



Urban nitrogen biogeochemistry: status and processes in green retention basins

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Abstract. Nitrogen (N) cycling has been poorly characterized in urban ecosystems. Processes involving N are of specific concern due to increasing anthropogenic inputs from fertilizer uses and fossil fuel combustion in cities. Here we report on a study of N biogeochemistry in city green retention basins and city parks in the Phoenix metropolitan area, Arizona, USA. City retention basins receive N inputs from street runoff, and along with city parks, fertilizer input from management, making these urban patches potential hot spots for biogeochemical cycling. We sampled soils from six retention basins and two non-retention city parks and measured soil organic matter (SOM) content, net N mineralization, net nitrification, denitrification potential, and intact core denitrification flux and nitrate retention. Our results showed significantly higher SOM, extractable nitrate, nitrification rates and potential denitrification rates in surface soils (0–7.5 cm; soil that is directly affected by fertilizer N input, irrigation, and storm runoff) than in deeper soils. We also observed a distinct horizontal trend of decreasing SOM and denitrification potentials from inlet to outlet (dry well) in the retention basins. Denitrification rates, measured both as potential rates with substrate amendment ($390\text{--}1151\text{ ng N}_2\text{O-N g}^{-1}\text{ soil h}^{-1}$), and as intact core fluxes ($3.3\text{--}57.6\text{ mg N m}^{-2}\text{ d}^{-1}$), were comparable to the highest rates reported in literature for other ecosystems. Management practices that affect biogeochemical processes in urban retention basins thus could affect the whole-city N cycling.

Introduction

Urbanization greatly alters ecosystem structures, components, and processes at levels never before seen (Pickett et al. 1997; Grimm et al. 2000). That humans have dramatically altered the global nitrogen (N) cycle is well known (e.g., Vitousek et al. 1997), but what is less appreciated is the extent to which cities, and demands urban populations place on their hinterlands, contribute to this alteration.

In cities, N transformations are altered in the following ways. First, fixation of N_2 within internal combustion chambers of automobile engines is a major source of reactive urban N. Baker et al. (2001) estimated that annual NO_x emissions from combustion processes alone produced $33.8 \times 10^6\text{ kg N}$, or $27.3\text{ kg N ha}^{-1}\text{ yr}^{-1}$, for the Phoenix metropolitan area they studied. The fate of the NO_x is unknown, but it is likely deposited relatively near the source at rates that depend in part on the city's ecosystem structure: the architecture and kinds and distributions of trees and buildings throughout the city. Second, large quantities of chemical fertilizers are

used daily in cities for maintaining lawns. The recommended rate of application of such fertilizers is $200 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Muchovej and Rechcigl 1994). Third, pets eat food (and the N contained within it) imported from outside the city, but deposit their urine and feces in public and private lawns and byways. Here we do not consider the N contained in human waste since in Phoenix metropolis it is mostly channeled into sewer systems where it is denitrified in the city wastewater treatment plant.

Not only has the input of N substantially increased in urban ecosystems, the distribution and transportation of N among various urban patches also has been altered dramatically. One unique characteristic of cities is the large percentage of paved, impervious surface. For example, Gromaire-Mertz et al. (1999) reported >90% impervious surface area (including roof, street, and impervious courtyards) for a residential catchment in central Paris, with the remainder being gardens, lawn, and bare soil. In the Phoenix metropolitan area, paved surfaces may comprise more than 50% of the residential and other urban properties (Stefanov et al. 2001). While N deposited on paved surfaces is not biologically transformed, during storms, stored N is picked up in storm runoff and transported to grassy channels or basins. There, soil and vegetation can actively take up N and various other N transformations could occur.

The large percentage of impervious area in cities makes urban runoff and pollutant control major issues in urban ecology and urban management. Since the 1960s, in most developed countries, the old practice of 'collecting and disposing urban runoff as completely and as quickly as possible' has been deemed mostly impossible with the fast pace of urbanization, and is increasingly being criticized as environmentally insensible (Scott et al. 1999). Instead, multilevel devices have been created to reduce peak runoff volume (and the pollutants in runoff). In many cities, surface runoff is separated from the city sewage system and channeled to retention basins or ponds. Moreover, water is a valuable resource in arid and semiarid regions. In some cities, runoff water is therefore actively collected and stored, and later reused for maintaining city lawns, thus simultaneously providing flood peak reduction, pollution control, and improved amenities (Argue and Pezzaniti 1999).

These storm water management practices create the potential for large quantities of non-point source pollutants such as N to be channeled and concentrated in relatively small catchment areas. While non-point source pollution of surface waters from urban and agricultural activities is a major concern of global ecology and its impact on neighboring natural ecosystems has been extensively documented (Tikkanen et al. 1997; Carpenter et al. 1998), the transformation and retention of N and phosphorus (P) in specific urban patches such as retention basins has not been addressed adequately by ecologists. The traditional engineering focuses of city retention basins mostly concern water infiltration rates (for flood control), sediment loading (for clogging evaluation), and heavy metal and hydrocarbon retention (for pollution control) (Maldonato et al. 1994; Bhaduri et al. 1995). Biogeochemical processes involving essential elements for ecosystems, such as N, P, cations, and organic matter, have not been considered. The few exceptions (Bhaduri et al. 1995;

Stanley 1996) treat the retention basin as a 'black box', calculating only input and output masses. These kinds of research, although valuable, ignore intra-system transformations – that is, those biogeochemical processes occurring within the retention basin, which can lead to an inability to explain observed patterns and hinder our ability to best manage the ecosystem.

Here, we report on a study of soil N mineralization, nitrification, and denitrification in city retention basins in the Phoenix metropolitan area. Phoenix is located in the northern Sonoran Desert of central Arizona, with annual precipitation about 15–20 cm and mean annual air temperatures between 20 and 23 °C. While the total rainfall amount is low, rain is concentrated in the summer monsoon season and in winter. Episodic rainfall usually creates high surface runoff, even in natural desert landscapes, owing to low soil percolation (Fisher and Minckley 1978; Fisher and Grimm 1985). In cities, storm runoff frequently causes flood damage that can incur costs of millions of dollars. Various retention devices have been created to prevent floods and to control non-point source pollutants, with community retention basins being the most broadly used. These basins are usually covered by winter grass, located in topographically lower areas, and collect runoff from a network of drainage ditches. They serve for water retention during flooding events and as community playgrounds the rest of the time.

Materials and methods

Site selection and soil sampling

Eight sites were selected in the east valley of the greater Phoenix metropolitan area, in the cities of Tempe and Mesa, Arizona. City retention devices have been given numerous names such as retention basins, detention basins, detention tanks, retention ditches, and retention ponds. Scott et al. (1999) defined 'detention' as the holding of runoff for short periods to reduce peak flow, followed by later release into watercourses to continue in the hydrologic cycle, and 'retention' as the procedures and schemes whereby storm water is held for considerable periods causing water to continue its hydrologic cycle via infiltration, percolation and evapotranspiration, and not via direct discharge to watercourses. In the Phoenix metropolitan area, stormwater management systems have both retention and detention functions. While surface runoff is channeled into the basins and covers the basin grass and soil, there are usually outlets (dry wells) for water to move out of the basin (to the deeper vadose zone). Water thus does not accumulate in the basins for extended periods of time; a management choice based on the public health concerns (mosquito outbreaks, for example). The basins serve as public playgrounds when there is no standing water (i.e., most of the time). Here we are using the term 'retention basin' in a broad sense and include those used for both retention and detention purposes. We selected six retention sites that collected channeled runoff from the surrounding urban or residential areas. For comparative purposes, we also sampled two city parks that did not collect any channeled runoff. All sites are

covered by winter grass and have no standing water during non-storm times. Sites are watered and fertilized by the city or respective neighborhood associations. Detailed information for each site is listed in Table 1.

In July 2000, we set a transect in each retention basin starting near the inlet, and spanning towards the outlet, sampling at four equidistant points along the transect. In non-retention city parks without visible inlets and outlets, we attempted to set transects covering representative landscape attributes. At each point, a 5.0 cm diameter soil core was taken to 15 cm depth. The soil core was sectioned into equal surface and deep parts and stored in Ziploc bags. A second soil core was taken to about 7–8 cm deep (surface soil only) and covered with caps for an intact core experiment. All soil samples were transported immediately to the nearby Arizona State University (ASU) laboratory and refrigerated at 4 °C before being processed (in <48 h). Samples were taken at least 48 h after any significant rain and no runoff water was noticed when we sampled the soil.

Chemical analyses of soils

Soils from the upper and lower parts of cores were separately hand sieved and sorted for root and rock material, and all weights were recorded. The soil weight per core allows us to calculate N contents and transformation rates on both a per gram soil basis and a per square meter area basis. Sieved soil samples (10 g) were extracted with 50 ml 2 M KCl solution, and filtered through pre-ashed glass fiber papers (GF/A, ashed at 550 °C for 2 h). The filtrate was acidified with 0.2 mL 6 M hydrochloric acid and stored at 4 °C before chemical analysis.

Filtrate was analyzed for ammonium-N (NH_4^+) and nitrate-N (NO_3^-) on a Bran-Luebbe TrAAcs 800 autoanalyzer, using standard alkaline phenol method (for NH_4^+) and cadmium reduction method (for NO_3^-). Method detection limit was 0.01 mg L^{-1} for both analyses. Filtrates were analyzed within 2 weeks. Our preliminary data indicated no change of NH_4^+ and NO_3^- concentrations in acidified solution during the 4-week storage period.

Sub-samples of sieved soils were oven dried at 60 °C for >48 h. Soil moisture content was calculated as g water 100 g^{-1} oven-dry soil. N contents were calculated as $\mu\text{g N g}^{-1}$ oven-dry soil. Additional soils were ashed at 550 °C (2 h) to obtain SOM content (loss on ignition method).

We measured net N mineralization and net nitrification rates using a 28-day lab incubation method. Sieved soil in the amount of 10 g was weighed into 250 ml bottles and adjusted to 20% soil moisture. The bottles were capped loosely to allow air movement while minimizing water loss. Incubation bottles were aerated weekly by removing their caps, and moisture contents were adjusted to 20%. Soils were extracted with 2 M KCl solution after the incubation and inorganic N (NH_4^+ and NO_3^-) were measured as described above. The difference between inorganic N contents before and after incubation was used to calculate net N mineralization rates. Net nitrification was defined as the difference between NO_3^- measurements before and after incubation.

Table 1. Site descriptions of retention basins and non-retention city parks. City parks include many non-grassy areas such as baseball fields, playgrounds and picnic grounds. Only the grassy area is included in size estimation.

Site name	Usage description	Size (m ²)	Watered?	Fertilized?
<i>Retention basins</i>				
Las Brisas site (LB)	Collects runoff from neighborhood residential area (high density single homes); pet activity high	~1500	Yes	Yes
Mesa Detention basin (MD)	Collects runoff from neighborhood, major street, and nearby canal; soccer field in the middle; pet activity likely	~50000	Likely	Likely
Mesa Retention basin (MR)	Collects runoff from neighborhood and major street; playground at the edge; pet activity likely	~25000	Likely	Likely
Corbel Park (CP)	Collects runoff from neighborhood and small street; playground at the edge; pet activity likely	~20000	Yes	Yes
Stroud Park (SP)	Collects runoff from neighborhood and possibly from nearby canal; playground at the edge; pet activity likely	~10000	Yes	Yes
Arizona Mills Mall (AM)	Collects parking-lot runoff from the commercial mall; fenced area, no human or pet access	~2000	No?	No?
<i>Non-retention city parks</i>				
Mitchell Park (MP)	Tempe city park, high human activity, very high pet activity	~10000	Yes	Yes
Daley Park (DP)	Tempe city park, high human activity, high pet activity	~3000	Yes	Yes

Denitrification measurements

Denitrification potential was assessed by measuring the maximum activity of the denitrifying enzyme presented in soil (Groffman et al. 1999). Approximately 50 g sieved soil was weighed into a 125 mL Wheaton bottle fitted with a rubber septum. Fifty milliliters of incubation medium containing the substrates NO_3^- (100 mg N/L) and dextrose carbon (100 mg C/L), and the reagent chloramphenicol, was added. The bottles were flushed with N_2 gas to produce anoxia and then sealed, and 10 ml acetylene (C_2H_2) was injected through the septum. The bottles were then incubated at room temperature with gentle swirling. Nitrous oxide (N_2O) gas samples were taken after 0.5 and 2.5 h. N_2O concentrations were measured in a Shimadzu gas chromatograph (GC) equipped with an electron capture detector. Denitrification rates were calculated as $\text{ng N denitrified g}^{-1} \text{ soil h}^{-1}$, after adjusting the N_2O in air and liquid phases using Bunsen coefficient (0.544 at 25 °C and 1 atm pressure) and the respective air and liquid volumes.

Denitrification rates of intact soil cores were measured according to Groffman et al. (1999). Intact soil cores containing 7–8 cm of topsoil were sealed at the bottom with rubber stoppers. The stoppers on the top were drilled and fitted with rubber septa and made gas tight with silicon gel caulking. A 10% C_2H_2 gas–air mixture was created in the headspace by injecting C_2H_2 into each intact core and repeatedly pumping the syringe to mix the column. Gas samples were collected after 0.5 and 4.5 h and analyzed for N_2O content by GC. The N_2O produced during the incubation was used to calculate *in situ* denitrification rates. To further evaluate the effect of surface runoff (containing NO_3^-) on soil denitrification rates, we added 60 mL 5 mg/L NO_3^- -N solution to each intact core, an equivalent of a 3 cm simulated rain with 300 $\mu\text{g N}$ per core (0.148 g N m^{-2}). This solution was allowed to percolate through the cores for 24 h. The filtrate was collected, acidified, and refrigerated for later chemical analyses. In more than half the cores, the added solution remained on top of the soil column due to impervious nature of the soil. We carefully decanted the standing water, filtered it and analyzed its water chemistry. We then performed the second round of denitrification measurements on these intact soil cores as described above.

Statistical analyses

We used two-way analysis of variance (ANOVA) to separate the effects of site (eight levels), soil depth (two levels), and site \times depth interactions. Contrasts were used to compare the six retention basins and two non-retention city parks. Residual plots were checked after each analysis to verify equal variance assumptions. We removed extreme outliers from the statistical analysis (we took a conservative approach, considering only those with Studentized Residual > 5.0) but report them in the text. For intact core measurement, only one-way ANOVA comparing site means was used. Data were reported as means and standard errors (SE). All calculations were done on SYSTAT 6.0 student version (SPSS Inc. 1997).

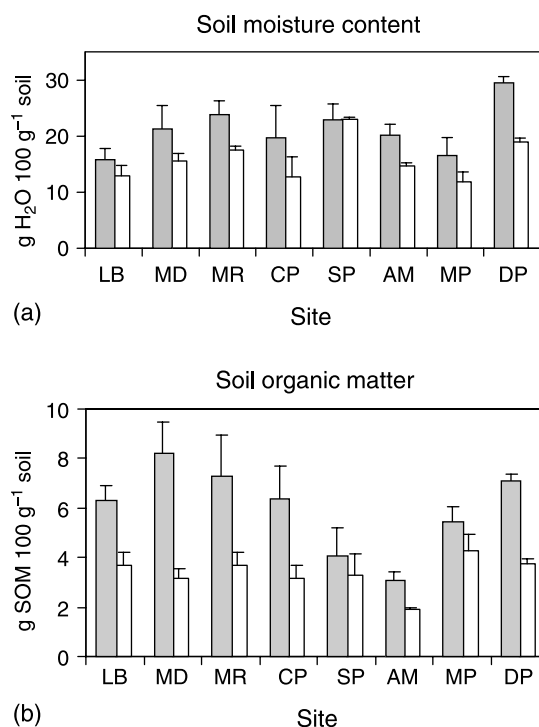


Figure 1. Soil moisture content (a) and SOM content (b) in city retention basins and non-retention city parks, showing the difference of surface (0–7.5 cm, strip bar) and deeper (7.5–15 cm, open bar) soils (mean \pm SE). Two city parks (MP, DP) are plotted at right; the six retention basins at left.

Results

Physical and chemical characteristics of soils

Average surface soil (0–7.5 cm) moisture content ranged from 15.58 to 29.23 g 100 g⁻¹ soil (Figure 1(a)) (an outlier datum, at 74.29 g 100 g⁻¹ at the MR site, was removed from further statistical analysis). Soil moisture in these sites was much higher than is typical for desert soils surrounding the Phoenix metropolis (2.02–3.07 g 100 g⁻¹, 95% CI, Zhu et al. manuscript in preparation). Soil moisture was significantly higher in the surface soils than in deeper ones (20.96 \pm 1.33 v.s. 15.88 \pm 0.81 g 100 g⁻¹, $P = 0.001$), despite high evapotranspiration rates expected in this desert environment.

Average surface soil organic matter (SOM) content ranged from 3.03 to 8.17 g 100 g⁻¹ (Figure 1(b)), varying significantly among sites. SOM content also was significantly higher in the surface soils than in deeper ones (5.93 \pm 0.44 v.s. 3.37 \pm 0.19 g 100 g⁻¹, $P < 0.001$), reflecting the long-term accumulation of dead plant biomass.

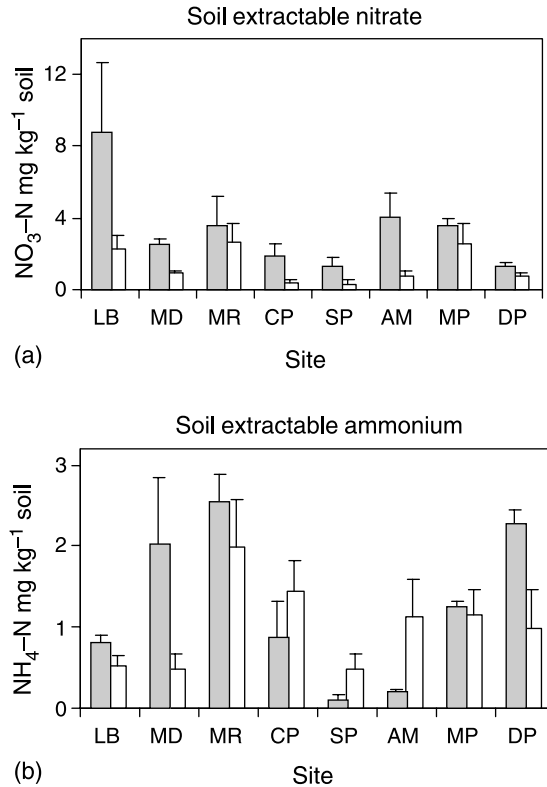


Figure 2. Extractable soil $\text{NO}_3\text{-N}$ (a) and $\text{NH}_4\text{-N}$ (b) contents in surface and deeper soils. Land use legends follow those in Figure 1.

Average extractable $\text{NO}_3\text{-N}$ in surface soils ranged from 1.22 to $8.67 \mu\text{g g}^{-1}$ soil (Figure 2(a)) (an outlier datum at $41.41 \mu\text{g g}^{-1}$, found at the MP site, was removed). There was significantly more $\text{NO}_3\text{-N}$ in the surface soils than in deeper soils (3.29 ± 0.68 v.s. $1.32 \pm 0.26 \mu\text{g g}^{-1}$, $P = 0.003$), despite anticipated higher plant uptake from the surface layer. The LB site, a retention basin managed by a neighborhood homeowners association, had the highest extractable NO_3^- . Extractable NH_4^+ was generally much lower than NO_3^- in all soils. Average $\text{NH}_4\text{-N}$ in surface soils ranged from 0.09 to $2.53 \mu\text{g g}^{-1}$ (Figure 2(b)). In contrast to the other soil variables, there were no differences between soil depths for NH_4^+ ($P = 0.250$), although there was a significant site \times depth interaction. Combined soil extractable inorganic N ($\text{NO}_3^- + \text{NH}_4^+$) in surface soils was almost twice the amount of deeper ones (4.53 ± 0.69 v.s. $2.34 \pm 0.30 \mu\text{g g}^{-1}$, $P = 0.002$). When converted to a per area basis and adding surface and deeper soils together (0–15 cm), average extractable $\text{NO}_3\text{-N}$ ranged from 0.121 to 0.877 g m^{-2} , and average inorganic N ranged from 0.177 to 0.997 g m^{-2} (Table 2).

There were no differences between the six retention basin sites and the two non-retention city parks regarding soil moisture content, organic matter content, or

Table 2. Extractable soil inorganic N ($\text{NO}_3 + \text{NH}_4\text{-N}$) and net N mineralization rates (per m^2 basis). Data are means with standard error in parentheses. Soil depth was 15 cm. For comparison, N data from a large-scale survey in the central Arizona–Phoenix (CAP) urban ecosystem, showing 95% confidence interval for natural desert and urban residential plots (calculated on the same per m^2 unit and contained the same soil depth), were provided.

Site	Inorganic N (g N m^{-2})	N mineralization ($\text{mg N m}^{-2} \text{d}^{-1}$)
<i>Retention basins</i>		
LB	0.997 (0.311)	26.43 (4.76)
MD	0.409 (0.078)	46.25 (4.96)
MR	0.922 (0.128)	38.02 (7.53)
CP	0.416 (0.097)	64.08 (25.60)
SP	0.177 (0.062)	19.20 (10.11)
AM	0.625 (0.137)	26.62 (7.45)
<i>Non-retention city parks</i>		
MP	0.674 (0.128)	61.92 (17.42)
DP	0.484 (0.081)	22.67 (16.21)
Natural desert (CAP)	(0.929, 1.403) ($n = 73$)	(17.62, 33.67) ($n = 44$)
Urban residential (CAP)	(1.806, 3.706) ($n = 54$)	(-3.95, 25.69) ($n = 29$)

extractable inorganic N (Figures 1 and 2, Table 2). Contrast analysis between two groups yielded no significant result for the indices listed above.

Laboratory incubation of soils

Nitrification dominated the process of N mineralization in the 28-day lab incubation. Average net nitrification rates in surface soils ranged from 0.186 to 0.642 $\mu\text{g g}^{-1} \text{d}^{-1}$ (Figure 3). Nitrification rates in surface soils on average were more than three times higher than in deeper soils (0.376 ± 0.058 v.s. $0.100 \pm 0.023 \mu\text{g g}^{-1} \text{d}^{-1}$, $P < 0.001$); but no differences among sites were found. Net N mineralization rates in the surface soils ranged from 0.199 to 0.668 $\mu\text{g g}^{-1} \text{d}^{-1}$, with net ammonification just a small portion of overall N transformation. Both net N mineralization rates and net nitrification rates were positively correlated with SOM content (Pearson correlation coefficient: 0.693 and 0.705 respectively, for both rates, $P < 0.001$, $n = 64$). The correlation between SOM and net nitrification rates was also stronger in surface soils than in deeper soils (Figure 4).

For soil depth from 0 to 15 cm, average nitrification rates ranged from 15.5 to 64.4 $\text{mg m}^{-2} \text{d}^{-1}$, and average N mineralization rates from 19.2 to 64.1 $\text{mg m}^{-2} \text{d}^{-1}$ (Table 2). These values are equivalent to the average production of $\text{NO}_3\text{-N}$ between 0.433 and 1.802 g m^{-2} in the 28-day laboratory incubation.

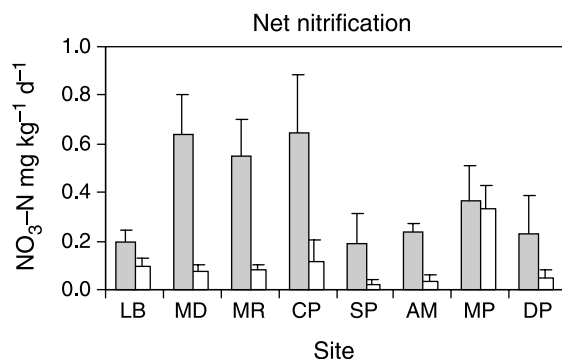


Figure 3. Net nitrification rates (lab incubation with water amendment) of soils collected from city retention basins and non-retention city parks. Land use legends follow those in Figure 1.

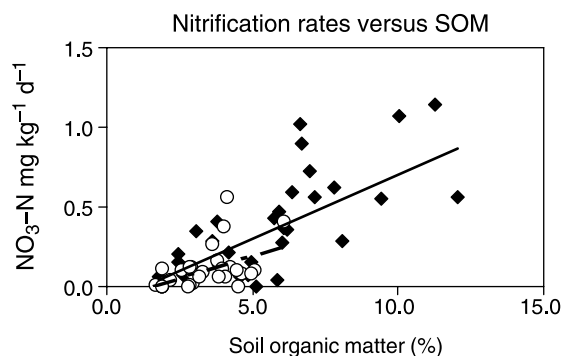


Figure 4. Correlations between soil net nitrification rate and organic matter content, separated according to soil strata. Surface soil (filled diamond): $r^2 = 0.38$, $P < 0.001$; deeper soil (open circle): $r^2 = 0.23$, $P < 0.01$, $n = 32$.

Denitrification potentials

Average potential denitrification rates for surface soils ranged from 390 to 1151 ng N₂O–N g⁻¹ h⁻¹ (Figure 5), or 9.37–27.62 μg N g⁻¹ d⁻¹. Denitrification potential was significantly higher in surface soils than in deep soils (730 ± 73 v.s. 149 ± 21 ng N₂O–N g⁻¹ h⁻¹, $P < 0.001$). Potential denitrification rates in our study sites were positively correlated with SOM content ($r = 0.616$, $P < 0.001$, Figure 6) and net nitrification rates ($r = 0.511$, $P = 0.001$), but not with extractable NO₃⁻ of soils.

While significant differences of N transformation rates were observed among the sites we studied, we found no difference in net nitrification rate, net N mineralization rate, and denitrification potential between the six retention basins and the two non-retention city parks (Contrast analyses: $P = 0.974$ and 0.237 for nitrification and denitrification potential, respectively).

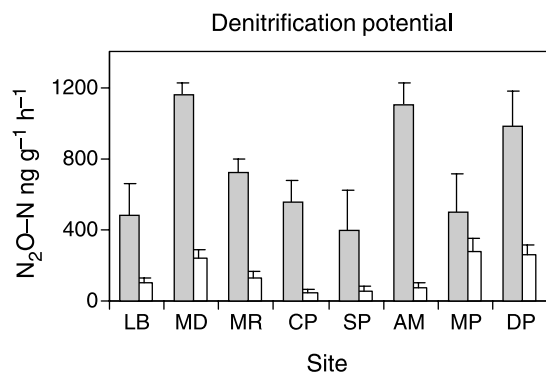


Figure 5. Potential denitrification rates of soils collected from city retention basins and non-retention city parks. Land use legends follow those in Figure 1.

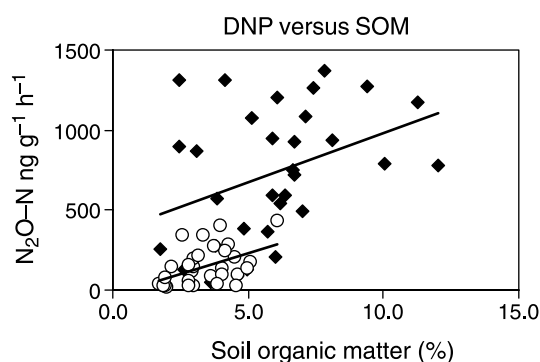


Figure 6. Correlations between potential denitrification rates and organic matter content of soil, separated according to soil strata. Surface soil (filled diamond): $r^2=0.14$, $P < 0.05$; deeper soil (open circle): $r^2=0.22$, $P < 0.01$, $n = 32$.

Denitrification – intact core fluxes and the change of water chemistry

Intact core denitrification fluxes varied substantially both within and between sites. Estimated 24 h denitrification rates ranged from 0 to 371 $\mu\text{g N}$ per core, or averaged from 3.3 to 57.6 $\text{mg N m}^{-2} \text{d}^{-1}$ (0–7.5 cm soil depth). Receiving a simulated runoff solution (with $\text{NO}_3\text{-N}$ concentration at 5 mg/L) produced very slight changes. Average denitrification fluxes 24 h after leaching with NO_3 solution ranged from 3.8 to 82.7 $\text{mg N m}^{-2} \text{d}^{-1}$. This range of actual denitrification flux is of the same magnitude of net nitrification rates reported previously.

While N_2O fluxes changed only moderately before and after receiving the simulated runoff solution, the change in water chemistry during the 24 h incubation period was dramatic and was largely determined by the pattern of leaching (Figure 7). Soil percolation was highly variable although usually slow: in less than

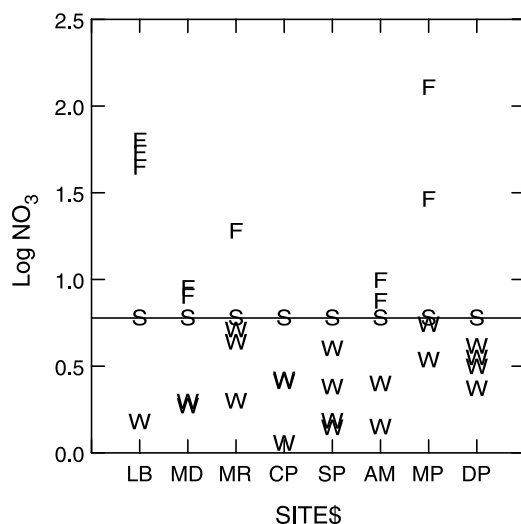


Figure 7. Nitrate-N concentration, expressed on a log scale ($\log_{10} [\text{NO}_3\text{-N} + 1]$), of water that did (F) or did not (W) infiltrate the soil column in laboratory experiments simulating runoff input to soils. 'S' represents control standard ($\text{NO}_3\text{-N}$: 5 mg/L).

1/3 of the cases simulated runoff passed through soil cores and was collected as filtrate. In the remaining cases, standing water remained and the NO_3^- was subject to substantial reduction. On the other hand, when water infiltrated the soil column, the filtrate chemistry was higher than the 5 mg/L standard level (the concentration of added solution), indicating an input of NO_3^- from the soil columns. The average $\text{NO}_3\text{-N}$ in standing water was 1.78 mg/L (95% CI: 1.20–2.35 mg/L), while average $\text{NO}_3\text{-N}$ in filtrates was 36.1 mg/L (95% CI: 9.02–63.1 mg/L).

Discussion

Nitrogen transformations in urban retention basin soils

Net N mineralization rates in the surface 7.5 cm soils we measured ranged from 0.199 to 0.668 $\mu\text{g g}^{-1} \text{d}^{-1}$ in this study. These rates were much higher than the rates reported in the parafluvial sediments of a Sonoran Desert stream (Holmes et al. 1996) and in Negev desert soils (Zaady et al. 1996), but were comparable to values reported for Chihuahuan Desert (Jornada basin; Reynolds et al. 1999). Zhu et al. (unpublished data) recently examined soil N transformations in a Sonoran Desert upland site and found average net N mineralization rates (same lab incubation method) ranging from 0.36 to 0.96 $\mu\text{g g}^{-1} \text{d}^{-1}$ in the top 0–2 cm, and 0.09–0.29 $\mu\text{g g}^{-1} \text{d}^{-1}$ at 2–12 cm depth; with NO_3^- the dominant form of inorganic N produced during the incubation. On an areal basis (0–15 cm soil depth), net N mineralization in these city retention basins ranged from 19.2 to 64.1 $\text{mg m}^{-2} \text{d}^{-1}$.

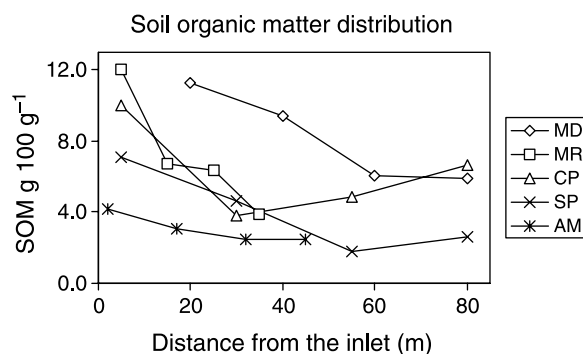


Figure 8. Distribution of SOM content along transects from inlet to 'sink' (outlet) in five urban retention basins. Lines are drawn for each site separately. Basin LB data were excluded from this figure as it does not have a clear inlet.

In comparison, net N mineralization measured in a broad-scale soil and vegetation survey in the central Arizona–Phoenix (CAP) urban ecosystem (a 6400 km² area covering whole Phoenix metropolis including all sites used in this study) in spring 2000 had a 95% confidence interval from 17.62 to 33.67 mg m⁻² d⁻¹ for natural desert sites and from -3.95 (net immobilization) to 25.69 mg m⁻² d⁻¹ (net mineralization) for the urban residential sites (Table 2). Thus city retention basins did not have substantially higher N mineralization (and nitrification) rates than surrounding ecosystems despite having received both managed and runoff inputs of water and nutrients.

N cycling in urban retention basins is likely stimulated by a combination of heterogeneous organic matter and nutrient inputs from runoff, and additions of these materials – and water – owing to on-site management. Net N mineralization and nitrification rates in this retention basin study were positively correlated with SOM content. SOM of the surface soils in retention basins ranged from 3.0 to 8.2%, much higher than what we found in the natural desert soils (95% CI: 1.92–2.29%; Zhu et al., manuscript in preparation). We plotted the distribution of SOM and denitrification potentials in the surface 7.5 cm of five retention basins against distance from the runoff inlets. A decrease in %SOM from the retention inlets is evident (Figure 8), indicating the importance of this runoff input. Statistic analysis showed a significant 'Position' factor ($F_{3,12} = 11.2$, $P = 0.001$) and the linear contrast of SOM against relative positions from the inlets is highly significant ($P < 0.001$). The spatial distribution of denitrification potential from the inlet to outlet generally followed the distribution pattern of SOM, but was more variable with no significant linear decline (linear contrast against the position $P = 0.110$, quadratic contrast $P = 0.088$). Jacopin et al. (1999) reported that solid particles collected in sediment traps when runoff water passed through a detention basin were fine-grained materials of high organic matter content (24%). Furthermore, these particles exhibited high affinities for heavy metals, and downward movement of pollutants was confined to the top 10 cm. In this study, we found major differences for SOM, N mineralization and nitrification, and

denitrification potentials between surface and deeper soils, suggesting the importance of surface soil (which is heavily affected by human management) in the overall biogeochemical processes in these basins.

Extractable soil inorganic N (dominated by NO_3^-) was surprisingly low in these human-managed urban ecosystems receiving direct fertilizer input and runoff from the nearby impervious surfaces. In the CAP survey conducted in spring 2000, extremely high $\text{NO}_3\text{-N}$ concentrations ($>100 \mu\text{g g}^{-1}$) and variations of several orders of magnitude in $\text{NO}_3\text{-N}$ (from <0.5 to $>1000 \mu\text{g g}^{-1}$) were found in 203 plots sampled, as well as in all major human land-use categories (54 urban residential plots, 36 non-residential urban plots, 23 agricultural plots, 6 transportation and 11 mixed plots; Zhu et al. manuscript in preparation). In contrast, the retention basins and city parks we studied here exhibited much lower variability ($\text{NO}_3\text{-N}$ ranged from 0.30 to $8.67 \mu\text{g g}^{-1}$) and had soil inorganic N content even lower than the natural desert (Table 2). Although the CAP survey was conducted in spring 2000 whereas we sampled retention basins in the summer, active site management (irrigation, fertilization, etc.) should maintain a relatively constant N status in these green retention basins. We suspect that active N transformations (nitrification and denitrification) in these sites, supported by high soil moisture, effectively reduced both the amount and the variability of extractable inorganic N. Indeed, soil moisture in these green basins ($20.96 \pm 0.98\%$, 0–7.5 cm; $15.88 \pm 0.96\%$, 7.5–15 cm) was not only much higher than the desert plots, but also higher than the urban residential plots of the CAP survey ($10.09 \pm 0.97\%$, based on the surface 10 cm of soil sampled from 54 urban residential plots). In addition, the higher average SOM in these managed desert ecosystems (Figure 1(b)) could also increase microbial immobilization, further reducing the level of soil inorganic N.

Denitrification likely plays a key role in maintaining low soil extractable inorganic N in these urban retention basins. Actual denitrification rates in retention basins of this desert city ($3.3\text{--}57.6 \text{ mg N m}^{-2} \text{ d}^{-1}$, 0–7.5 cm soil depth), as well as potential denitrification rates measured using the denitrification enzyme assay, were among the highest rates of denitrification reported in the literature (Groffman 1994, Table 3). Pinay et al. (1995) however, reported a substantially higher summer denitrification rate ($250 \text{ mg N m}^{-2} \text{ d}^{-1}$) in riparian forest soils in southern France exposed to extremely high riverine NO_3^- concentrations. Groffman (1994) reported denitrification flux in natural and heavily polluted wetland soils to be from <0.1 to $20\text{--}36 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. Our measured actual denitrification rates, extrapolated to annual rates by assuming 200 d of active denitrification per year (which is conservative for the central Arizona climate), would be equivalent to $6.6\text{--}115.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. While this annual denitrification estimate must be interpreted with caution since it is based on a one-time soil sampling and does not reflect possible interannual, interseasonal, and diurnal variations, nevertheless the denitrification estimate explains well the status of low extractable soil inorganic N in places receiving large exogenous N and SOM input, and the denitrification flux estimated is in the same range of our independently measured net N mineralization and nitrification rates. Our denitrification estimate is also in sharp contrast with those estimated for natural deserts in the Southwest United States. Virginia et al.

Table 3. Cross ecosystem comparison of denitrification rates.

Ecosystem type/location	Actual denitrification ($\text{mg N m}^{-2} \text{d}^{-1}$)	Denitrifying enzyme activity ($\text{ng N g}^{-1} \text{h}^{-1}$) ^a	Reference
Urban retention basins/Phoenix, AZ	3.3–57.6 (0–7.5 cm)	0–7.5 cm soil: 390–1151 7.5–15 cm: 48–248	This study
Wooded swamp/Michigan	Sand: 0.2, clay loam: 11 ^b 0.08–8.04	Sand: 54, clay loam: 558	Groffman and Tiejde (1989)
Red maple swamp/Minnesota	Unenriched sites: 1.7–5.9 ^c Enriched sites: 2.6–13.9	Not reported	Zak and Grigal (1991)
Red maple swamp/Rhode Island	0.11–3.79 ^d 0.047	Not measured	Hanson et al. (1994)
Semi-arid grassland/Yellowstone Park	0.009–0.344 (0–10 cm)	4–1249	Frank and Groffman (1998)
Old field/Michigan		Not reported	Robertson et al. (1988)
Spruce forest/Austria		O horizon: 304–995 A horizon: 20–258	Henrich and Haselwanderter (1997)
Sonoran Desert/South California	27.84 under <i>Prosopis</i> (Mesquite) 0.48 bare soil (after 50 mm H ₂ O)		Virginia et al. (1982)
Desert/Southwest USA	7.90 (after 31.5 mm H ₂ O)	89.7	Peterjohn and Schlesinger (1991)
Desert Stream/Arizona	Paraffluvial: 3.6–4.8 River bank: 0.12	15 60–80	Holmes et al. (1996)
Negav Desert – Macrophytic patch/Israel	19.8 (2–10 days after rewetting) ^e 79.2 (20–30 days after rewetting)		Zaddy et al. (1996)

^aPotential denitrification rate or denitrification potential, as used in this paper.

Actual denitrification rates in several studies were calculated based on ^byearly average rates, ^cyearly average except 88 days winter date when denitrification not measured, ^dactive season average, ^eunit conversion from $\mu\text{g N kg}^{-1} \text{h}^{-1}$ assuming 7.5 cm soil depth and 1.1 bulk density.

(1982) measured denitrification under *Prosopis glandulosa* (a woody legume, thus a spatial resource hot spot) within 48 h of a simulated 50 mm rain (a temporal hot moment), and reported mean rates at $1.16 \text{ mg N m}^{-2} \text{ h}^{-1}$ and estimated annual denitrification flux at 0.5 kg N ha^{-1} . Similarly, Peterjohn and Schlesinger (1991) sampled soil cores along a vegetation transect in the Jornada LTER over a 8-d period and found water, followed by N and C, to be the major limiting factors of denitrification. Their extrapolated annual denitrification flux at $7.22 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ is at the low end of our denitrification estimate for urban retention basins. The pulsed denitrification flux after soil rewetting in desert soils could be quite high since elevated soil respiration could quickly deplete soil O_2 , while inorganic N accumulated during prior dry conditions and N mineralized during the rewetting event provide substrate NO_3^- (Peterjohn and Schlesinger 1991; Zaddy et al. 1996; Belnap et al. 2004). Such pulsed denitrification fluxes, unlike those maintained in managed urban retention basins and lawns, cannot be sustained due to likely water and inorganic N limitation, resulting in much lower annual rates (Virginia et al. 1982).

Denitrification rates measured *in situ* in this study were within the range of net nitrification rates (Tables 2 and 3); however, potential denitrification rates were 10–100 times higher. It is likely that both intra-system NO_3^- production (through N mineralization and nitrification) and exogenous N inputs (from runoff, fertilizer, or pet deposits) were needed to sustain denitrification in these urban sites. In contrast, denitrification in natural systems such as forested wetlands is mostly supported by intra-system nitrification and usually consumes only a small portion of the NO_3^- being produced (Zak and Grigal 1991: denitrification consumed less than 14% of net nitrification). In riparian forests where, like urban retention basins, exogenous N inputs are substantial, denitrification rates are more commonly within the range of nitrification rates (e.g., Pinay et al. 1995). In wetlands constructed specifically for treating agricultural and urban runoff, even greater N removal rates were reported (Mitsch et al. 2001), likely due to combined vegetation uptake, sediment organic matter accumulation, and denitrification.

Buildup of denitrification potential in urban retention basins

Denitrification *in situ* is extremely heterogeneous and is the integrated product of multiple factors, including: (1) size of the denitrifier population (estimated by denitrification enzyme assay, or denitrification potential); (2) low O_2 conditions; (3) high NO_3^- supply; and (4) availability of labile C (Groffman 1994). Potential denitrification rates measured in this study were among the highest ever reported, significantly higher in surface soils than in deeper soils, and positively correlated with SOM content, net N mineralization rates, and nitrification rates (Table 3, Figures 5 and 6). Groffman (1994) suggested that long-term favorable conditions for denitrification eventually lead to a distinctive denitrifier biomass (which produces high levels of denitrification enzymes), and this level is a function of total microbial biomass, soil moisture, and C and N dynamics. The accumulation of

SOM in urban retention basins, fueled by various N inputs and favorable water content in a warm climate, could be the ultimate control of potential denitrification in urban systems. Accumulation of SOM is likely affected by site age and management policies. For example, if grass were left in place after mowing, given time, soil development would be substantial under favorable temperature, moisture, and nutrient conditions. The resulting high SOM, high total soil N, as well as the fine soil particles could support large denitrifier populations.

Urban retention basins also generally meet other criteria for high actual denitrification. Besides the obvious runoff and fertilizer inputs that supply the NO_3^- substrate, the creation of low O_2 conditions is a key factor for retention basin denitrification. Standing water accumulates in retention basins after major storms, and this can generate low O_2 conditions. Desert soils are generally impervious and we found water filtration to be extremely slow, which, coupled with active microbial respiration, would lead to O_2 depletion in standing water. During non-storm seasons, the irrigation management (daily watering) and high soil respiration can create low O_2 microspots in retention basin soils and favor *in situ* denitrification.

In the last two decades, numerous researches have evaluated the role and mechanisms of the vegetated riparian zone in removal of N pollutants from surface runoff and shallow groundwater (Peterjohn and Correll 1984; Lowrance 1992; Haycock and Pinay 1993; Hanson et al. 1994). While urban retention basins are not riparian ecosystems, they do share some characteristics. Both retention basins and riparian ecosystems receive exogenous N (in the forms of NO_3^- , NH_4^+ and organic N), organic C, and soil/sediment deposition via hydrologic input. Both endure dry-wet cycles caused by flooding, and their biogeochemical cycling of N is affected by the change of soil redox status. In unmanaged riparian zones, low primary production in winter results in lower N uptake, and denitrification may be limited because N in groundwater does not interact significantly with surface soils with high denitrification potentials (Lowrance 1992; Haycock and Pinay 1993). In urban retention basins of this desert region, however, plant growth occurs year round and NPP is high due to favorable temperature and moisture conditions. Furthermore, N in both runoff and fertilizer interacts directly with the grass-covered topsoil, which is rich in organic matter and has high denitrification potentials, creating favorable conditions for actual denitrification.

Retention basins versus city parks

We are surprised to find no significant differences between urban retention basins and non-retention city parks in terms of the soil characteristics we quantified. Although city parks do not receive storm runoff, they are fertilized (and subject to pet activity) and watered to maintain year-round green coverage. Low oxygen conditions (after irrigation or rain), high soil respiration, high NO_3^- (as direct inputs or through nitrification), and high C content (due to high primary production) thus could support high rates of denitrification and other N transformations in city parks.

Intact soil cores collected from both retention basins and non-retention city parks substantially reduced NO_3^- in standing water and substantially increased NO_3^- con-

centration in water that passed through soil columns quickly (Figure 8). The loss of $\text{NO}_3\text{-N}$ in the standing water (from 48–220 $\mu\text{g core}^{-1}\text{d}^{-1}$) is in the range of intact core $\text{N}_2\text{O-N}$ flux (from 3 to 247 $\mu\text{g core}^{-1}\text{d}^{-1}$, an equivalent of 1.3–110.2 $\text{mg m}^{-2}\text{d}^{-1}$), providing independent support for our denitrification estimate. On the other hand, the increase of NO_3^- in water passed through the soil column can be explained as an additional input of NO_3^- from the soil itself (the increase of $\text{NO}_3\text{-N}$ in leachate was positively correlated to the soil extractable $\text{NO}_3\text{-N}$ pool, $r^2 = 0.69$).

The removal of pollutant NO_3^- via denitrification in urban retention basins and other grass-covered areas, however, must be viewed in the broad context of human management and urban landscape. The estimated yearly denitrification rates of between 6.6 and 115.2 kg N ha^{-1} in these sites were less than half the normal fertilization rate (200 kg N ha^{-1}), and equivalent to the rate of NO_x production by automobiles. Therefore, large amounts of urban runoff would have to be channeled into these sites to achieve effective N removal of this large input, but in fact, many neighborhoods drain directly to storm pipes and surface waters, even in this relatively new city. Furthermore, the NO_3^- that is not denitrified in retention basins may make its way into groundwater via the drywell outlets, potentially contributing to groundwater NO_3^- pollution. Thus, while our study showed that retention basins have very high denitrification fluxes and could represent useful tools for reducing NO_3^- pollution, we suggest that unless N inputs into the urban ecosystem are substantially reduced, the city likely will remain a source of N pollution to the surrounding landscape.

Conclusions

We measured net N mineralization, net nitrification, and denitrification in urban retention basins, managed ecosystems that receive large energy and material inputs from human activities. Denitrification rates, measured both as actual and potential rates, were among the highest reported in literature. Detailed analyses illustrated that retention basins have ideal ecological conditions for denitrification: accumulation of denitrifier populations, periodic low O_2 , input of NO_3^- , production of NO_3^- within the system, and an ample supply of labile C. Additional modification of management practices, such as increasing C stock (by leaving grass on site after mowing) or maintaining standing water in the basins for extended periods of time (instead of draining water as quickly as possible to the deeper vadose zone), could increase the removal of urban non-point source N pollution. Such practices, however, have drawbacks, such as increasing breeding sites for pests and potential disease vectors, or contributing N_2O , a greenhouse gas, to the global atmospheric pool. Therefore, further studies on the N removal potential of green retention basins and other productive urban patches are urgently needed.

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