2127 (114)	95	2.5
Gai05−01	1.6	1938	13	9	5.0	0.13	44	0.72−1.7	41	17	78 (86)	34 (38)	22	1.3
Gai05−02	8.9	1938	30	21	4.2	0.10	55	3.0−45	8.2	47	108 (13)	640 (78)	231	2.2
Lam05−01	3.4	1979	38	36	6.4	0.15	89	1.6−9.6	20	33	161 (53)	224 (74)	90	2.8
Mar05−02	2.2	1947	23	34	66	0.09	59	3.7−5.9	34	77	94 (61)	212 (139)	175	2.2
Mar05−04	3.4	1953	31	32	25	0.10	71	2.6−8.5	21	32	109 (40)	160 (58)	87	3.4
Ter05−01	5.9	1969	35	28	26	0.13	74	3.9−57	10	83	114 (22)	874 (169)	287	2.2
Median					13	0.12	64	2.0−9.6	19	33	108 (39)	212 (74)	90	2.2
rainfed agriculture, chloride flushed—young water (postcultivation)														
Daw03−02	5.0	1938	22	9	2.1	0.15	34	3.8−31	5.5	30	50 (13)	288 (73)	58	3.5
Daw03−03	4.3	1938	25	7		0.08	62	0.06−0.6	25	2.2	100 (30)	9 (2.6)	10	1.1
Daw03−04	2.9	1938	30	14		0.09	62	0.11−1.4	36	3.1	91 (48)	8 (4.0)	16	1.0
Daw03−05	4.4	1937	14	5	2.2	0.14	36	1.8−10	7.0	12	54 (16)	85 (25)	38	1.3
Daw05−01	4.0	1938	25	10	1.0	0.13	16	4.2−33	4.4	13	25 (8.2)	80 (26)	26	1.0
Daw06−02	9.2	1938	28	10	6.1	0.12	33	1.1−61	3.5	37	50 (6.1)	552 (67)	91	3.4
Daw06−03	7.9	1938	25	10	6.6	0.10	58	3.6−27	8.4	34	88 (13)	366 (53)	78	4.6
How05−01	6.2	1936	20	14	26	0.13	35	3.1−59	5.3	63	57 (11)	647 (125)	254	2.2
Mar05−01	7.5	1947	20	27	12	0.13	23	5.3−40	4.1	15	55 (8.4)	214 (33)	26	3.4
Mar05−03	6.5	1953	34	33	21	0.15	15	0.51−13	4.7	4.8	55 (10)	63 (11)	8.0	1.0
median					6.3	0.13	34	2.5−29	5.4	14	55 (12)	149 (29)	32	1.8

[a] Borehole settings include natural ecosystems, rainfed agricultural ecosystems (chloride partially flushed: old water and young water, and chloride flushed: young water). Depths refer to borehole depths, with the exception of partially flushed young water where depths refer to the flushed zone, historical depth to water (DTW) and associated measurement year, DTW (~year 2000), matric potentials (MP), water contents (WC), chloride mass balance (CMB) ages, range of NO_3−N/Cl molar ratios (based on concentrations in mg/L), Cl and NO_3−N concentrations and inventories, and peak NO_3−N concentrations and associated depths. CMB ages for natural and partially flushed old water are for the entire profile. CMB ages for young water profiles are for the base of the Cl-flushed profile and do not include the root zone age (1 m depth). MP, WC, and concentration values represent depth-weighted means below the root zone (1 m). Inventory values in parentheses are normalized by the sampled borehole depth.

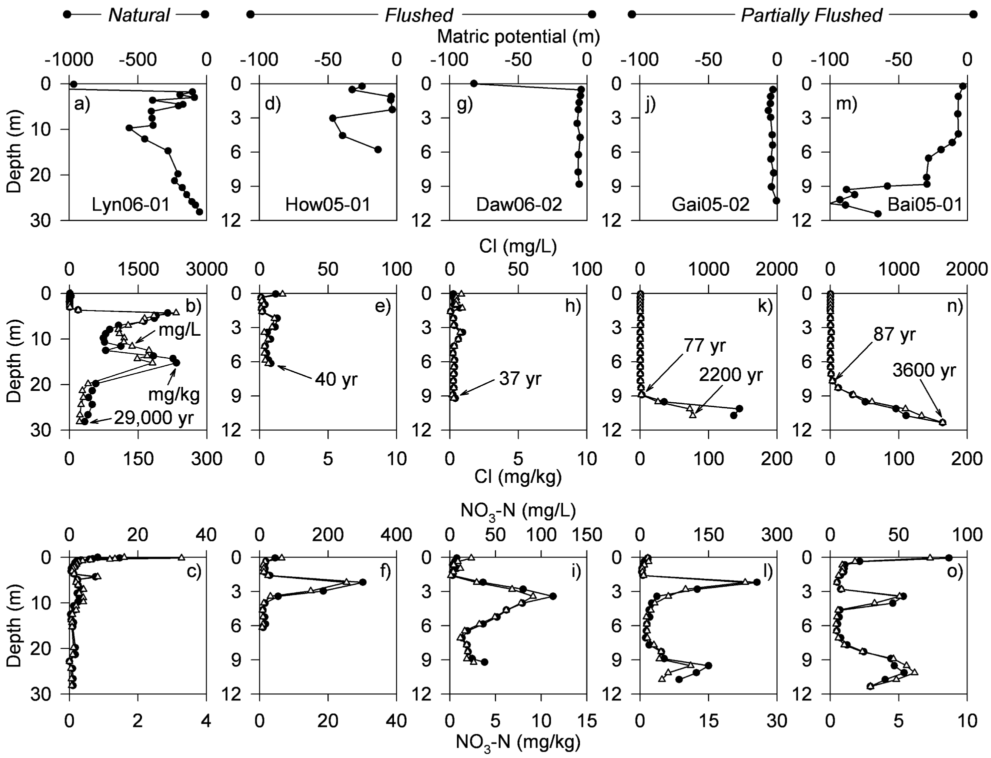

FIGURE 3. Representative matric potential, Cl and NO_3—N profiles in a natural grassland/shrubland ecosystem (Lyn06—01), rainfed agricultural ecosystems where Cl is flushed (young soil water only; How05—01 and Daw06—02), and Cl is partially flushed (young and old soil water; Gai05—02 and Bai05—01). Concentrations are shown in mg/L soil pore water and mg/kg of dry sediment. Chloride mass balance ages for soil pore water are shown at the base of the Cl flushed zone and the base of the profile.

and/or N from long-term atmospheric deposition stored in organic matter in the soil. Previous studies in this region reported ^{15}N recoveries in plants ranging from 19 to 28%, resulting in ~70—80% of the N partially volatilizing and/or remaining in the soil (*7*). Therefore, rates of fertilizer application and SON mineralization are sufficient to account for NO_3 inventories measured in these profiles.

3.3. Nitrate Inventories in Old Soil Water Representing Land Use Change Impacts. The partially flushed Cl profiles (nine profiles) have old (precultivation) soil water toward the base of the profiles with CMB ages up to 7600 years (Table 1). High NO_3 concentrations are found toward the base of these profiles, surrounding the zone where Cl concentrations increase and where soil water ages predate agricultural fertilizer applications (Figure 3l and o). The NO_3—N inventories in this zone range from 28 to 578 kg N/ha/m (median: 135 kg N/ha/m) with peak NO_3—N concentrations of 36—303 mg/L and peak depths from 2.8—10.1 m (Figure 3l and o, Table 1). Some of the profiles did not extend deep enough to sample the entire NO_3—N inventory. The NO_3—N inventories in the mineralized zone (86—1057 kg N/ha) represent 18—89% (median 74%) of total inventories in these profiles below the root zone (1 m). There are several possible explanations for the high NO_3 in this transition zone.

(1) It could reflect high NO_3 concentrations that accumulated under natural ecosystems prior to cultivation. However, the fact that none of the profiles under contemporary natural ecosystems have high NO_3 concentrations does not seem to be consistent with this scenario (Figures 2, 3c; Table 1).

(2) It could result from preferential flow of water with NO_3 from fertilizers or mineralization of SON from shallow zones. However, the gradual changes in NO_3 concentrations would not be expected if preferential flow was the transport mechanism (Figure 3l and o). Uniformly low Cl concentrations in the flushed portion of these profiles provide strong evidence for predominantly piston-type flow in these settings (Figure 3k and n) (*13*).

(3) The most likely source of this high NO_3 zone in old water beneath cropland is mineralization and nitrification of SON that occurred during initiation of cultivation. Isotopes in soil water extracts from the proposed mineralized zones of profiles range from +5.3 to +11.6‰ for $\delta^{15}N_{NO_3}$ and from +3.6 to +12.1‰ for $\delta^{18}O_{NO_3}$, which are consistent with nitrification of reduced SON (Supporting Information, Figure S2, Table S1). The similarity in $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ values in deep NO_3 peaks in old soil water and shallow NO_3 peaks in young soil water indicates that the source of the NO_3 in these two zones is not distinguishable using isotopes. Both old and young NO_3 may be derived from mineralization and nitrification of SON. SON does not represent the original source of the NO_3, which could be atmospheric deposition, N fixation by vegetation or bacteria, and/or a geologic source. Molar ratios of NO_3/Cl in the old soil water are ≤7 (Table 1), which are generally less than ratios found in precipitation (3.8—18.2) and could be derived from atmospheric deposition. Much larger total inventories of NO_3—N are found in other semiarid regions from atmospheric deposition in the southwest U.S. and central High Plains (≤13 600 kg N/ha (*8*)). The lack of high NO_3 under natural ecosystems in the SHP could indicate that the NO_3 from atmospheric deposition over the past 10 000 to 30 000 years was assimilated and immobilized in organic matter in the SHP, or the N as NH_4 could have been adsorbed onto clays, or partially adsorbed onto clays and volatilized as NH_3. Much more enriched N isotopes in paleogroundwater in the SHP ($\delta^{15}N_{NO_3}$ +12.3‰) than in the northern high plains (+1.3‰) was attributed to loss of N from the system (*25*), possibly through ammonia volatilization.

How do SON mineralization and nitrification occur in old soil water? The most likely mechanism is related to increased soil wetness beneath cropland. Mineralization is a microbially mediated process and is thus affected by soil

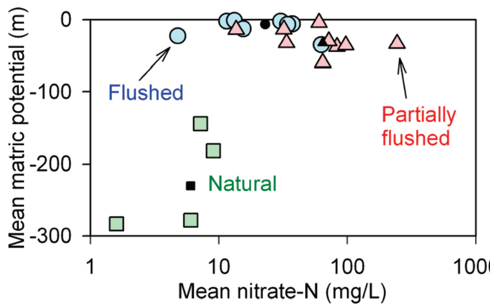

FIGURE 4. Mean matric potential versus mean NO_3—N concentration below the root zone (1 m) in profiles in natural ecosystems, and Cl partially flushed and flushed profiles in rainfed agricultural ecosystems.

water content and temperature (*4, 26*). Experimental results from previous studies indicate that net N mineralization is linearly related to matric potential between −400 and −1 m (*4*). Median matric potentials in the mineralized zones (−2.5 to −78 m; median for all profiles: −42 m) are much higher than median matric potentials in profiles beneath natural ecosystems (−144 to −283 m; median −211 m), indicating wetter conditions that would enhance microbial mineralization and nitrification (Table 1; Figure 4). Cultivation results in downward movement of a wetting (pressure) front and solute (chloride) front (*13, 27*) (Supporting Information, Figure S3). The wetting front is marked by an increase in moisture content and matric potential and migrates ahead of the chloride front. The velocity of the wetting front (v_{wf}) and chloride front (v_{cf}) are as follows:

$$v_{wf} = \frac{q_w}{\theta_w - \theta_d};\quad v_{cf} = \frac{q_w}{\theta_w};\quad \frac{v_{wf}}{v_{cf}} = \frac{\theta_w}{\theta_w - \theta_d} \qquad (3)$$

where q_w is water flux (drainage or recharge rate), θ_w, and θ_d are water contents above and below the wetting front, and v_{wf} / v_{cf} is the ratio of the velocities of the wetting and chloride fronts. The chloride front represents the interface between new water above and old water below (Supporting Information Figure S3). The zone between the chloride front and wetting front does not represent newly infiltrated water but downward displacement of stored water in the profile. This is the main zone where SON mineralization occurs. The mineralization proposed in this study at the beginning of cultivation may be similar to N mineralization flushes associated with drying/rewetting of soils that occurs at much shorter timescales (*28*).

Similar processes may have occurred in semiarid regions in southern Australia, where shallow rooted crops and pasture replaced native eucalyptus vegetation in the early 1900s. High NO_3 concentrations extend into the zone of high Cl concentrations at depth in partially flushed profiles (Figure 5) (Supporting Information, Figure S4, Table S2) (*29, 30*), beneath rainfed cropland, similar to the relationship between NO_3 and Cl in the SHP. The BEM23 profile is from a sandy area at the Borrika site, with a postcultivation drainage rate at least 23 mm/year (*29, 31*). The 6HC profile is also from a sandy location in the Riverlands region, near the Murray River, with a postcultivation recharge rate of 14.8 mm/year (*30*). However, similar NO_3 bulges were also found in the shallow zone of two natural profiles at the Borrika site (*29*); therefore, additional profiles would be required to better understand processes related to LUC in this region.

Many previous studies have shown that SON decreases with cultivation along with SOC (*1, 32, 33*). Bronson (*33*) reported that total N in the 0−0.3 m sampled soil in the SHP was 2500 kg N/ha for native vegetation and 2100 kg N/ha for rainfed cropland, respectively, equivalent to a 400 kg N/ha decrease with cultivation. The reduction in SON is within

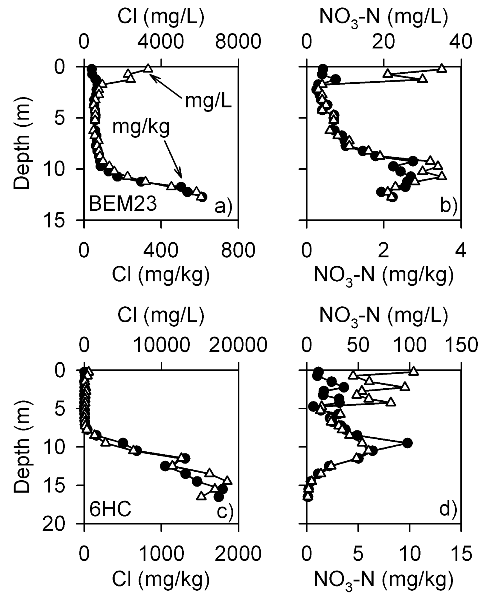

FIGURE 5. Profiles of Cl and NO_3—N in the Borrika region (BEM23) (*29*) and in the Murray Riverlands region (6HC) in rainfed agricultural ecosystems with partially flushed Cl in S. Australia (Supporting Information, Table S2).

the range of increases in NO_3—N from mineralization and nitrification of SON in old water with cultivation in the current study (86−1057 kg N/ha). The organic carbon (OC) reduction (0.25%) reported by Bronson (*35*) from natural ecosystems (0.76% OC) to rainfed cropland (0.51%) in the upper 0.3 m is also consistent with the amount of OC required to explain mineralized N inventories in this study (0.2% OC required for largest measured N inventory, 1000 kg N/ha, Table 1) (Supporting Information).

3.4. Impact of Mobilization of Unsaturated Zone Nitrate on Groundwater Contamination. Contamination of the Ogallala aquifer with NO_3 is widespread in the SHP. Most NO_3 contamination is concentrated in the southern half of the SHP (SHP-S) with 25% of wells exceeding the MCL (10 mg/L NO_3—N) whereas only 1% of wells exceed the MCL in the northern half of the SHP (SHP-N) (Supporting Information, Figure S5). High NO_3—N concentrations in the SHP-S region are attributed in part to the shallow water table (median depth ~ 30 m) relative to the SHP-N region (median depth ~ 63 m) (Figure 5) and to a lower aquifer saturated thickness (median ~15 m) in the SHP-S relative to the SHP-N region (median ~21 m) providing less water to dilute incoming contaminants.

The potential impact of mobilizing NO_3 by increasing recharge beneath cropland areas was evaluated by estimating the groundwater concentration from transport of the unsaturated zone NO_3 inventory and mixing within the aquifer (median saturated thickness, 15 m in the SHP-S, porosity 0.3) (Supporting Information). Mobilizing the entire NO_3—N inventories (100−1270 kg/ha) in the partially flushed profiles into the aquifer would increase groundwater NO_3—N concentrations by 2−26 mg/L (median 17 mg/L). This calculation ignores dispersion. In addition, boreholes were not drilled to the water table; therefore, measured inventories underestimate total inventories. The NO_3—N inventory in the mineralized zone represents 74% (median) of the total sampled inventories in the partially flushed profiles and should continue to contribute substantially to groundwater NO_3 contamination in the SHP. Mobilizing NO_3—N inventories (8−874 kg/ha) in young water (postcultivation) should increase groundwater concentrations relative to current values by 0.2−18 mg/L (median 4.4 mg/L). Unsaturated zone NO_3 profiles provide an excellent archive of past impacts of

LUC on N cycling and indicate that mineralization and nitrification of SON associated with the beginning of cultivation represents a substantial source of NO_3 in this system. Mineralization and nitrification also represent a continuous source of NO_3 that needs to be considered when estimating crop fertilizer requirements.

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Supporting Information Available

Plots of water content, matric potential, chloride, and nitrate for all sampled profiles (Figure S1), stable isotopes of nitrate (Figure S2, Table S1), schematic of relative movement of wetting and chloride fronts (Figure S3), Australian profiles and summary data (Figure S4, Table S2), and example calculations for organic carbon requirements for nitrogen mineralization and for estimating impacts of mobilizing unsaturated zone nitrate into the underlying aquifer. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Murty, D.; Kirschbaum, M. U. F.; McMurtrie, R. E.; McGilvray, A. Does conversion of forest to agricultural land change soil carbon and nitrogen? a review of the literature. *Global Change Biol.* **2002**, *8*, 105–123.

(2) Campbell, C. A.; Souster, W. Loss of organic-matter and potentially mineralizable nitrogen from Saskatchewan soils due to cropping. *Can. J. Soil Sci.* **1982**, *62*, 651–656.

(3) Knops, J. M. H.; Tilman, D. Dynamics of soil nitrogen and carbon accumulation for 61 years after agricultural abandonment. *Ecology* **2000**, *81*, 88–98.

(4) Myers, R. J. K.; Campbell, C. A.; Weier, K. L. Quantitative relationship between net nitrogen mineralization and moisture-content of soils. *Can. J. Soil Sci.* **1982**, *62*, 111–124.

(5) Kaplan, N.; Magaritz, M. A nitrogen isotope study of the sources of nitrate contamination in groundwater of the Pleistocene Coastal Plain aquifer, Israel. *Water Res.* **1986**, *20*, 131–135.

(6) Scanlon, B. R.; Jolly, I.; Sophocleous, M.; Zhang, L. Global impacts of conversions from natural to agricultural ecosystems on water resources: Quantity versus quality. *Water Resour. Res.* **2007**, *43*, article no. W03437.

(7) Chua, T. T.; Bronson, K. F.; Booker, J. D.; Keeling, J. W.; Mosier, A. R.; Bordovsky, J. P.; Lascano, R. J.; Green, C. J.; Segarra, E. In-season nitrogen status sensing in irrigated cotton: I. Yields and nitrogen-15 recovery. *Soil Sci. Soc. Am. J.* **2003**, *67*, 1428–1438.

(8) Walvoord, M. A.; Phillips, F. M.; Stonestrom, D. A.; Evans, E. C.; Hartsough, P. C.; Newman, B. D.; Striegl, R. G. A reservoir of nitrate beneath desert soils. *Science* **2003**, *302*, 5647.

(9) Deans, J. D.; Edmunds, W. M.; Lindley, D. K.; Gaye, C. B.; Dreyfus, B.; Nizinski, J. J.; Neyra, M.; Ingleby, K.; Munro, R. C. Nitrogen in interstitial waters in the Sahel; Natural baseline, pollutant or resource? *Plant Soil* **2005**, *271*, 47–62.

(10) McMahon, P. B.; Dennehy, K. F.; Bruce, B. W.; Bohlke, J. K.; Michel, R. L.; Gurdak, J. J.; Hurlbut, D. B. Storage and transit time of chemicals in thick unsaturated zones under rangeland and irrigated cropland, High Plains, United States. *Water Resour. Res.* **2006**, *42*.

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

(12) Kinniburgh, D. G. the Unsaturated Zone: Key to the Past, Guide to the Future. *2004 GSA Denver Annual Meeting*, November 7−10, 2004, Paper No. 137-1, 2004.

(13) Scanlon, B. R.; Reedy, R. C.; Tachovsky, J. A. 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.* **2007**, *43*, article no. W06423.

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

(15) USDA Soil Survey Geographic Data Base, SSURGO; Natural Resourse Conservation Service, USDA, Misc. Pub. 1527, variably paginated, 1995.

(16) Qi, S. L.; Konduris, A.; Litke, D. W.; Dupree, J. Classification of Irrigated Land Using Satellite Imagery, The High Plains Aquifer, Nominal Data 1992; U.S. Geological Survey Water Resourses Inventory Report 02−4236, 2002.

(17) Wood, W. W.; Sanford, W. E. Chemical and isotopic methods for quantifying ground-water recharge in a regional, semiarid environment. *Ground Water* **1995**, *33*, 458–468.

(18) Nativ, R. Hydrogeology and hydrochemistry of the Ogallala Aquifer, Southern High Plains, Texas Panhandle and Eastern New Mexico; University of Texas, Bureau of Economic Geology, Report of Investigations No. 177,1988.

(19) Casciotti, K. L.; Sigman, D. M.; Hastings, M.; Bohlke, J. K.; Hikert, A. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. *Anal. Chem.* **2002**, *74*, 4905–4912.

(20) Kreitler, C. W. Nitrogen-isotope ratio studies of soils and groundwater nitrate from alluvial fan aquifers in Texas. *J. Hydrol.* **1979**, *42*, 147–170.

(21) Heaton, T. H. E. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere−A review. *Chem. Geol.* **1986**, *59*, 87–102.

(22) Kendall, C. Tracing nitrogen sources and cycling in catchments. In *Isotope Tracers in Catchment Hydrology*; Kendall, C., McDonnell, J. J., Eds.; Elsevier: New York, 1998; pp 519−576.

(23) Andersson, K. K.; Hooper, A. B. O_2 and H_2O are each the source of one O in NO_2- produced from NH_3 by Nitrosomonas - N-15-Nmr evidence. *FEBS Letters* **1983**, *164*, 236–240.

(24) Bronson, K. F.; Boman, R. K. Nutrient management for Texas High Plains cotton production. Texas AgriLife Research and Texas AgriLife Extension. http://lubbock.tamu.edu/soilfertility/pdfs/nutrmgmtforcot.pdf. 2008.

(25) McMahon, P. B.; Bolke, J. K. Regional patterns in the isotopic composition of natural and anthropogenic nitrate in groundwater, high plains USA. *Env. Sci. Technol.* **2006**, *40*, 2965–2970.

(26) Paul, K. I.; Polglase, P. J.; O'Connell, A. M.; Carlyle, J. C.; Smethurst, P. J.; Khanna, P. K. Defining the relation between soil water content and net nitrogen mineralization. *Eur. J. Soil Sci.* **2003**, *54*, 39–47.

(27) Jolly, I. D.; Cook, P. G.; Allison, G. B.; Hughes, M. W. Simultaneous water and solute movement through unsaturated soil following an increase in recharge. *J. Hydrol.* **1989**, *111*, 391–396.

(28) Appel, T. Non-biomass soil organic N - the substrate for N mineralization flushes following soil drying-rewetting and for organic N rendered $CaCl_2$-extractable upon soil drying. *Soil Biol. Biochem.* **1998**, *30*, 1445–1456.

(29) Cook, P. G. The Spatial and Temporal Variability of Groundwater Recharge in the Western Murray Basin, Australia. Ph.D. thesis, Flinders University of South Australia, Bedford Park, 1992.

(30) Cook, P. G.; Leaney, F. W.; Miles, M. Groundwater recharge in the north-east mallee region, South Australia. CSIRO Land and Water Report, Technical Report, 25/04, 2004.

(31) Cook, P. G.; Leaney, F. W.; Jolly, I. D. Groundwater recharge in the Mallee Region and salinity implications for the Murray River-A review. CSIRO Land and Water Technical Report 45/01, 2001.

(32) Davidson, E. A.; Ackerman, I. L. Changes in soil carbon inventories following cultivation of previously untilled soils. *Biogeochemistry* **1993**, *20*, 161–193.

(33) Bronson, K. F.; Zobeck, T. M.; Chua, T. T.; Acosta-Martinez, V.; van Pelt, R. S.; Booker, J. D. Carbon and nitrogen pools of southern High Plains cropland and grassland soils. *Soil Sci. Soc. Am. J.* **2004**, *68*, 1695–1704.

(34) Brady, N. C.; Weil, R. R. *The Nature and Properties of Soils*; 13th ed.; Prentice Hall: NJ, 2002.

(35) Schwartz, R. C.; Dao, T. H. Phosphorus extractability of soils amended with stockpiled and composted cattle manure. *J. Environ. Qual.* **2005**, *34*, 970–978.

ES800792W