



Spatial variation in soil inorganic nitrogen across an arid urban ecosystem

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Abstract. We explored variations in inorganic soil nitrogen (N) concentrations across metropolitan Phoenix, Arizona, and the surrounding desert using a probability-based synoptic survey. Data were examined using spatial statistics on the entire region, as well as for the desert and urban sites separately. Concentrations of both NO₃-N and NH₄-N were markedly higher and more heterogeneous amongst urban compared to desert soils. Regional variation in soil NO₃-N concentration was best explained by latitude, land use history, population density, along with percent cover of impervious surfaces and lawn, whereas soil NH₄-N concentrations were related to only latitude and population density. Within the urban area, patterns in both soil NO₃-N and NH₄-N were best predicted by elevation, population density and type of irrigation in the surrounding neighborhood. Spatial autocorrelation of soil NO₃-N concentrations explained 49% of variation among desert sites but was absent between urban sites. We suggest that inorganic soil N concentrations are controlled by a number of 'local' or 'neighborhood' human-related drivers in the city, rather than factors related to an urban-rural gradient.

Keywords: soil NO₃-N, soil NH₄-N, urban ecosystem, desert, spatial autocorrelation, integrated inventory, CAP LTER

Introduction

Cities represent extreme cases of human influence on ecosystem function (McDonnell *et al.*, 1993; Pickett *et al.*, 1997; Collins *et al.*, 2000; Grimm *et al.*, 2000). This is particularly

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the case for biogeochemical patterns and processes. In non-human dominated ecosystems, inorganic nitrogen (N) pools and fluxes are governed by natural processes such as microbial mineralization and nitrification, inputs in atmospheric deposition, microbial N-fixation rates, and losses in surface and ground waters (Schlesinger, 1997). However, in cities the effects of human management on the N cycle are profound, with the pathways and pools being radically altered by urbanization (Baker *et al.*, 2001; Faerge *et al.*, 2001). Work to date on how inorganic soil N is affected by urbanization shows that it may be significantly changed (Pouyat *et al.*, 1997; Pouyat and Turechek, 2001; Zhu and Carreiro, 2004).

The urban-rural gradient approach has proved a useful organizing framework for understanding the soil patterns and processes in cities of the temperate northeastern US (McDonnell and Pickett, 1990; Pouyat and McDonnell, 1991; Pouyat *et al.*, 1994, 1995; Goldman *et al.*, 1995; McDonnell *et al.*, 1997; Pouyat *et al.*, 1997). However, such gradients are sometimes more complex than a simple linear urban-rural gradient (Adams, 1970; Ley, 1983; McDonnell *et al.*, 1997; Alberti *et al.*, 2001). Across the natural landscapes of the Sonoran desert in the southwestern US, the distribution of soil nutrients is governed primarily by geomorphic features and water availability (Whittaker and Niering, 1975; McAuliffe, 1994). However, urbanization fragments these natural landscapes, increasing spatial heterogeneity of various landscape pattern metrics (Clark *et al.*, 1997; Wu, 1998; Jennerette and Wu, 2001; Luck and Wu, 2002) and also potentially changes the distribution of soil nutrients as well.

Understanding the heterogeneity of nutrient pools and fluxes across ecosystems is a subject of considerable interest in ecology (McClain *et al.*, 2003). High spatial heterogeneity of soil nutrients may affect interspecific plant competition and the diversity, invasibility, and composition of plant communities (Loreau, 1998; Stohlgren *et al.*, 1999). The particular pattern of nutrient distribution in terrestrial components of landscapes also may have consequences for the subsequent delivery of nutrients to streams, lakes, wetlands, and marine ecosystems (Creed and Band 1998; Gergel *et al.*, 1999; Grimm *et al.*, 2003). Development of a better understanding of such heterogeneity is also important for the construction of elemental budgets and modeling of biogeochemical cycles, as well as for the effective management of soil (and water) resources (e.g. Baker *et al.*, 2001; McClain *et al.*, 2003).

We therefore used a one-time 'snapshot' sampling approach in order to characterize variation in soil inorganic N concentrations across the large, rapidly urbanizing region encompassing the Phoenix metropolitan area. We wanted to answer the following three questions. Firstly, to what extent does urbanization alter the geomorphic controls determining the spatial patterning of inorganic soil N across this arid ecosystem? Secondly, to what extent can patterns in soil N across the urbanized region be explained by a linear urban-rural gradient? Thirdly, do human variables other than measures of the urban-rural gradient (e.g., income levels, age of housing) contribute to explaining spatial variation in soil inorganic N concentrations, given that humans are an integral part of the ecosystem? We focused on the two main forms of inorganic soil N-nitrate ($\text{NO}_3\text{-N}$) and ammonium ($\text{NH}_4\text{-N}$), which are the dominant forms of available, inorganic N in these soils (W. Zhu, SUNY-Binghamton, personal communication) and which, along with water, co-limit plant growth in southwestern desert ecosystems (Schlesinger *et al.*, 1996).

Material and methods

Study area and survey design

The study was conducted at the Central Arizona-Phoenix Long Term Ecological Research (CAP LTER) research site, one of two urban ecosystems in the National Science Foundation's LTER network (Kaiser, 2001). The central Arizona region consists of a large alluvial plain and eroded mountain remnants which together provide the geomorphic template upon which the city has developed. The climate of the region is hot and dry, with an average annual daily (1948–2003) maximum temperature of 30°C and average daily minimum of 15°C, with an annual average rainfall of 193 mm. During the period Nov 1999–May 2000, rainfall was 30% lower than average and fell mostly in March 2000—the middle of the survey period (M. Kaye, Arizona State University, personal communication). The CAP study site includes the rapidly expanding metropolitan Phoenix area, surrounding farmland and desert (figure 1). The main urbanized core abuts agricultural land to the west and southeast and is surrounded by sparsely populated, largely undeveloped Sonoran Desert. The population has increased by 47% since 1990 to over 3.5 million people (US Census Bureau, 2000), living in 23 municipalities that comprise the Phoenix metropolitan area. Growth and development of the present city, which has reoccupied the site of a large prehistoric settlement of some 250,000 people (Bayman, 2001) has occurred mostly during the second half of the 20th century. Modern agricultural and subsequent urban development has been made possible by the construction of large dams on the Salt and Verde Rivers, which store spring runoff from higher elevations. Since the early 1990s, this water supply has been augmented with water from the Colorado River, delivered via the Central Arizona Project canal. Widespread urbanization followed the development of air conditioning and use of the personal motor vehicle (Gammage, 1999). This has been accompanied by the establishment of urban residential landscapes which rely on irrigation, initially using pre-existing flood irrigation systems (where land was previously in agricultural use), but more recently by installation of overhead and drip systems (Martin, 2001). Hence, there is an abrupt delineation in vegetation between irrigated areas and undeveloped desert, the latter having been replaced or supplemented with numerous imported non-native species (Hope *et al.*, 2003). A similar abrupt difference might also be expected in the spatial patterning of soil inorganic N concentrations.

We chose a geometrically defined, roughly rectangular area of 6400 km² which covered most of the CAP LTER site. This sampling universe goes well beyond current incorporated municipal boundaries to include surrounding agricultural and desert land. It allows for comparisons among land use types, but ensures that there will continue to be a number of desert sites that will remain undeveloped in this region of rapid urban growth. A probability-based sampling scheme was used to obtain a spatially dispersed, unbiased sample of soil and other ecosystem variables (Stevens, 1997; Peterson *et al.*, 1999). A randomized, tessellation-stratified design was achieved by superimposing a 4 × 4 km grid on the study area, giving 462 potential sampling units of which over half fell outside the current urban core area. To capture the much greater landscape heterogeneity within the developed metropolitan core (Luck and Wu, 2002) a random sample point was as-

signed within every square inside the beltway and in every third square outside that area, which gave a total sample size of 206 (figure 1). No *a priori* stratification according land cover, land use type, or other characteristics was used, for two main reasons: (i) to allow results to be extrapolated to the entire study area, while minimizing the variance of parameter estimates for subsequent spatial estimation and modeling applications; (ii) to cover the whole area systematically. This scheme was used to achieve our goal of a broad characterization of the study area, even though it sacrificed representation of rarer patch types.

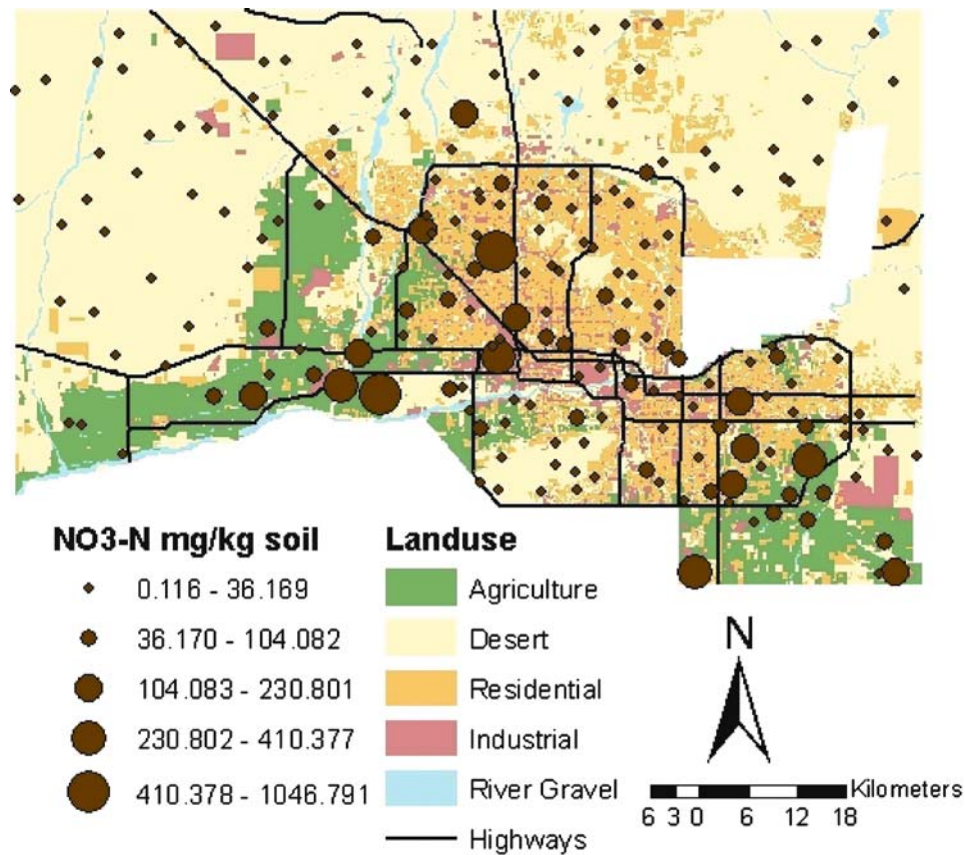


Figure 1. Map showing (a) soil $\text{NO}_3\text{-N}$ concentrations and (b) soil $\text{NH}_4\text{-N}$ concentrations in the top 10 cm of the soil profile (mg kg^{-1}) and at the 204 sample sites across the CAP LTER region. Also shown are the major land use categories as designated by the Maricopa Association of Governments (MAG). Blank areas in the east central and south west valley are Indian reservation land for which permission to sample was not obtained.

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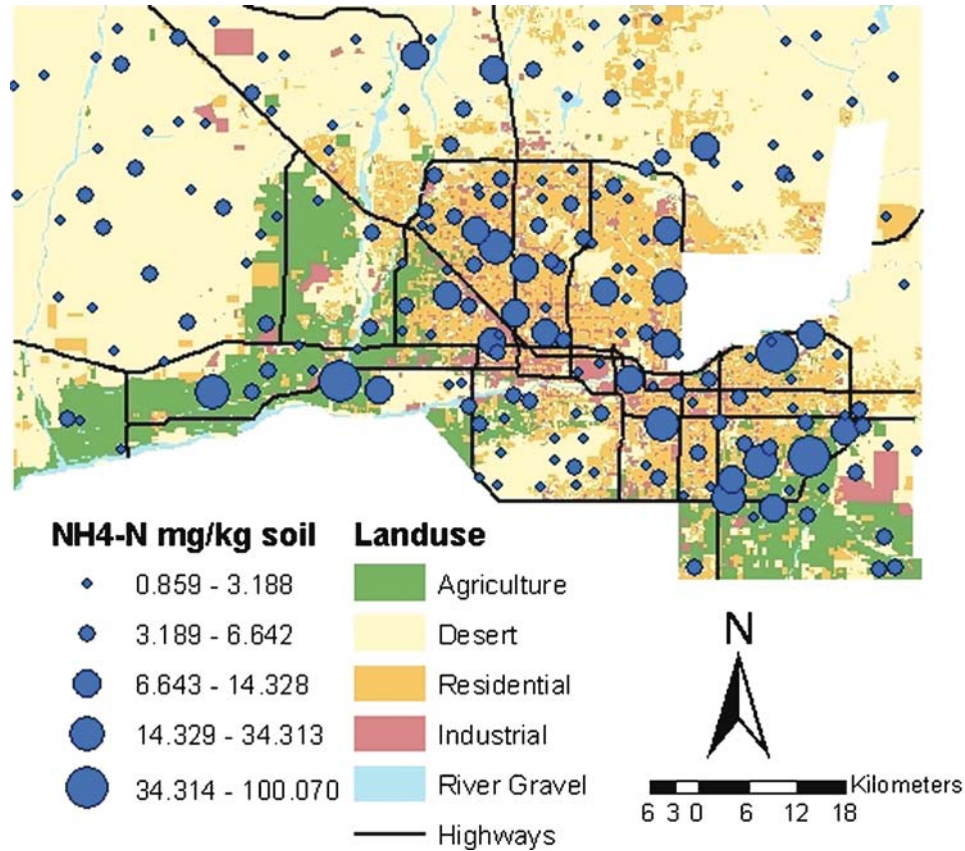


Figure 1. (Continued).

Data acquisition

Integrated field inventory. Sample collection was carried out over a 3.5 month period in spring 2000. Each survey site consisted of a 30 × 30 m plots (the size of a Landsat Thematic Mapper pixel) centered on the randomly assigned sites located with the aid of a Global Positioning System (Trimble 'Pro XRS' real-time satellite corrected mapping grade unit). Sites were sampled exactly where the randomly generated coordinates fell, which included residential lots, street surfaces, vacant urban lots and undeveloped desert. Many of the survey plots fell across more than one property boundary, but access was successfully negotiated for all but 8 sites, of which 6 were relocated to the nearest (within 100 m) similar accessible site. There were only 2 sites for which access was denied and no suitable surrogate could be found, giving a total of 204 sample sites.

Soil cores were taken using a hand-impacting corer (2.5 cm diameter to a depth of 30 cm) at four points in each plot. Core samples were separated into 0–10 cm (top) and

10–30 cm (bottom) depth intervals. The top soils from the four replicate cores were mixed, to give one integrated top soil sample for each plot, and refrigerated. The bottom samples were treated the same way. At a small number of survey plots where the entire surface was covered by impervious urban surface, soil samples were collected from the nearest accessible site within 50–100 m of the plot boundary. For subsequent analyses soil samples were sieved at field moisture through a 2 mm mesh sieve and homogenized. A 10 g sub-sample was extracted with 2 M KCl solution in a reciprocal shaker for 1 h. The extract was filtered through pre-ashed glass fiber (Whatman GF/A) filters, acidified and stored at 4°C. Extracts were analyzed using a Bran-Luebbe TrAACs 800 auto-analyzer within 1–2 weeks of collection, using the alkaline phenol method for $\text{NH}_4\text{-N}$ and cadmium reduction method for $\text{NO}_3\text{-N}$. The sample detection limit was 0.01 mg L^{-1} for both analyses. Sub-samples of sieved soils were weighed, oven dried at 60°C for >48 hours and re-weighed, in order to determine soil water content. Extractable soil N was calculated as mg N per kg oven dry soil. Only the data for the surface (0–10 cm depth) samples are considered here, since surface soils are more likely to respond to N inputs from urban and agricultural activities.

An additional sample of top soil was taken using a 5 cm diameter corer from the central point of each plot; particle size analysis was carried out on these samples using the hydrometer method (Gee and Bauder, 1986). Other key biotic, abiotic, and human variables collected during the field survey included noting the cover of all surface types (e.g., turf, bare soil and impervious surfaces such as concrete, asphalt, tile, gravel, roofs of permanent structures), from which the percentage of impervious surface cover for each plot was calculated. The irrigated area and type of irrigation on each plot was also recorded.

Data from other sources. The field data were supplemented with several key geographic and socioeconomic variables. Land use at each of the 204 surveyed sites was classified according to the Maricopa Association of Governments' (MAG, 1997) land use definitions, modified in accord with the land cover classification developed by Stefanov *et al.* (2001). Managed 'open space' within the urban area was subsumed under the 'urban' top level category and a 'mixed' category was added where more than one of the main land uses was present in the same survey plot (Table 1). The five main land use categories were: urban ($n = 90$), desert ($n = 73$), agriculture ($n = 23$); transportation ($n = 6$) and a 'mixed' class ($n = 11$).

Elevation was obtained from the US Geological Survey Digital Elevation Model (USGS DEM) for the region (resolution $30 \times 30 \text{ m}$). Distances of each site from the urban center (defined as Central Ave and Washington St.) and from the nearest major freeway were calculated using ARCVIEW GIS. Historic land use analyses carried out for each survey point (Knowles-Yáñez *et al.*, 1999) were used to assign an indicator variable showing whether the site had ever been in agriculture. Three socioeconomic variables (per capita income, median age of housing stock and human population density) were taken from the U.S. Census of Population and Housing for the appropriate block group within which each survey point was located. Since U.S. Census block group boundaries are drawn up to contain a standardized number of people, they vary in spatial extent across the CAP region.

Table 1. Summary statistics for soil NO₃-N and NH₄-N concentrations (mg extractable N kg⁻¹ soil) measured in soil cores taken from the 0–10 cm depth interval at each site during the synoptic survey

	All Sites (<i>n</i> = 204)	Urban (<i>n</i> = 91)	Desert (<i>n</i> = 73)	Agriculture (<i>n</i> = 23)	Transport (<i>n</i> = 6)	Mixed (<i>n</i> = 11)
Soil NO ₃ -N in top 10 cm						
Mean	39.6	42.6	6.9	45.9	107	160
Median	7.3	10.0	4.3	18.8	75.5	50.8
Std. dev.	104	92.0	7.9	65.9	112	303
CV	262	216	114	143	104	189
Range	0.1 to 1047	0 to 39	0.4–36.2	2.0–303.2	1.8–290.0	2.0–1046.8
Soil NH ₄ -N in top 10 cm						
Mean	5.3	7.1	3.5	6.0	3.1	6.7
Median	3.0	3.9	2.5	2.8	2.8	3.4
Std. Dev.	10.4	12.9	3.8	13.8	1.5	9.4
CV	194	182	78	231	50	141
Range	0.9–100	1.0–100	0.9–25.1	1.0–68.8	1.6–5.8	1.4–34.3

However, we consider them to well represent the neighborhoods surrounding our survey sites (Hope *et al.*, 2003). For brevity, in this paper the block group within which a sample site was located is referred to as the ‘surrounding neighborhood’.

Statistical analyses

The suite of independent variables chosen to represent the main site characteristics in terms of physical setting were: site latitude; site longitude, elevation, distance from urban center, distance from the site to the nearest major freeway, percentage cover of impervious surface on the plot. Biophysical site characteristics were represented by percentage vegetation cover, percentage clay content in the soil and percentage impervious surface cover. Land use legacy influences were represented by an indicator variable showing whether the site had ever been in agriculture, how many years a site had been in agriculture and median age of the housing stock. Socioeconomic influences were represented by human population density and per capita income, with two additional variables indicating landscape management at the site: presence of irrigation and percentage turf cover. The variables were also chosen to ensure minimal co-linearity. None of the variance inflation factors between the independent variables exceeded seven (the level considered to indicate significant covariance) and most were substantially less, indicating that co-linearity was not a significant problem (Gujarati, 1995). Although many additional factors might also help explain variation in the dependent variables, some (e.g., ethnicity, % college educated, soil type) were strongly correlated with the chosen variables, while others were unavailable for all or many of the sites (e.g., potential evapotranspiration, real estate values). Some attributes traditionally used as descriptors of

geomorphic setting (e.g., slope, aspect, position on hillslope), were tested in preliminary analyses, but found to be uninformative because the large majority of sites were on flat or only very gentle slopes and did not make a significant contribution to explaining site-to-site variability. We chose *not* to use land use *per se* as a variable in these analyses, since so many other variables co-vary with land use. However, we did test the difference in NO₃-N and NH₄-N concentrations between the five main land use types separately. We used an ANOVA and two-sample *t*-tests for the NO₃-N data, while for the NH₄-N data, which differed greatly from normality assumptions, we used a non-parametric Kruskal-Wallis test.

Our prediction was that the underlying geomorphic template would be a primary control on spatial patterns in inorganic soil N concentrations in the undeveloped native Sonoran Desert across the region (Whittaker and Niering, 1975; McAuliffe, 1994; Parker and Bendix, 1996), but that such factors would be modified by deliberate management activities related to land use (e.g., manipulation of irrigation regime and vegetation cover). The urban-rural gradient concept has been useful in older cities with clearly delineated centers (e.g., McDonnell *et al.*, 1997) where it has largely been applied to remnant fragments of native ecosystems within and outside of the city (e.g., White *et al.*, 1988; Pouyat *et al.*, 1995). However, metro Phoenix is a large, young, rapidly urbanizing region with a more complex urban morphology and we wanted to include all land use types, even the heavily modified, human-managed components of the system. Therefore we conducted our statistical testing so that any urban-rural gradient emerged from the analysis, rather than being determined *a priori*.

We used spatial autocorrelation analysis to investigate the spatial dependence of inorganic N in soils across CAP (Cressie, 1993; Schaebenberger *et al.*, 2001). This technique examines how soil nitrate-N and ammonium-N concentrations co-vary as a function of the distance between sites. Statistical modeling was performed using PROC MIXED of SAS/STAT software, Version 9 of the SAS System for Windows (SAS Institute Inc., 2004) which allows for spatially correlated error structures. Where spatial dependence was found, we used a semi-variogram to show how differences in concentrations change with increasing separation between sites, using the *geOR* package in *R* (Ribeiro and Diggle, 2001).

Soil nitrate-N and ammonium-N were then modeled as a function of the independent variables, after transformation of the data to normalize the distributions. The model can be written as

$$y_s = \beta_0 + \beta_1 x_{1s} + \beta_2 x_{2s} + \beta_3 x_{3s} + \beta_4 x_{4s} + \beta_5 x_{5s} + \beta_6 x_{6s} + \beta_7 x_{7s} + \beta_8 x_{8s} \\ + \beta_9 x_{9s} + \beta_{10} x_{10s} + \beta_{11} x_{11s} + \beta_{12} x_{12s} + \beta_{13} x_{13s} + \beta_{14} x_{14s} + \beta_{15} x_{15s} + e_s$$

where x_{1s}, \dots, x_{15s} represent the 15 independent variables to be used in the analysis and $s = 1, \dots, 204$ indicate each of the 204 sample sites. In this model, e_s represents the remaining error not accounted for by the independent terms in the model. This additional error is potentially correlated over space where the relationship between sites decreases as the distance between them increases. For this data, as has been found in previous studies of spatial patterning in soil nutrients (Schlesinger *et al.*, 1996; Guo *et al.*, 2001), the spherical model was deemed appropriate. This means that e_s for $s = 1, \dots, 204$ is assumed to follow

a normal distribution with mean 0 and variance σ^2 . The corresponding correlation decreases as the distance between sites increases by the order of

$$(1 - 3/(2\theta)\|h\| + 1/(2\theta^3)\|h\|^3)$$

where h represents distance between sites and θ is a spatial scale parameter. For examples of other correlation functions see Cressie (1993) or Schabenberger *et al.* (2001).

Model residuals were examined for outliers and tested for spatial autocorrelation. Values that appeared to be outliers were examined to check for errors in analysis, but none were found. We therefore chose to leave all data points in the analysis rather than excluding them by statistical outlier tests, because extreme heterogeneity appears to be a fundamental aspect of urban soils. The selection of the final model used for each analysis depended primarily on the probability distribution used to model the response variable. When making inferences about the parameters, we used an $\alpha = 0.05$ significance level unless otherwise noted. The detailed procedure followed for each dependent variable is described below.

Soil NO₃-N

For the entire data set, soil NO₃-N concentrations were spatially independent. Hence Ordinary Least Squares (OLS) regression, the most widely used estimation procedure for building regression models, was applied (Myers, 1990) using a log transformation to stabilize the error variance and engender a Gaussian error distribution. Several variable selection techniques were applied, with backward elimination being relied on most heavily (Berk, 1978). Distributional properties were investigated using both residual and normal plots; the residual plots along with various other diagnostic techniques (e.g., Cook's distance, studentized residuals) were used to detect unusual observations (Cook and Weisberg, 1982; SAS, 2001). The data for the 91 urban sites were also spatially uncorrelated; log transformation was again used to obtain a homogeneous, Gaussian error distribution and the same techniques applied as described above.

The empirical semi-variogram for the log-transformed data from the 73 desert sites showed that soil NO₃-N concentrations were more similar at sites closer together (i.e., spatially autocorrelated) and that the model residuals were best fitted by a spherical model. The spatial autocorrelation in the errors necessitated that we used generalized linear mixed model techniques. Within this framework we make transformations on the original variable and allow for a random spatial component in the model in order to make inferences about the parameters and the error covariances. Residual plots were used to investigate the error distribution and potentially unusual observations (outliers), as describe above.

Soil NH₄-N

There was no significant spatial autocorrelation in soil NH₄-N concentrations for urban, desert or all-site data, so OLS techniques were implemented for all three analyses. In

this case, a power (-0.333) transformation of the $\text{NH}_4\text{-N}$ data was used to obtain a normal distribution of the residuals for the urban and all-sites data sets, while a log transform was used for the desert sites.

Interpreting the model output and graphs.

We do not report r^2 values for the resultant models, since in linear mixed modeling there is no statistic that is the counterpart of the r^2 measure. Instead, estimates for the β coefficients for each variable are given for the best fit model in every case, along with the corresponding significance level; i.e., the marginal t -test P value (Table 2). Estimates for the β coefficients for each of the aforementioned variables are listed from the smallest P value to the largest. This gives an order of importance of the variables (with a smaller P value representing a more important variable) as the P value gives an indication of the contribution of the variable above and beyond the information supplied by the other variables already in the model. The value of the estimate of β_k represents the increase in y_s if x_k were to increase by a unit of one and all other independent variables remain unchanged; i.e., it indicates the 'marginal effect' or strength of each variable's contribution simultaneously *together with* the other variables in the model.

Results

Soil $\text{NO}_3\text{-N}$

Variation in soil $\text{NO}_3\text{-N}$ concentrations across the whole CAP region spanned four orders of magnitude, from 0.1 to 1047 mg kg^{-1} dry mass of soil (figure 1(a), Table 1). Mean $\text{NO}_3\text{-N}$ concentrations differed significantly ($P < 0.001$) with land use type (figure 2); desert sites had significantly lower concentrations (mean = 7 mg N kg^{-1} , $n = 73$) than each of the other land use types ($P < 0.001$). The mean $\text{NO}_3\text{-N}$ concentration for the urban sites (43 mg N kg^{-1} , $n = 91$) was similar to the mean for agricultural sites (46 mg N kg^{-1} , $n = 23$) and significantly lower ($P = 0.006$) than that for the mixed sites (mean = 160 mg N kg^{-1} , $n = 11$); the transportation category had the highest mean concentration, although the smallest number of sites (107 mg N kg^{-1} , $n = 6$).

Across the study area as a whole, the overall F -test showed that variation in soil $\text{NO}_3\text{-N}$ concentration was significantly explained by a regression model containing a combination of geomorphic and human-related variables ($P < 0.0001$). These variables were human population density, percentage impervious surface cover, percentage lawn cover, whether the land was ever in agricultural use, and latitude; the marginal t -test P values are shown in Table 2. Estimates for the β coefficients for each of the aforementioned variables are listed from the smallest P value to the largest i.e. in order of importance (with a smaller P value representing a more important variable). Soil $\text{NO}_3\text{-N}$ concentrations showed a tendency to be higher at sites with more people per km^2 in the block group within which a sample site was located and where the land had been used for agriculture at some time previously. This was combined with a tendency for $\text{NO}_3\text{-N}$ to be lower at sites where the percentage cover

Table 2. Best fit models of spatial variations in soil NO₃-N and NH₄-N concentrations (mg N kg soil⁻¹ from 0–10 cm depth interval)

	Variable*	Estimate	P-value
= NO ₃ -N			
All Sites (n = 204)			
	Latitude	-2.058	0.014
	Land ever in agriculture	0.913	0.001
	Population density	<0.001	<0.001
	% impervious surface	-0.011	0.008
	% lawn cover	-0.017	0.029
Urban sites (n = 91)			
	Elevation	-0.011	0.002
	Population density	0.001	0.029
	% impervious surface	-0.016	0.013
	Income per capita	<0.001	0.011
	Irrigation (non-flood)	-1.293	0.016
Desert sites (n = 73)			
Spatially autocorrelated			
NH ₄ -N			
All Sites (n = 204)			
	Latitude	0.2439	<0.001
	Population density	-0.001	<0.001
	% clay content	-0.004	0.012
Urban sites only (n = 91)			
	Elevation	0.001	0.023
	Population density	-0.001	0.029
	% lawn cover	-0.002	0.035
	Irrigation (non-flood)	0.123	0.014
Desert sites only (n = 73)			
	Percent clay content	0.022	0.038

*Sources of data: elevation was derived from the USGS DEM using site latitude and longitude; percent impervious surface and lawn cover, along with irrigation (non-flood i.e. overhead sprinkler and/or drip systems) were recorded during the field survey; percent clay content was determined on core samples using the hydrometer method (Gee and Bauder, 1986); income per capita and population density are derived for the US Census of Population and Housing for the block group within which each survey point was located; whether a site was ever in agriculture was determined by reference to Knowles-Yáñez *et al.* (1999).

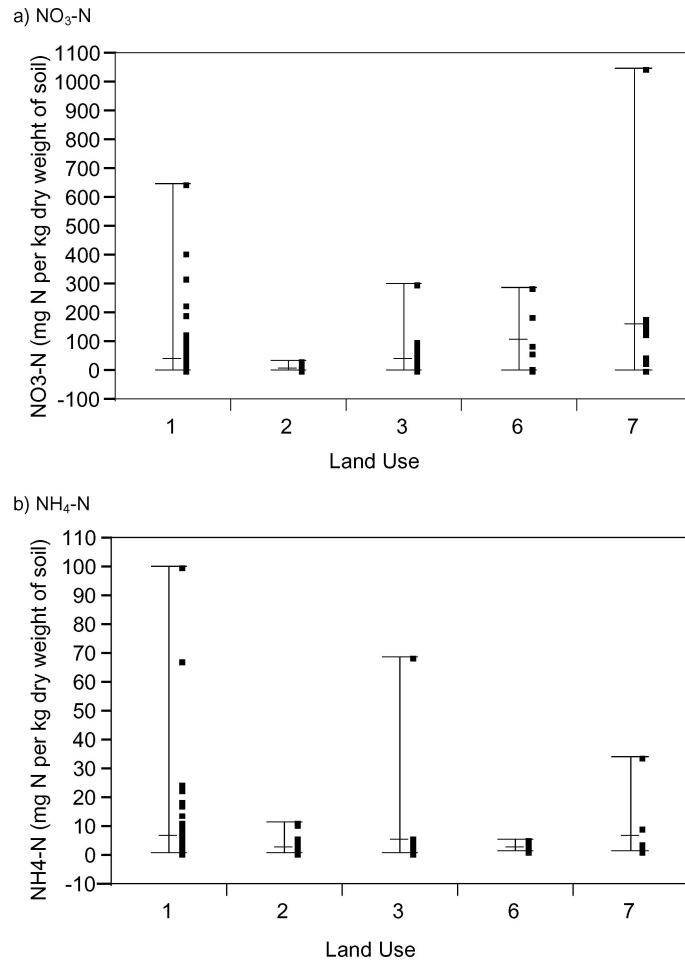


Figure 2. Variation in soil inorganic N concentrations with land use; bars show range and mean of values, dots show individual data points. Land use types are 1—urban ($n = 91$), 2—desert ($n = 73$), 3—agriculture ($n = 22$), 4—transportation ($n = 6$) and 5—mixed ($n = 11$).

of impervious surface and lawn cover were high and to decrease from south to north across the study area.

The overall F -test on soil NO₃-N concentrations for urban sites (figures 2 and 3(a)) showed that large variation amongst sites was significantly predicted by a regression model containing a combination of the five independent variables ($P < 0.0001$). These were elevation, human population density, percentage impervious surface cover, per capita income in the surrounding neighborhood and the presence of irrigation (Table 2). Urban soil NO₃-N concentrations were more likely to be higher in neighborhoods with higher human population density (figure 4(a)), higher income levels and low impervious surface cover,

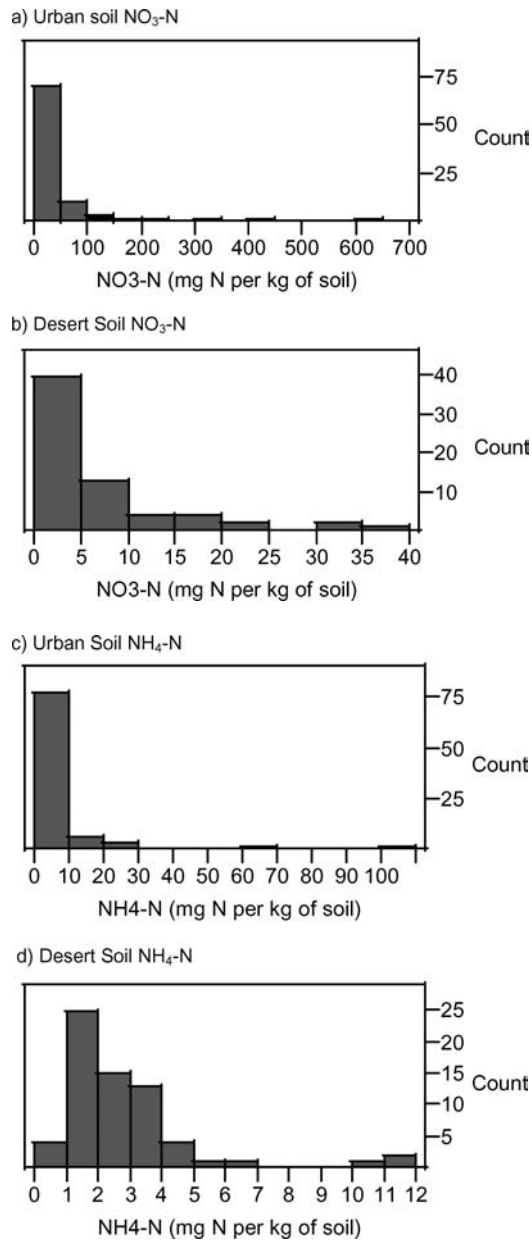


Figure 3. Frequency distributions for (a) urban soil NO₃-N (b) desert soil NO₃-N, (c) urban soil NH₄-N (this graph is shown truncated at 50 mg N kg⁻¹, omitting the highest 18 values so that the graph can be shown at the same scale as for the desert sites) and (d) desert NH₄-N concentrations (mg N kg⁻¹).

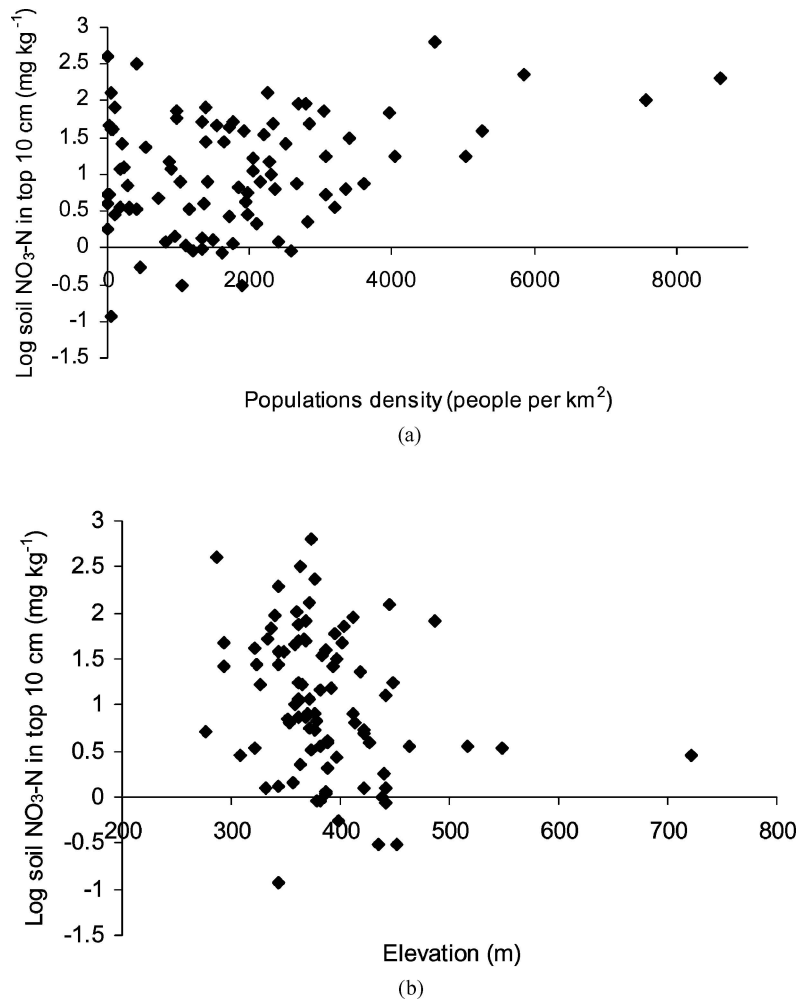


Figure 4. Variation in soil $\text{NO}_3\text{-N}$ with (a) human population density (number of people per km^2) and (b) elevation (m) for the urban sites. Population density is derived from the US Census block group surrounding each sample site.

as found for the region as a whole. In addition, soil $\text{NO}_3\text{-N}$ concentrations tended to be lower at higher elevation urban sites (figure 4(b)) and where there was irrigation (Table 2). However, while these variables were significant in the multivariate models, scatter plots of individual variables show that bivariate relationships are typically indistinct (figure 4).

Desert soils had less variable $\text{NO}_3\text{-N}$ concentrations than at the developed sites (Table 1; figures 2 and 3(b)). Since none of the independent variables tested were found to be significant predictors of variations in soil $\text{NO}_3\text{-N}$ between desert sites and the errors were not identically and independently distributed, the typical overall F-test used in regression was

not applicable here. We instead performed a likelihood ratio test where the null model is a regression equation and only the intercept is fitted. The alternative method was a mixed model where the intercept was fitted by spatially correlated errors and a resulting likelihood ratio test had one degree of freedom. In this approach, rejection of the null hypothesis is an indication that including the spatially correlated errors significantly adds to the model. Since the likelihood ratio test statistic was 5.9 ($P = 0.0086$) this suggests a significant spatial correlation in the errors of $\text{NO}_3\text{-N}$ among the desert sites. The semi-variance of soil $\text{NO}_3\text{-N}$ concentrations was best fit by a spherical model (figure 5), in which semi-variance increased

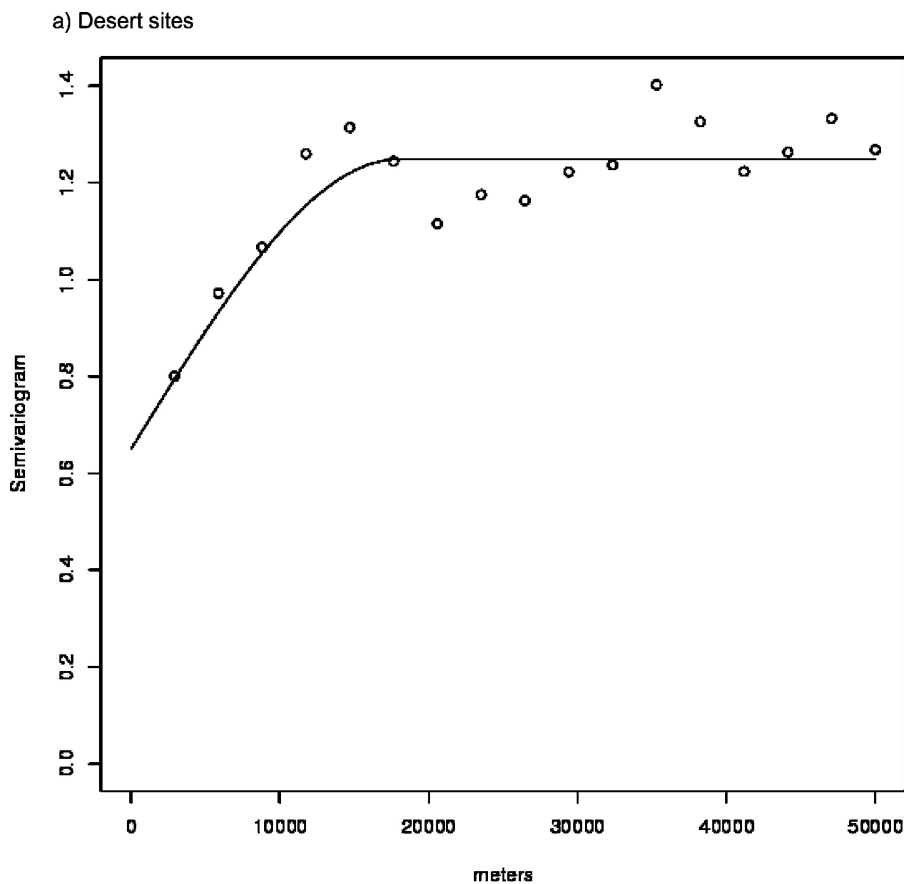


Figure 5. Semi-variogram of soil $\text{NO}_3\text{-N}$ concentrations. (a) For the desert sites semi-variance scores from the semi-variogram (unit-less) increased with separation between sites up to a distance of 10 km (known as the 'range') beyond which it leveled off at a maximum value known as the 'sill' and soil $\text{NO}_3\text{-N}$ concentrations were independent of one other beyond that distance, hence the data are said to be fit by the 'Spherical Model'. The range indicates that soil $\text{NO}_3\text{-N}$ concentrations are correlated up to a distance of 10 km apart, which may be interpreted as average patch size. The y-intercept (called the 'nugget') represents either measurement error or variability occurring at scales smaller than the sampling grain (Rossi *et al.*, 1992). (b) For the urban sites the semi-variogram is a straight line, due to the lack of spatial autocorrelation.

(Continued on next page.)

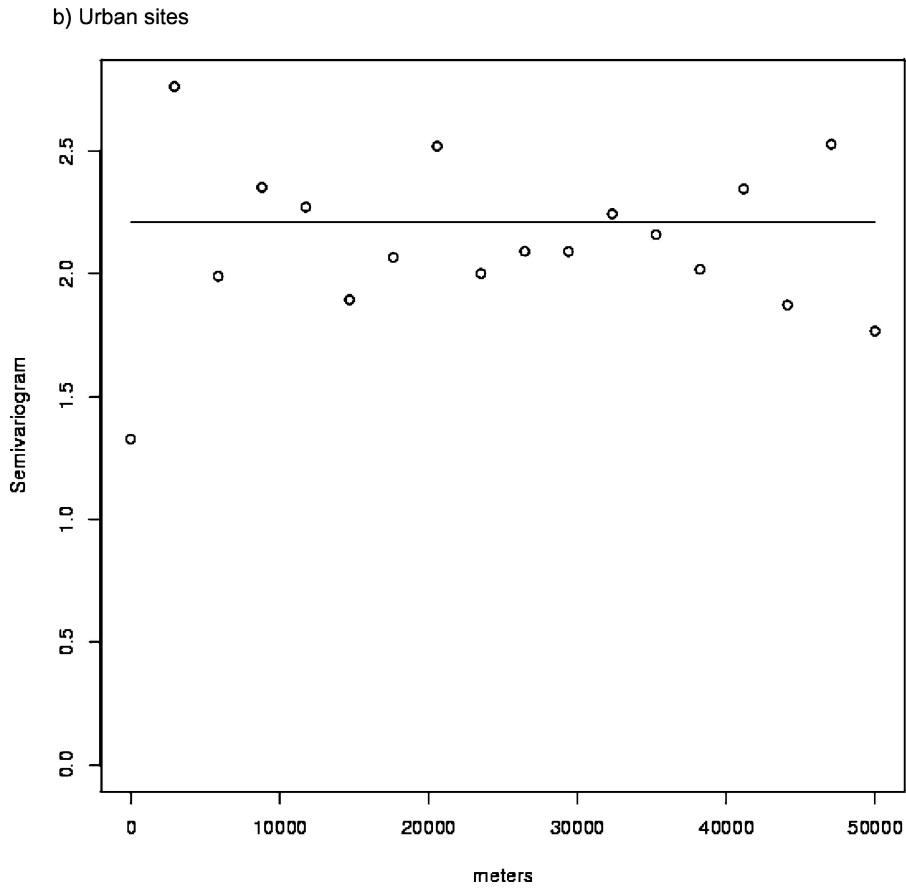


Figure 5. (Continued).

with separation between desert sites up to a distance of 10 km (known as the 'range'). Above 10 km the semi-variance levels off at a maximum value (known as the 'sill') of 1.2184, with soil $\text{NO}_3\text{-N}$ concentrations independent of one other beyond that distance. Variance at the y -intercept (called the 'nugget') was 0.6191 and may represent either variability occurring at scales smaller than the sampling grain, or measurement error (Rossi *et al.*, 1992). The proportion of the total variation attributable to spatial autocorrelation (represented by the difference between the sill and the nugget) was 0.5993. Dividing this value by the sill gives the proportion of total variation in desert soil $\text{NO}_3\text{-N}$ attributable to autocorrelation, in this case 0.49 or 49% of the total.

Soil $\text{NH}_4\text{-N}$

Soil $\text{NH}_4\text{-N}$ concentrations showed variation across two orders of magnitude, from 0.9 to 100.0 mg kg^{-1} dry weight of soil (figure (1)) and there were significant differences between

several of the land use types (figure 2(b)): urban and desert ($P < 0.001$), desert and agriculture ($P = 0.025$), and desert and mixed ($P = 0.008$). Soil $\text{NH}_4\text{-N}$ concentrations were greatest at urban (mean = 7.1 mg N kg^{-1} , $n = 91$) and agricultural (mean = 6.0 mg N kg^{-1} , $n = 23$) sites and lowest (mean = 3.5 mg N kg^{-1} , $n = 73$) at desert sites (Table 1). The ratio of inorganic soil N present as $\text{NO}_3\text{-N} : \text{NH}_4\text{-N}$ was 8.2 across the region as a whole, but was only 3.0 in desert soils, compared to 9.2 in urban soils and 10.5 in agricultural soils.

There was no spatial autocorrelation in soil $\text{NH}_4\text{-N}$ concentrations between neighboring sites for the urban area, or whole sampling region. Spatial variation in soil $\text{NH}_4\text{-N}$ concentrations across the entire CAP region was best predicted by percentage clay, along with latitude and human population density, with the overall F -test for the regression model significant at $P < 0.0001$ (the marginal t -test P values for each variable are listed in Table 2). Soil $\text{NH}_4\text{-N}$ concentrations showed the same tendency as $\text{NO}_3\text{-N}$ to decrease from south to north across the study area, but tended to be lower where there was higher human population density in the surrounding neighborhood and at sites with higher clay contents. Urban soil $\text{NH}_4\text{-N}$ concentrations (from 0.9 to 100.0 mg kg^{-1} dry weight) were best predicted by a regression model using human population density, in combination with elevation, percentage lawn cover and irrigation (the overall F -test having a significance of $P = 0.0008$, marginal t -test P values for each variable are shown in Table 2). In contrast to the urban soil $\text{NO}_3\text{-N}$, concentrations of urban $\text{NH}_4\text{-N}$ tended to be *lower* at sites with higher human population densities and *higher* at greater elevations and in the presence of irrigation (Table 2). Lawn cover had the same inverse contribution to the model of urban soil $\text{NH}_4\text{-N}$ as seen for urban soil $\text{NO}_3\text{-N}$. Desert soil $\text{NH}_4\text{-N}$ concentrations were best modeled by clay content and were significantly higher at sites with soils containing higher amounts of clay (Table 2). The overall F test suggested a P level for this regression model of 0.0375.

Discussion

Natural factors affecting soil $\text{NO}_3\text{-N}$

Spatial dependence in soil properties is known to occur over short distances. This can be as little as 10 m in desert shrub lands, where spatial patterning in available soil nutrients have been found to vary with shrub and inter-shrub position (Schlesinger *et al.*, 1996; Schlesinger and Pilmanis, 1998), or up to 100 m in agricultural fields (Robertson *et al.*, 1997). However, only one previous study to date has analyzed spatial autocorrelation in soil nutrients at the regional scale. In the Hebei Province of China, an area of alluvial plains and hills with cropland, forest and grassland, Guo *et al.* (2001) found the range of spatial autocorrelation varied from 5 km to 25.5 km, the shortest range being for available N and the largest for available K, with the semi-variance of soil N, P and K concentrations best fit by a spherical model, as with the CAP data. Our semi-variogram model for $\text{NO}_3\text{-N}$ concentrations in the top 10 cm of desert soils indicated that 49% of the variance was spatially structured, with spatial dependence between concentrations at neighboring sites up to 10 km apart. We interpret this to indicate the average 'patch size' for soil nitrate in this landscape, a typical patch being determined by geomorphic features (e.g., landscape position, similarly aged

depositional surfaces, elevation and erosion features) which in turn influence soil physical and chemical properties at the regional scale (Whittaker and Niering, 1975; McAuliffe, 1994; Parker and Bendix, 1996; Wondzell *et al.*, 1996).

Human influences on inorganic soil N

Urbanization appears to have had a significant effect on inorganic soil N across the CAP region at the scale and grain size of our sampling. The natural patterning seen across undeveloped desert sites was completely absent for urban sites. Urban and other developed sites also had higher and much more variable inorganic soil N concentrations compared to undeveloped desert (Table 1, figures 2 and 3). They also had higher soil water and organic matter contents and lower bulk densities, differences which are unlikely to result merely from pre-existing soil characteristics related to the underlying geomorphic template (Zhu, personal communication). Similar patterns in urban soil properties have been reported elsewhere, although these studies report a smaller range of concentrations (Pouyat *et al.*, 1994, 1997, 2002; Carreiro *et al.*, 1999; Pouyat and Turechek, 2001; Zhu and Carreiro, 2004).

Unlike the previous studies mentioned we found no relationship between soil NO₃-N or NH₄-N and distance from urban center, perhaps not surprising in such a patchy environment. Some classic measures of an urban gradient (human population density, impervious surface and lawn cover) did appear as predictor variables in our models, but as part of a complex, interacting suite of social, geomorphic, and ecological factors which appear to govern soil properties across this rapidly urbanizing arid ecosystem. An alternative model treating the same data with a Bayesian approach, gave almost identical results to those presented here (Oleson *et al.*, in review). Similarly complex controls were also found to explain spatial variations in plant diversity across the CAP region (Hope *et al.*, 2003). We suggest that in such new, rapidly growing urban environments it may be more appropriate to think of the landscape as a patchwork of very small gradients, interacting in complicated ways.

The tendency for higher soil NO₃-N concentrations to occur in locations with higher surrounding human population density (figure 4(a)) and with more impervious surface area is likely to be due to more deliberate fertilizer applications at such sites, as well as more inadvertent fertilization from pets and livestock (horses, goats, and other farm animals were present at several sites). Then tendency to find higher soil NO₃-N concentrations in wealthier neighborhoods is perhaps the most surprising finding. This may be due to soils being more intensively managed and fertilized in wealthier neighborhoods, even when other significant variables are taken into account. This observation parallels a previous finding that plant species diversity increases with income (Hope *et al.*, 2003).

The variables in the urban model also largely dominate soil NO₃-N concentrations across the CAP region as a whole (Table 3). There was a clear legacy effect of former agricultural land use on soil NO₃-N across the CAP region, with sites that had ever been in agriculture having significantly higher, a phenomenon which has been reported previously for other soil characteristics in studies elsewhere (Sandor and Eash, 1991). In addition, at the regional scale soil NO₃-N increased from south to north. The apparent presence of a broad regional gradient unrelated to the variations in elevation within the desert and urban data

sub-sets may, in part, result from an urban heat island effect, which gives rise to higher soil temperatures (and potentially higher soil N pool turnover rates) in the urbanized parts of the region (Baker *et al.*, 2002). Regional and localized enhanced N deposition may also have elevated inorganic soil N at some sites, with the presence of some of the highest soil NO₃-N concentrations at sites adjacent to major freeways, as seen on a regional scale elsewhere in the western US (Padgett *et al.*, 1999; Padgett and Bytnerowicz, 2001; Fenn *et al.*, 2003).

High soil NO₃-N concentrations also occurred in several other widely varying locations (e.g. former sewage storage pond, edge of a fallow agricultural field), highlighting the importance of very site-specific factors not captured by our predictor variables. These may include short-term variations in site management practices (e.g. irrigation, fertilization), as well as seasonal effects. Soil NO₃-N and NH₄-N concentrations (and N transformations) typically show marked rainfall and temperature-related seasonal variations in arid environments periods (Xie *et al.*, 2001; Sadras and Baldock, 2003). Hence the occurrence of a peak of rainfall in the middle the sampling period is likely to have contributed to between-site variation, although it would not have caused systematic bias since the sites were visited in random order.

Comparing soil NO₃-N and NH₄-N

Soil NH₄-N concentrations were generally lower and somewhat less variable from site to site than for NO₃-N, but showed the same general differences between land use types (Table 1). Modeling showed that spatial variations in desert soil NH₄-N were primarily related to clay content (Table 2) which, although low compared to the range seen across the region as a whole, showed a positive relationship to NH₄-N concentrations. This was presumably due to ammonia being less likely to volatilize in fine textured soils where a greater number of exchange sites allowed NH₄-N to accumulate (Xie *et al.*, 2001). However, soil texture was replaced by a combination of geomorphic and human-related variables in the model for urban soil NH₄-N (Table 2). These were mostly the same predictor variables as for NO₃-N (elevation, latitude, population density and presence of irrigation). Urban (and agricultural soils) had higher clay contents than found in desert soils (Zhu *et al.*, in review). This leads us to speculate that the long-term repeated watering of soils in this environment may have increased clay content and depleted the soil NH₄-N pool over time (Schlesinger and Hartley, 2000), or more likely that urban sites tend to occur on the flatter areas where soils had higher clay contents prior to development.

The magnitude of vegetation uptake, microbial immobilization, leaching and denitrification losses are likely to vary significantly with moisture (Fisher *et al.*, 1987; Hefting *et al.*, 2004). Across CAP, irrigation is associated with lower soil NO₃-N and NH₄-N concentrations, compared to non-irrigated sites. Urban soils without irrigation ($n = 12$ sites) had higher mean inorganic N concentrations (NO₃-N = 71.4 mg kg⁻¹, NH₄-N = 10.4 mg kg⁻¹) than sites with irrigation ($n = 77$, NO₃-N = 38.1 mg kg⁻¹, NH₄-N = 6.6 mg kg⁻¹). A similar trend was seen for mean concentrations in irrigated agriculture ($n = 20$, NO₃-N = 33.1 mg kg⁻¹, NH₄-N = 3.1 mg kg⁻¹) compared with un-irrigated farmed sites ($n = 3$, NO₃-N = 131 mg kg⁻¹, NH₄-N = 24.7 mg kg⁻¹). Our hypothesis is that the much greater

variability in $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in the urban area reflects the much more variable management (irrigation and fertilization) regimes from site to site within the city compared to the desert. On any given day, some irrigated sites will be wet, and others will be dry (similarly with agricultural sites). Meanwhile in the desert, moisture regimes vary only with precipitation and so NO_3^- and NH_4^+ would be expected to be less variable. The coefficients of variation support this, decreasing in the order: urban \gg ag $>$ desert for $\text{NO}_3\text{-N}$ and in order: ag $>$ urban \gg desert $>$ for $\text{NH}_4\text{-N}$ (Table 1).

Why do variables in the urban soil $\text{NH}_4\text{-N}$ model tended to have the *opposite* sign to those found in the model of urban soil $\text{NO}_3\text{-N}$? Rates of net N mineralization measured in laboratory incubations showed desert sites across CAP to have net inorganic N production, while urban soils showed a mixture of production and consumption, with an average close to zero (Zhu, personal communication). We suggest that frequent irrigation, interspersed with dry periods, promotes net mineralization and nitrification. Yet although nitrate removal is higher in irrigated systems (Peterjohn and Schlesinger, 1991), N production is greater than removal, resulting in the elevated $\text{NO}_3\text{-N}$ concentrations observed in urban and agricultural soils ($\text{NO}_3\text{-N} : \text{NH}_4\text{-N}$ ratios of 9 and 6 respectively) compared to desert sites ($\text{NO}_3\text{-N} : \text{NH}_4\text{-N}$ ratio of 3). The low $\text{NO}_3\text{-N}$ in desert soils may be due to low N supply and rapid denitrification during wet periods, with $\text{NH}_4\text{-N}$ accumulation being favored during the extended dry periods (Xie *et al.*, 2001; Sadras and Baldock, 2003; Welter, 2004). However, since pools of soil NO_3^- and NH_4^+ are quite labile, our one-time sampling may not reflect long-term average concentrations. The extent to which the patterns reported here differ during periods of low precipitation and after heavy rains needs to be tested in future work.

Conclusions

We postulate, based on the extent and grain size (resolution) of this study, that many urban systems have greater heterogeneity in soil inorganic N concentrations than the surrounding landscape. Geomorphic and edaphic controls on inorganic soil N in the desert surrounding the Phoenix metropolitan area fail to explain the variability seen within the city. Instead, these “natural” controls are replaced or modified by a suite of social and management factors in our models of spatial variation across the CAP region. This leads us to conclude that humans impart this variability to the urban soils. Why are soil $\text{NO}_3\text{-N}$ concentrations in samples even relatively close to one another completely independent in the city? At the scale of the region this is likely to result from direct and legacy effects of land use decisions, while at small scales, the decisions of individual homeowners and farmers on the types of plant cover, irrigation and fertilization regimes are all likely to be important. Such controls can be very site-specific and show abrupt changes across property boundaries. We suggest that future work focus on determining how much of this site-specific variation arises from predictable variation versus essentially unpredictable contingent events that make each site unique. Intensive human actions, both deliberate and inadvertent, appear to generate a high spatial heterogeneity in urban soil nutrients—a complexity accentuated by economic and social forces.

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