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Soil Characteristics and the Accumulation of Inorganic Nitrogen in an Arid Urban Ecosystem

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Abstract

Urbanization represents the extreme case of human influence on an ecosystem. Biogeochemical cycling of nitrogen (N) in cities is very different from that of non-urban landscapes due to the large input of reactive forms of N and the heterogeneous distribution of various land uses that alters landscape connections. To quantify the likely effects of human activities on soil N and other soil properties in urban ecosystems, we conducted a probability-based study to sample 203 plots randomly distributed over the 6,400 km^2 Central Arizona-Phoenix Long-Term Ecological Research (CAP LTER) area, which encompasses metropolitan Phoenix with its 3.5 million inhabitants. Soil inorganic N concentrations were significantly higher in urban residential, non-residential, agricultural, transportation, and mixed sites than in the desert sites. Soil water content and organic matter were both significantly higher under urban and agricultural land uses, whereas bulk density was lower compared to undeveloped desert. We calculated that farming and urbanization on average had caused an accumulation of 7.23 g m^{-2} in soil inorganic N across the CAP study area. Average soil inorganic N of the sampled desert sites (3.23 g m^{-2}) was much higher than the natural background level reported in the literature. Laboratory incubation studies showed that many urban soils exhibited net immobilization of inorganic N, whereas desert and agricultural soils showed small, but positive, net N mineralization. The large accumulation of inorganic N in soils (mostly as nitrate) was highly unusual in terrestrial ecosystems, suggesting that in this arid urban ecosystem, N is likely no longer the primary limiting resource affecting plants, but instead poses a threat to surface and groundwater contamination, and influences other N cycling processes such as denitrification.

Key words: urban; land use; soil; nitrogen; nitrate; Central Arizona-Phoenix LTER.

Introduction

Human activities are now shaping every part of the global ecosystem (McDonnell and Picket 1993; Vitousek and others 1997). Nowhere have human behaviors and activities altered ecosystem structures and functions more radically than in cities (McDonnell and Pickett 1990; Rebele 1994; McDonnell and others 1997; Pickett and others 2001). Today, urbanization is a true global trend and an important component of land transformation worldwide (Vitousek and others 1997; Collins and others 2000). Despite this, nitrogen (N) and carbon (C) cycling of cities and their surrounding ecosystems are still poorly understood due to the lack of extensive, interdisciplinary, and long-term ecological studies (Grimm and others 2000; Pickett and others 2001).

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Cities are open, heterotrophic ecosystems with large inputs and outputs of energy and materials (for example, Folke and others 1997; Luck and others 2001). Human activities in cities increase N inputs to terrestrial ecosystems through: (1) large imports of N in food for humans and their pets; (2) large inputs of commercial fertilizer to support agriculture surrounding cities and public and private ''greenlands'' within cities; (3) N fixed from the atmosphere as a by-product of high-temperature, high-pressure combustion in automobiles and power plants; and (4) in some areas, N fixed by legume crops in the fringing agricultural subsystem (for example, Baker and others 2001). The N released from such activities could change structure and function of ecosystems within the city and, through atmospheric and hydrological transport, affect regional recipient ecosystems surrounding the city (Howarth and others 1996; Lovett and others 2000; Fenn and others 2003a).

The Central Arizona-Phoenix Long-Term Ecological Research area (CAP LTER) is home to 3.5 million people in an ecosystem of 6,400 km^2 (most live in the central urban core that comprises 25% of the total land), with intensified human activities that have profound impacts on N cycling. In a mass balance study, Baker and others (2001) identified commercial fertilizer input and fixation by combustion as two major sources of N input to the CAP ecosystem, with atmospheric NO_x export and denitrification as major N outputs. They estimated an annual net N accumulation of 16.9 kg N ha^{-1} for the CAP ecosystem, but direct measurements with which to quantify the accumulation were lacking. Moreover, it is uncertain where and in what forms N accumulates within the region; various land-use types in the CAP ecosystem could differ dramatically in their ability to store the excess N derived from intensive human activities.

Like other cities, the CAP ecosystem is spatially heterogeneous, with many patches (that is, relatively homogeneous land-use and land-cover types) that vary in ecological content and context (Zipperer and others 2000; Luck and Wu 2002). Land-use change is a dominant force shaping patterns and processes in urban ecosystems, is itself affected and constrained by both environmental context (physical–chemical factors) and socioeconomic factors (Grimm and others 2000), and can directly affect N and C cycling (Boyle and others 1997). Direct human interventions, such as converting desert landscape to irrigated and fertilized lawns, for example, could substantially alter local ecosystem primary production and decomposition rates and consequently the accumulation of N and C. Legacies of past land use, especially in cities like Phoenix that have a long agricultural history, may explain current distributions of N and C. In addition, indirect or inadvertent effects of human action that vary with distance from urban centers (that is, urban–rural gradient concept; McDonnell and Pickett 1990; Pouyat and others 1995; McDonnell and others 1997; Lovett and others 2000; Zhu and Carreiro 2004)—for example, pollutant distributions associated with traffic patterns or housing density—could influence ecosystem processes within a given land-use patch.

To gain a thorough understanding of the CAP urban ecosystem with its diverse land-use types and complicated socioeconomic connections, we used a dual-density, stratified-random sampling design to characterize the entire 6,400 km^2 CAP ecosystem, which contains the rapidly expanding metropolitan Phoenix area, fringing agricultural lands, and surrounding undeveloped Sonoran Desert (Figure 1, Hope and others 2003). The sample will be repeated once every 5 years, to gain long-term perspectives of the urban development and ecosystem variations of the study area. This paper uses a space-for-time substitution approach to determine how urbanization has affected the storage of inorganic N, based on the first sample result. We focus on inorganic N because its availability directly affects terrestrial ecosystem structure and function, and its excess in urban ecosystems is a public health concern in terms of both water and air quality (Townsend and others 2003). We report differences in soil inorganic N and N transformations between major land-use types, using these differences to draw conclusions about the effects of urbanization. Our main research questions are: (1) Does N availability differ between natural desert and human-created land-use types? (2) Does the form of soil N differ between natural desert and human-created land-use types? and (3) To what extent does our field-based estimate of the increase in soil N match the annual N accumulation predicted by an earlier analysis of the whole-ecosystem N budget (Baker and others 2001)?

Methods

Sample Design and Site Selection

We applied a dual-density, randomized, tessellation-stratified design to obtain a large number of spatially dispersed, unbiased sample sites that allow for maximum a posteriori stratification (Hope and others 2003). A grid of four hundred 4 km × 4 km cells was superimposed on the entire 6,400 km^2

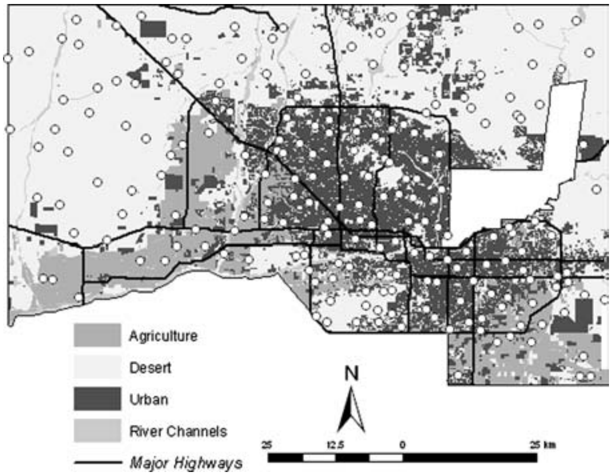

Figure 1. Distribution of study sites in the year 2000 CAP LTER field sampling. The study area encompasses the central urban core, major highways, fringe agricultural area, and hinterland Sonoran Desert. Native American Indian reservation lands on the east corner were excluded from the sample area.

CAP ecosystem, and a random sample point was assigned within every grid cell inside the developed urban core and in every third grid cell outside the urban core, yielding a total sample size of 206 sites (Figure 1). Among them, 203 sites were used for the soil sampling (one site was located on 100% paved parking structure and no soil was available, whereas permission to access was denied for the other two sites). The probability-based sampling design ensured a representative and unbiased characterization of ecological resources in highly heterogeneous urban centers and vast fringe areas subject to potential urban sprawl (Stevens 1997; Peterson and others 1999). Because the sample was designed to collect data for a wide range of applications and is intended to be repeated every 5 years, no a priori stratification according to land cover, land-use type, or other characteristics was used, which ensured flexibility for post-stratification tests. The multiple replicates generated for each land-use type allow the results to be extrapolated to the entire study area while minimizing the variance of parameter estimates and to cover the whole area systematically (Hope and others 2003). The resultant sites consisted of 73 desert (DES), 54 urban residential (URR), 36 urban non-residential (URN), 23 agricultural (AGR), 6 transportation (TRA), and 11 mixed land-use sites (MIX), based on the major land-use categories defined in the CAP LTER (Hope and others 2003). Each site is 30 m × 30 m, with latitudinal and longitudinal coordinates of the plot center chosen randomly prior to the study. Urban residential sites are small, medium, and large single-family lots, with a few multiple-family residential sites, containing both xeric and mesic landscaping. Urban non-residential sites include those used for commercial, industrial, and institutional purposes, urban open spaces like parks, golf courses, and vacant lots, and sites under construction. Agricultural sites include active and fallow croplands, pastures and orchards. Transportation sites include major roads, highways, and airports. There were 11 sites where the 30 m × 30 m field plot covered two or more land-use categories; these are classified as mixed land use. The CAP urban ecosystem is located in the northern Sonoran Desert (33°30′N, 112°10′W), with annual precipitation of 15–20 cm and mean annual air temperatures between 22 and 23°C. Soils ranging from moderate alkalinity to highly calcareous are formed from alluvial fans in the river valleys to various mountainous substrates (Soil Survey of Maricopa County, Arizona 1977).

Soil Sampling

Soils were collected over a 3.5-month period in spring 2000. Plots sampled on any given date were chosen randomly to minimize potential bias that could have been introduced by sampling in a more systematic way (that is, according to land-use type, Hope and others 2005). Plot center was located using a Trimble 'Pro XRS' Global Position System (GPS) with real-time satellite correction. Soil samples were taken at four points: 10 m due north, east, south, and west of plot center, or the nearest possible location in cases where there was a paved surface or nearby power or water lines. Because the GPS coordinates of plot centers were generated randomly within the sample grids prior to the survey, we are confident that our soil collection was objective (for example, not biased towards collecting soils from lawns in urban plots).

Soil cores were taken to a depth of 30 cm using a hand-impacting, 2.5 cm diameter core. Samples were collected with a plastic liner which was retrieved from the corer and capped at both ends with color-coded caps (to distinguish top and bottom) for transport back to the laboratory. Core samples were subsequently separated into 0 to10 cm (surface) and 10 to 30 cm (deeper) depth intervals and soils from the same depth interval of the four replicate cores were pooled, to give one surface and one deeper soil sample for each plot. In addition, one 5.0 cm diameter soil core was taken 1 m north of plot center at each site. In this case it was possible to collect a core only for the 0–15 cm depth interval, because at many sites extraction of deeper 5.0 cm cores proved to be impossible due to highly compacted, stony or very dry soil. These cores were used for the determination of bulk density and stone content, because large-diameter cores create less soil compaction and give better estimates of soil bulk density (Elliott and others 1999).

Soil N Analyses

Soils were sieved (2-mm sieve) within 24 h at field moisture conditions. Ten grams sieved soils were weighed and extracted in 50 ml 2 M KCl solution in a reciprocal shaker for 1 h, and filtered through pre-ashed glass-fiber filters (Whatman GF/A). The filtrate was acidified with 6M hydrochloric acid to pH lower than 2 and stored at 4°C. Filtrates were analyzed for NH_4–N and NO_3–N in the ASU Goldwater Environmental Analytical laboratory on a Bran-Luebbe TrAAcs 800 autoanalyzer, using the alkaline phenol method for NH_4^+ and cadmium reduction method for NO_3^-. The sample detection limit was 0.01 mg L^{-1} for both analyses. Filtrates were analyzed within 1–2 weeks of collection; quality-control checks indicated no change of N concentrations in acidified solutions during a 4-week storage period.

Sub-samples of sieved soils were oven dried at 60°C for more than 48 h and all extractable soil N values were expressed first as mg N per kg oven-dry soil. Additional soils were ashed at 550°C for 2 h for the measurement of soil organic matter (SOM; loss-on-ignition method). Soil moisture content is expressed as g water per 100 g oven-dry (60°C) soil and SOM as g organic matter per 100 g dry mass of soil.

Bulk Density Determination

Bulk density (g cm^{-3}) for each site was determined from the total dry mass (including stone) of the 5 cm soil core (Elliott and others 1999). As an independent check, bulk densities were also calculated based on the combined total dry mass from the 2.5 cm cores. Bulk density showed little difference between the two depth intervals sampled (mean deeper:surface soil bulk density ratio = 1.05; W. Zhu, unpublished data). We thus use a uniform bulk-density dataset (from the 5 cm cores) for all subsequent N-mass calculations. When processing bulk-density samples, stone content (assumed to contain no N) was quantified and corrected to calculate soil mass (particles passing the 2-mm sieve) for each site. Soil mass data were then used to convert soil NO_3–N and NH_4–N concentrations (mg kg^{-1}) to N content (g m^{-2}, 0–30 cm combined) for each site.

Net N Mineralization and Nitrification Potentials

Net N mineralization and net nitrification rates were measured on soils collected from 117 sites, randomly selected from the total 203 sites and covering all land-use groups identified in this survey. The 28-day lab-incubation protocol (Robertson and others 1999) entailed placing 10 g (fresh mass) sieved soils into 250 ml bottles, adjusting soil moisture content to 20% and loosely capping bottles to allow air movement but minimize water loss. Preliminary measurements suggested that 20% soil moisture content was approximately 50% of the water holding capacity of soils collected under various land uses. Incubation bottles were aerated once every week by removing their caps and moisture contents were adjusted. Soils were extracted with 2 M KCl solution after incubation, and inorganic N (NH_4^+ and NO_3^-) in the filtered solution was measured as described above. The difference of inorganic N contents before and after incubation was used to calculate net N mineralization rates. Net nitrification was defined as the difference of NO_3–N before and after the incubation. The moisture adjustment during the lab incubation generated *potential* mineralization and nitrification rates, not *actual* rates expected in the field. The impact of moisture adjustment on interpretation of these potential N mineralization and nitrification rates will be discussed later.

Statistical Analyses

A two-factor analysis of variance (ANOVA) was conducted to quantify the effects of land uses (six levels), depth (two intervals), and their interaction on soil moisture content, organic matter content, and extractable NH_4–N and NO_3–N (mg kg^{-1}). N mass (0–30 cm combined) across land-use groups was analyzed by one-way ANOVA. Data transformations—arcsine square root transformations for the percentage data (moisture, SOM), and log transformations for N data—were performed before statistical analyses to accommodate extremely skewed distributions and unequal variances. Data outliers were removed only under ''extreme'' circumstances, that is, a ''Studentized Residual'' greater than 4.0 after data transformations, and are reported in the text. Residuals were plotted after each ANOVA to examine the validity of the underlying assumptions of the statistical analysis. For comparisons between different land-use groups, means and 95% confidence intervals were calculated based on the transformed data, but were ''back transformed'' to the original units for the

Table 1. Estimates of Population Means and their 95% Confidence Intervals (CI, in parentheses) of Measurements Conducted on Soils from the year 2000 Sampling in the Central Arizona-Phoenix Long-Term Ecological Research (CAP LTER) Study Area

Soils	Moisture (g 100 g^{-1})	Soil organic matter (g 100 g^{-1})	NH_4–N (mg kg^{-1})	NO_3–N (mg kg^{-1})
Surface soils (*0–10 cm*)				
Desert (*n* = 73)	2.52 (2.02, 3.07)	2.10 (1.92, 2.29)	2.35 (2.04, 2.69)	4.36 (3.41, 5.52)
Urban residential (*n* = 54*)	9.13 (7.40, 11.03)	3.22 (2.83, 3.64)	3.98 (3.23, 4.86)	11.46 (7.44, 17.38)
Urban non-residential (*n* = 36*)	8.18 (6.27, 10.31)	3.11 (2.65, 3.61)	4.35 (3.36, 5.55)	14.27 (7.85, 25.35)
Agriculture (*n* = 23*)	7.56 (5.43, 9.99)	2.96 (2.54, 3.42)	2.88 (2.36, 3.48)	19.87 (10.61, 36.52)
Transportation (*n* = 6)	4.74 (2.44, 7.75)	2.24 (1.57, 3.03)	2.89 (1.70, 4.61)	46.20 (6.45, 297.9)
Mixed (*n* = 11)	7.16 (4.46, 10.44)	2.66 (1.97, 3.47)	4.48 (2.30, 8.10)	37.73 (8.62, 154.9)
Deeper soils (*10–30 cm*)				
Desert (*n* = 73)	3.54 (2.96, 4.17)	1.88 (1.71, 2.04)	1.89 (1.61, 2.21)	4.10 (3.00, 5.52)
Urban residential (*n* = 54*)	9.93 (8.63, 11.31)	2.31 (2.09, 2.54)	2.17 (1.82, 2.55)	6.18 (3.89, 9.55)
Urban non-residential (*n* = 36)	9.55 (8.09, 11.10)	2.43 (2.20, 2.68)	2.71 (2.11, 3.43)	12.01 (6.64, 21.14)
Agriculture (*n* = 23)	10.04 (8.03, 12.24)	2.53 (2.15, 2.94)	1.73 (1.30, 2.24)	14.00 (6.79, 27.89)
Transportation (*n* = 6)	9.46 (6.00, 13.60)	2.21 (1.32, 3.32)	2.03 (0.94, 3.73)	28.04 (4.91, 141.6)
Mixed (*n* = 11)	9.22 (6.63, 12.16)	2.43 (1.76, 3.20)	2.49 (1.50, 3.85)	34.82 (8.86, 129.1)

*Soil moisture and organic matter data were arcsine square-root transformed, and NH_4–N and NO_3–N data were natural-log transformed. Estimates for the population means and their 95% CI were calculated based on the transformed data (*outliers were removed, which reduces sample size for the specific measurements and specific land-use groups; see text for details) and back-transformed to their original measurement units.*

ease of interpretation (Zar 1999). Tukey tests were used for multiple comparison analyses. For net N mineralization and net nitrification measurements, data transformation failed to restore normality, so we used the Kruskal–Wallis non-parametric rank statistical method to test for differences among all land-use categories, followed by Dunn multiple comparisons to test for significant difference between specific land-use groups (Zar 1999). The α-value for statistical significance was set at 0.05 unless otherwise stated. All analyses were conducted on SYSTAT 10.2 software (SYSTAT Software Inc. 2002).

Results

Soil Physical–Chemical Properties and Inorganic N Concentrations

Soil characteristics varied dramatically among major land-use types across the CAP ecosystem. Soil moisture content was significantly lower in the desert than in all developed land uses (Tables 1, 2). In the 0–10 cm surface soils, desert sites had a mean moisture content of 2.52 g 100 g^{-1} vs. 9.13 g 100 g^{-1} in the urban residential sites. For the deeper soil interval, desert sites had a mean moisture content of 3.54 g 100 g^{-1}, much less than the 10.04 g 100 g^{-1} in the agricultural sites (Table 1). Soil moisture was significantly lower in the surface than at deeper depth intervals across all land-use types (Table 2). Soil moisture content also varied widely—from less than 1 g 100 g^{-1} in the desert sites to more than 20 g 100 g^{-1} in some urban residential, urban non-residential, and agricultural sites.

Conversely, SOM content was significantly higher in the surface soils than in the deeper soils (Tables 1, 2). Urban residential, urban non-residential, and agricultural sites had significantly higher SOM content than the desert sites (Table 2). Mean SOM content in these three land-use types (that is, the majority of the non-desert sites) was approximately 150% that of desert soils (Table 1).

Extractable NH_4–N in soils varied widely, from less than 1 mg kg^{-1} to more than 100 mg kg^{-1} (Figure 2A). After log transformation, four outliers were further removed from the dataset before statistical analysis (an urban residential site, surface soil: 100.1 mg kg^{-1}, deeper soil: 27.4 mg kg^{-1}; an agricultural site, surface soil: 68.6 mg kg^{-1}; and an urban non-residential site, surface soil: 67.8 mg kg^{-1}), to obtain approximately equal variance across all land-use types. Outlier removal did not change the results of the statistical analysis (Table 2). Urban residential, urban non-residential, and mixed land-use sites had significantly higher extractable NH_4^+ than the desert sites (Tables 1, 2). There was also significantly lower NH_4^+ in agricultural soils than in urban residential soils (Table 2). We found a significant difference in NH_4^+ concentrations between the surface and deeper soil depths, with a mean in the surface soils 1.2–1.8

Table 2. Statistical Summary of the ANOVA Analyses for the Soil Measurements Reported in Table 1

Variables	Sources	Sum of squares	*df*	*F*-value	*P*-value	Tukey comparison summary
Moisture	Land use	5,264.0	5	43.15	0.000	DES < all others
(g 100 g^{-1})	Depth	265.6	1	10.89	0.001	Surface < deep
	L × D	72.8	5	0.597	0.702	
	Residual	9,613.8	394			
SOM	Land use	187.6	5	11.68	0.000	DES < URR, URN, ARG
(g 100 g^{-1})	Depth	28.1	1	8.749	0.003	Surface > deep
	L × D	25.5	5	1.588	0.162	
	Residual	1,262.9	393			
NH_4–N	Land use	8.59	5	7.398	0.000	DES < URR, URN, MIX; AGR < URR
(mg kg^{-1})	Layer	5.63	1	24.21	0.000	Surface > deep
	L × L	1.71	5	1.471	0.198	
	Residual	90.62	390			
NO_3–N	Land-use	143.6	5	15.94	0.000	DES < all others; URR < MIX, TRA; URN < MIX
(mg kg^{-1})	Layer	3.79	1	2.104	0.148	
	L × L	4.45	5	0.494	0.781	
	Residual	710.2	394			

The two-factor analysis of variance (ANOVA) was performed on transformed datasets. Land-use categories were: DES, desert; URR, urban-residential; URN, urban-nonresidential; AGR, agricultural; TRA, transportation; and MIX, mixed. The ''depth'' factor is a categorical variable with two values: surface (0–10 cm soil) and deep (10–30 cm soil). Several outliers had to be removed for the ANOVA, which reduced sample size for particular analyses (see change in residual degree of freedom).

times that of the respective deeper soils (Figure 2A; Table 1). Among the surface soils, low NH_4–N (< 2 mg kg^{-1}) was found in all land-use types; however, samples that had NH_4–N concentrations greater than 15 mg kg^{-1} (9 out of the 203 samples) were found exclusively in urban and agricultural sites (Figure 2A).

Extractable inorganic N in CAP soils was dominated by NO_3^-. The concentration of soil NO_3–N was extremely variable, ranging over four orders of magnitude from less than 1 mg kg^{-1} to over 1,000 mg kg^{-1} (Figure 2B). Log transformation successfully equalized the variance among all land-use types and data distributions after transformation were approximately ''normal''. Analysis of variance and Tukey comparisons demonstrated that the desert sites had significantly lower NO_3^- than all other land uses, with mean NO_3^- concentration in developed land uses 2–10 times higher than in the desert (Table 2). Among the various developed land-use types, mixed and transportation sites had significantly higher NO_3^- than urban residential sites; mixed land-use sites also had significantly higher NO_3^- than the urban non-residential sites (Tables 1, 2). Unlike extractable NH_4^+, the difference between the surface soils and the deeper soils for NO_3^- was not statistically significant (Table 2). Like NH_4^+, low concentrations of extractable NO_3–N (< 2 mg kg^{-1}) were found in both desert and developed sites; the extremely high NO_3–N concentrations, however, were found almost exclusively in non-desert sites (Figure 2B). Among all surface soils sampled, the highest NO_3–N concentration of desert plots was 36.2 mg kg^{-1}, but there were 17 non-desert sites with NO_3–N greater than 100 mg kg^{-1}.

Physical characteristics of soils also differed markedly between land-use types across the CAP ecosystem. Soil bulk density was significantly lower at urban (residential and non-residential) compared to desert sites (Table 3, $P < 0.001$). The highly variable stone proportions (that is, > 2 mm) were likely affecting both bulk density and the actual soil mass contained per unit volume (Table 3). Agricultural sites had a significantly lower stone content, with a mean of 6.43% ($P < 0.001$, Table 3). Corrected for stones, average soil mass per unit volume (particle size < 2 mm) ranged from 0.95 g cm^{-3} in the desert sites to 1.14 g cm^{-3} in the agricultural sites, and was not statistically different among land-use types.

Net N Mineralization and Nitrification Potentials

The change in inorganic N concentration during laboratory incubations (with water content adjusted to 50% of the soil water holding capacity, see Methods) was highly variable, ranging from positive (net N mineralization) to negative (net N immobilization). Variability also was very high

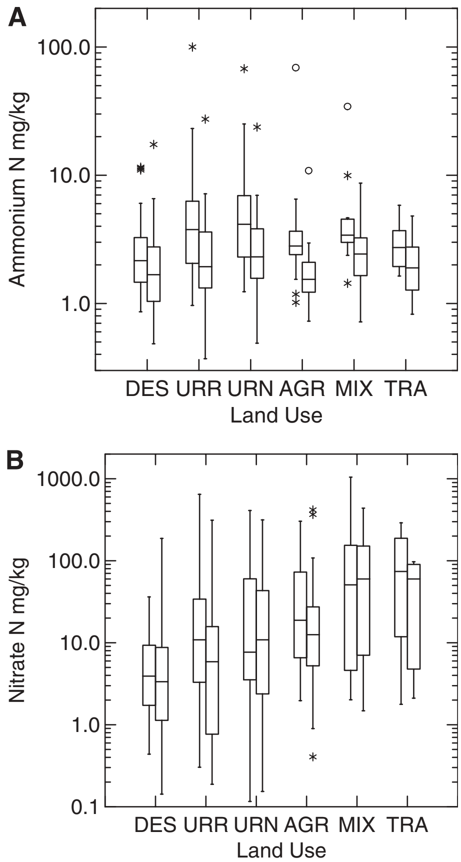

Figure 2. Box plots of soil extractable NH_4–N (**A**) and NO_3–N (**B**) in the six major land-use types, separated by those in the surface 0–10 cm interval (*left box*) and the deeper 10–30 cm (*right box*). Units of mg kg^{-1} were displayed in log scale. *DES* desert; *URR* urban residential; *URN* urban non-residential; *AGR* agricultural; *MIX* mixed; *TRA* transportation. Box plot shows median, inter-quartiles, and ''outliers''. Most of these outliers were ''corrected'' after log transformation, four outliers in (**A**) were removed from further statistical analyses (see text for detail).

within any single land-use category (Table 4). In general, desert and agricultural sites exhibited net production of inorganic N, urban residential sites had either production or consumption but averaged near zero, whereas urban non-residential, transportation, and mixed sites showed net consumption of inorganic N (Table 4). Kruskal–Wallis tests revealed highly significant differences in net N mineralization between land-use types (H_6 = 32.92, P < 0.001). Agricultural sites had significantly higher inorganic N production than mixed and transportation sites, whereas desert sites had significantly higher inorganic N production than mixed, transportation, and urban non-residential sites (Dunn non-parametric multiple comparison tests). N transformations were dominated by NO_3^- production or consumption; most NH_4^+ that was present initially was converted to NO_3^- during the incubation (Table 4).

Estimating the Effects of Land-Use Change on the Accumulation of Inorganic N in Soils

To estimate the effects of land-use change on inorganic N pools in sites across the diverse land-cover types in the CAP ecosystem, we took several steps and made several assumptions. We first calculated N mass using inorganic N concentration (NH_4^+ + NO_3^-, mg N kg^{-1} soil) in each depth interval, and the soil mass per unit volume (bulk density corrected for stone content), summed to give one N value for each site (g m^{-2}, 0–30 cm). Inorganic N content in the developed land-use groups was on average 2–7 times higher than N content of desert soil (F = 10.02, P < 0.001, Table 5). Compared to net N mineralization potential rates (Table 4), that is, N released through microbial mineralization under optimal conditions, initial inorganic N accumulation in this arid urban ecosystem was much higher (Table 5).

Direct calculation of the change using existing differences in N mass between deserts and developed land-use types, however, is subject to several constraints. Firstly, land-use change and development across the CAP study area has been concentrated mostly on the alluvial valley floor, where more readily workable soils and a supply of water for irrigation have been available since pre-historic times. Hence, soils at developed sites may have had inherently higher soil N concentrations to begin with due to the nature of alluvial deposits. This would mean that our calculations over-estimated the amount by which land-use change has elevated soil N compared to the currently undeveloped sites, many of which have poor, thin, rocky soils. Secondly, the proximity of many desert sites to the urban core may result in their containing more N than pre-development regional background levels due to enhanced N deposition (for example, Fenn and others 2003a). The latter would result in our over-estimating the natural background, and hence under-estimating the amount by which land-use change has increased inorganic soil N pools.

In order to evaluate the extent to which the higher inorganic soil N was a result of pre-existing differences rather than a change in response to development, we compared soil properties between undeveloped desert and developed sites found on the same mapped soil types and associations (Ta-

Table 3. Estimates of Population Means and their 95% Confidence Intervals (CI, in parentheses) of Soil Physical Measurements Conducted on Soils from the year 2000 Sampling in the CAP LTER Study Area

Land use	Bulk density[1] ($g\ cm^{-3}$)	Stone %[2]	Soil mass ($g\ cm^{-3}$)
Desert (n = 73)	1.36 (1.32, 1.40)	26.9 (22.0, 32.1)	0.95 (0.89, 1.01)
Urban residential (n = 54)	1.26 (1.21, 1.30)	21.6 (16.4, 27.2)	0.96 (0.88, 1.03)
Urban non- residential (n = 36)	1.21 (1.13, 1.29)	18.2 (12.6, 24.5)	0.95 (0.86, 1.03)
Agricultural (n = 23)	1.25 (1.19, 1.31)	6.4 (2.9, 11.2)	1.14 (1.06, 1.21)
Transportation (n = 6)	1.40 (1.21, 1.59)	27.7 (8.4, 52.8)	1.00 (0.61, 1.38)
Mixed (n = 11)	1.31 (1.20, 1.43)	15.1 (4.7, 30.0)	1.06 (0.87, 1.26)

[1]Bulk density values contained stone whereas soil mass did not.
[2]Stone (%) data were arcsine square-root transformed to calculate means and 95% CI, and then back-transformed to the percentage unit.

Table 4. Net Nitrogen (N) Mineralization and Nitrification Rates ($g\ m^{-2}\ 28\ d^{-1}$, 0–30 cm soil) from the CAP LTER Sampling, Based on the Laboratory Incubation with Soil Moisture Adjusted to 20%

	Net N mineralization		Net nitrification	
Land uses	Median	Mean (SD)	Median	Mean (SD)
Desert (n = 46)	0.766	1.126 (4.287)	1.106	1.705 (4.236)
Urban residential (n = 31)	0.030	−0.053 (3.827)	0.412	0.992 (4.584)
Urban non-residential (n = 21)	−0.894	−2.472 (5.540)	0.202	−1.066 (6.012)
Agriculture (n = 8*)	0.652	4.51 (9.02)	0.978	4.87 (8.98)
Transportation (n = 6)	−1.446	−2.045 (1.715)	−0.888	−1.495 (1.564)
Mixed (n = 3*)	−1.838	−1.631 (0.387)	−1.116	−0.725 (0.677)

Positive values indicate net inorganic N production, whereas negative values indicate net inorganic N consumption. Two outliers, one agricultural site (109.3 $g\ m^{-2} 28\ d^{-1}$) and one mixed site (−170.9 $g\ m^{-2} 28\ d^{-1}$), were removed from the mean and standard deviation (SD) calculation.

Table 5. Estimated Increase in Soil Inorganic N Storage ($NH_4 + NO_3$–N, $g\ m^{-2}$ soil, 0–30 cm) from Pre-urbanization Levels, Calculated from Simple Arithmetic Means of Current Pools for each Land-use Category

Land uses	Current inorganic N[1] ($g\ m^{-2}$)	Impervious cover (%)	Mean N increase ($g\ m^{-2}$)	Land area (km^2)	Estimated N increase (1 Gg = 10^9 g)
Desert (n = 73)	3.23 (5.58)	0.0 (0.0)	2.28	3,093.6	7.06
Urban residential (n = 54)	10.18 (24.92)	47.1 (21.7)	4.45	1,145.8	5.09
Urban Non-residential (n = 36)	13.05 (17.87)	35.7 (32.9)	9.01	851.2	7.67
Agriculture (n = 23)	16.29 (26.29)	0.0 (0.0)	15.35	736.6	11.31
Transportation (n = 6)	24.25 (22.51)	65.8 (31.6)	6.76	163.7	1.11
Mixed (n = 11)	42.80 (66.66)	26.7 (34.6)	34.29	409.2	14.03
Total				6,400	46.27
Area weighted average N increase ($g\ m^{-2}$)					7.23

Standard deviations are in parentheses.
Current soil inorganic N mass was calculated based on N concentrations and soil mass corrected for stone content; the arithmetic mean and SDs in each land-use groups are affected by the large values often found in urban and agricultural plots.
Nitrogen increase from the pre-urbanization level was calculated as the difference between the N mass of each sample plot and the ''baseline estimate'' (0.9437 $g\ m^{-2}$, see text for details), corrected for the percentage impervious cover in each plot, and then averaged for each land-use group.

ble 6). Of the five soil groups that had a sufficient sample size with which to make a comparison, four showed significantly higher soil NO_3^- at developed than at desert sites; NH_4^+ also tended to be higher in soils at developed sites, although the magnitude of the difference was much smaller than for NO_3^-

Table 6. Comparison of Soil Properties between Desert and Developed Sites Located on the Same Soil Associations and Soil Types

	Number of samples		Mean NO_3–N (mg kg^{-1})		Mean NH_4–N (mg kg^{-1})	
Soil association/type[1]	Desert	Developed	Desert	Developed	Desert	Developed
Antho/Typic Torrifluvent	3	4	3.46	10.11	3.00	2.97
Ebon/Typic Haplargid	4	2	5.00	0.43	3.30	4.68
Gilman/Typic Torrifluvent	3	22	7.26	79.44	2.92	4.31
Mohall/Typic Haplargid	5	21	14.04	60.04	2.47	5.41
Tremant/Typic Haplargid	4	2	11.73	17.48	1.99	3.44

[1]Major soil associations and soil types are from the Natural Resources Conservation Service's Soil Survey Geographic Database (http://www.az.nrcs.usda.gov/soils/ssurgo.html).

(Table 6). We thus conclude that the elevation in inorganic N is real and not a bias due to pre-development difference.

To address the potential effect of an increase in background levels of soil N at undeveloped desert sites due to adjacent urban impact, we took a statistical approach and selected the lower quartile (Q_1= 0.944 g m^{-2}) of soil inorganic N mass from the 73 desert sites as the baseline estimate representing situations before urban development. We then calculated the increase of soil inorganic N in each of the 203 plots (including desert) against this baseline.

A large increase in percentage impervious surface has accompanied urban development in the CAP ecosystem, which affected our estimate of N accumulation. Mean impervious surface cover ranged from 0% in desert and agriculture sites to 47.1% in the urban residential sites and 65.8% in the transportation sites (Table 5). We made the assumption that impervious surface cover blocked the entry of new anthropogenic N into soils in these parts of the landscape. The net N accumulation in each survey plot was thus calculated as the difference between its N content and the baseline value, corrected for its impervious cover; the average N accumulation in each land-use group was then calculated (Table 5).

The land area of each land-use type was estimated based on the number of plots of each type sampled, and adjusted for different sample densities within and outside the urban core (Figure 1, see Methods). For example, each desert plot located outside the urban core represented three grid cells (3×16 km^2) whereas each urban plot represented just one grid cell (16 km^2) of the CAP LTER ecosystem. The land area of each land-use group and its mean N increase was then multiplied to get an estimate of N increase for that group (Table 5).

We estimate that agricultural and mixed land uses, representing 11.5 and 6.4%, respectively, of the total land cover in the CAP study area, have accumulated 11.31 and 14.03 Gg of inorganic N, respectively, compared to the natural ''background'' N content of desert soil (Table 5). The high N increment for agricultural soils is due in part to the lack of impervious cover, whereas the high N increment for mixed land use was chiefly the result of very high N concentrations in the exposed soils. Meanwhile, urban residential and non-residential sites occupied 31.2% of the study area but together contributed only 12.76 Gg inorganic N above the ''pre-urban'' values, due to a combination of relatively low soil N concentrations and high impervious surface cover. Desert sites accumulated 7.06 Gg inorganic N above the pre-development background. Overall, we estimate that land-use conversion and indirect input to the desert led to an average accumulation of inorganic N of 7.229 g m^{-2}, mostly in the form of NO_3–N, over the pre-urbanization background value of 0.944 g m^{-2}.

Discussion

This paper presents one of the first systematic inventories of soil properties (along with other ecological variables, Hope and others 2003) to be carried out across an entire urban ecosystem. The differences in soil characteristics found between undeveloped and developed land uses across the CAP ecosystem were large. Mean soil moisture at all developed (residential, non-residential, agricultural, transportation, and mixed) sites was significantly higher than at undeveloped desert sites, whereas soil organic matter at urban (residential and non-residential) and agricultural sites was significantly higher than at the desert sites (Tables 1, 2). In the urban residential and non-residential area, the availability of water (a key resource in the desert environment) in surface soils was more than three times greater than in the desert (Table 1). However, the wide range and often extremely elevated concentration of inorganic N in soils at developed compared to desert sites, mostly in the form of nitrate (Figure 2), was the most remarkable finding.

Elevated Soil Inorganic N Concentrations Associated With Urban Land Uses

Enriched soil inorganic N concentrations in the vicinity of metropolitan areas, mostly associated with enhanced dry deposition resulting from urban NO_x production, have been reported previously (Fenn and others 2003a; Padgett and others 1999; Lovett and others 2000). Padgett and others (1999) examined soils from the coastal-sage scrub ecosystem in the Los Angeles Basin of southern California, and found surface soil (0–2 cm) NO_3–N reached 50–60 mg kg^{-1} at sites under heavy pollution, but was near detection limits at low-pollution sites. Some of the highest soil NO_3^- concentrations in this study occurred at transportation sites, suggesting enrichment due to elevated deposition from automobile exhaust, as reported by Padgett and others (1999). However, the highest soil NO_3^- concentrations found in our study were far greater than those reported by Padgett and others (1999) and elsewhere, and spanned a much wider range of more than four orders of magnitudes. For example, the estimated population mean for NO_3–N (surface 0–10 cm soil) in urban transportation sites was 46.2 mg kg^{-1} (with an upper 95% confidence limit of 297.9 mg kg^{-1}), more than ten times that of the desert sites (Table 1). Sites with very high soil NO_3^- concentrations were varied in character. They included areas of bare soil on margins adjacent to major highways, where enhanced NO_x derived from atmospheric deposition of automobile exhaust, in combination with a lack of plant uptake, were likely the major factors contributing to inorganic N enrichment. Other high soil NO_3^- concentrations were found at a small holding for livestock, the bare margin of an agricultural field, as well as the site of a former sewage holding pond. We retained plots with unusually high concentrations in our data analyses because they were real values; indeed, the varied nature of sites having very high inorganic N suggests that soil chemistry is a product of highly localized, site-specific factors (Hope and others 2005). This site-specific and idiosyncratic nature of controls may be a ubiquitous feature of human-dominated ecosystems, giving rise to unique patterns in soil nutrients such as that seen across the CAP region. Nevertheless, the overall statistically significant differences between developed and undeveloped sites (after data transformations that accounted for the extreme data range) show convincingly that urbanization and other human practices can lead to dramatic increases in soil inorganic N concentrations.

The Sonoran Desert, like other southwestern arid lands, is limited by N and water, with inorganic N being scarce and concentrated in shrub ''resource islands'' (West and Klemmedson 1978; Schlesinger and others 1996; Reynolds and others 1999). Atmospheric deposition inputs to non-urban areas are usually low. Schlesinger and others (1982) and Ellis and others (1983) reported atmospheric N inputs to southern California chaparral of 0.96–1.5 and 0.5 kg ha^{-1} y^{-1} for NO_3–N and NH_4–N respectively. Rapidly developing urban centers in the Southwest could dramatically alter this pattern; for example, a recent estimate of N deposition in and adjacent to metro Phoenix was 13.5 kg N ha^{-1} y^{-1}, mostly as dry deposition (Fenn and others 2003a). The elevated N input from atmospheric deposition, plus site-specific input from various human activities, are likely changing the extent of N limitation in this arid urban ecosystem.

Soil NO_3–N Accumulation in the CAP Urban Ecosystem

The probability-based (that is, unbiased random) sampling design provided us with a solid basis to evaluate the likely effect of land-use change on soil properties and the change of N biogeochemistry. The result that urban and agricultural sites had much higher inorganic N concentrations than desert sites suggests that substantial N accumulation has accompanied urbanization of the CAP ecosystem. Significant accumulation of inorganic N in soil is rare in natural terrestrial ecosystems, where N is rapidly assimilated by soil microbial organisms and plants, and the turnover of soil inorganic pools is rapid through N mineralization and nitrification processes (Paul and Clark 1996). In a study of remnant deciduous forests along an urban–rural gradient, Zhu and Carreiro (2004) found that turnover time of the soil inorganic N pool due to microbial N transformations was 2–4 days in the summer growing season. In soils collected from a remote desert site, N released in a 28-day lab incubation exceeded extractable inorganic N pools of approximately 1 mg kg^{-1} by two-to five fold (Reynolds and others 1999), whereas in desert soils collected from the CAP ecosystem, N released in the 28-day lab incubation was just one-third of the initial standing pools (Tables 4, 5). Although large quantities of inorganic N were found accumulating in urban and agricultural sites, mostly in the form of NO_3^-, net N mineralization and nitrification rates were surprisingly low, often negative, and highly variable within any single land-use category (Table 4). Even though we adjusted soil moisture to the optimal conditions during the lab incubation (see Methods), N mineralized was still a minor component compared to the initial inorganic pools. Thus in this urban ecosystem a fundamental shift of N biogeochemistry pathway may have occurred, from dominance by internal N cycling (plant uptake and microbial mineralization) to external N input (mostly from anthropogenic sources).

We estimate that N enrichment in the undeveloped desert surrounding Phoenix metro contributed an extra 7.06×10^9 g inorganic N to the CAP ecosystem. The assumed background pool size of 0.944 g m^{-2} inorganic N is a conservative estimate compared to published data (Mun and Whitford 1989; Padgett and others 1999; Reynolds and others 1999). Soil N enrichment in urban non-residential, agricultural, and mixed land-use sites, covering 13.3, 11.5 and 6.4% of the CAP study region, respectively, are estimated to contribute a combined accumulation of more than 30×10^9 g inorganic soil N. These hot spots of N enrichment, at concentrations 10–1,000 times higher than natural desert soils (Figure 2A, B), contributed greatly to the overall storage of inorganic N in the CAP ecosystem (Table 5). The total estimated inorganic N accumulation attributable to development across the entire CAP ecosystem was 7.23 g N m^{-2}, a value equivalent to 4 years of the N imbalance calculated by Baker and others (2001). Because our estimate did not include deep (that is, below 30 cm) soil storage, it is possible that even greater accumulations have occurred (for example, Walvoord and others 2003). In addition, significantly higher SOM content in urban sites (Table 1) indicates that some soil N could be accumulating as organic N in the CAP ecosystem.

An alternative approach was also used to estimating the baseline inorganic N pool size in the CAP ecosystem. Fifteen desert sites located in the northwestern and western parts of the study area were selected, avoiding sites near major roads and urban and agricultural land uses (Figure 1). Western locations of our study area are outside the main southwest–northeast movement of the Phoenix urban pollution plumes (Ellis and others 1999). Among these 15 plots, 2 were dropped because they were directly on a floodplain. The median inorganic N pool size of the remaining 13 plots was 1.669 g m^{-2}. Thus it is possible we have under-estimated the background N pool size and consequently over-estimated the accumulation of inorganic N in the CAP ecosystem by 0.725 g m^{-2} (Table 5). The higher background N value in our system is possibly due to the abundance of biological N_2 fixation from legumes and cyanobacterial crusts common in the Sonoran Desert (Whitford 2002).

Comparison of soil properties between developed and native Sonoran Desert sites located on the same soil types and major soil associations (Table 6) gives us confidence that the differences observed are largely a result of changes brought about by urbanization. However, in the absence of sample data at locations before and after development, the presence of some a priori differences cannot be ruled out. Moreover, current land use at some sites may have changed since the soil mapping was carried out, so that changes in soil properties may in some cases be a result of importation of topsoil to a site, rather than modification of the original soil profile. Indeed such manipulations are likely to be a common feature of urban soils, for which there is as yet no comprehensive soil taxonomy developed (Effland and Pouyat 1997).

Implications of Enhanced N Availability for Ecological Processes in the Urban Ecosystem

The major soil characteristics we quantified in this study indicated that urbanization in the CAP ecosystem creates favorable water and N conditions in the otherwise water- and N-limited desert environment. Enhanced dry deposition from combustion-derived NO_x products may also have impacts on the surrounding Sonoran Desert, potentially affecting plant growth and species diversity (Fenn and others 2003b), even though analyses so far indicate that factors other than soil NO_3–N content are largely responsible for spatial variation in plant diversity across the CAP ecosystem (Hope and others 2003). Within the urban area, plant productivity is most likely to show effects of elevated N availability, whereas plant diversity (composed mostly of exotic species) is heavily influenced by factors such as economic resource (household income), legacy effects of former agricultural land use, and age of developments (Hope and others 2003).

Intensive management of the soil–plant system within the urban landscape (for example, mowing, setting aside agricultural land for fallow periods, preventing adventitious plants from colonizing vacant lots and street margins), along with urban pollution and competition from exotic plants, could all affect N uptake. When combined with deliberate and inadvertent N inputs, these may push urban ecosystems towards N saturation (Aber and others 1998; Fenn and others 2003b). A large inorganic N soil pool, mostly in the form of NO_3^-, could result in both vertical and horizontal transfers. Vertical downward transfer of NO_3^- in natural desert environments is believed to be low because evapotranspiration exceeds precipitation (Peterjohn and Schlesinger 1990; but see Walvoord and others 2003). In the present study, although NH_4^+ concentrations were significantly higher in the surface soils than in the deeper soils, there was no statistically significant difference for NO_3^- (Tables 1, 2), indicating that some downward movement of NO_3^- is possible even in this arid environment. Downward NO_3^- transport is likely to be more significant in regulating N pollution in mesic environments such as those in the Northeast (Aber and others 1998) than in deserts, yet irrigation of urban landscapes and agricultural fields could greatly facilitate such vertical NO_3^- movement (Walvoord and others 2003). Baker and others (2001) estimated that 1400-1600 kg ha^{-1} leacheable NO_3–N could be stored in the vadose zone underneath the cropland in the CAP ecosystem, which varies in depth from 30–200 m.

Nitrate accumulated in surface soil also can be exported horizontally as urban storm water runoff. Precipitation in the Sonoran Desert is highly episodic, often generating flash floods of short duration (Fisher and Grimm 1985), which in the urban area are channeled into retention basins. Denitrification may be substantial in these basins, which are located in topographically low areas and typically covered by turf grass. Zhu and others (2004) measured denitrification rates in retention basin soils at rates of 3.3–57.6 mg N m^{-2} d^{-1}; such high values were probably supported by the conditions of low oxygen and high organic C content in the retention basin. Denitrification in desert ecosystems is largely associated with wetting and drying events (Virginia and others 1982; Peterjohn and Schlesinger 1991). Elevated soil NO_3–N concentrations and high organic matter content and soil moisture in the CAP urban ecosystem could favor this process for regulating excessive N accumulation.

Conclusions

An extensive, probability-based sampling at 203 sites across the entire CAP LTER region was used to quantify soil chemical and physical characteristics under different land-use types. Soil inorganic N, mostly in the form of NO_3^-, was 2–10 times higher in urban and agricultural sites than the surrounding Sonoran Desert, which we estimate may itself have elevated soil N concentrations compared to pre-urban conditions. Other soil properties differed among land uses; urban and agricultural lands had higher moisture content, higher organic matter quantity, and reduced bulk density compared to undeveloped desert sites. In a related paper, Hope and others (2005) analyzed spatial variation of soil inorganic N in the CAP ecosystem and reported strong spatial autocorrelation of NO_3^- among desert sites but strong 'local', human-related controls on NO_3^- concentration in the city. In this paper, we calculate that soil N pools may have increased by 7.23 g N m^{-2} in the upper 30 cm of the soil profile, which could account for a large proportion of the N predicted to have accumulated in a mass balance study of the CAP ecosystem (Baker and others 2001). The large accumulation of inorganic NO_3^- highlights that N cycling in this urban ecosystem is both quantitatively and qualitatively different from the natural Sonoran Desert where much agricultural and urban development has occurred.

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