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Soil N_2O and NO emissions from an arid, urban ecosystem

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[1] We measured soil nitrogen (N) cycling and fluxes of N_2O and NO in three land-use types across the metropolitan area of Phoenix, Arizona. Urbanization increased N_2O emissions compared to native landscapes, primarily due to the expansion of fertilized and irrigated lawns. Fluxes of N_2O from lawns ranged from 18 to 80 μg N m^{-2} h^{-1} and were significantly larger than managed xeric landscapes (2.5–22 μg N m^{-2} h^{-1}) and remnant desert sites within the urban core (3.7–14 μg N m^{-2} h^{-1}). In contrast, average NO fluxes from lawns were not significantly different from native desert when dry (6–80 μg N m^{-2} h^{-1} lawn; 5–16 μg N m^{-2} h^{-1} desert) and were lower than fluxes from deserts after wetting events. Furthermore, urbanization has significantly altered the temporal dynamics of NO emissions by replacing pulse-driven desert ecosystems with year-round irrigated, managed lawns. Short-term, pulse-driven emissions of NO from wetting of dry desert soils may reach 35% of anthropogenic emissions within a day after summer monsoon storms. If regional O_3 production is NO_x-limited during the monsoon season, fluxes from warm, recently wet arid soils may contribute to summer O_3 episodes.

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1. Introduction

[2] Global emissions of nitrous oxide (N_2O) and nitric oxide (NO) have increased dramatically during the last century, primarily due to human activity [*Holland et al.*, 1999; *Khalil*, 1999]. Nitrous oxide is a stable greenhouse gas in the troposphere with a global warming potential 300 times that of CO_2, and when in the stratosphere, it has the capacity to catalyze the destruction of ozone (O_3 [*Intergovernmental Panel on Climate Change*, 2007]). Concentrations of N_2O in the atmosphere are rising exponentially at $\sim$0.3% a^{-1}, driven mostly by microbial activity in nitrogen (N)-rich soils associated with agriculture. Nitric oxide is also produced by microorganisms in soils, but rising global atmospheric concentrations are due primarily to combustion processes associated with power generation and transportation [*Galloway et al.*, 2004]. Nitric oxide is oxidized rapidly to nitrogen dioxide (NO_2) in the troposphere (together abbreviated as NO_x), and these compounds can react with hydroxyl and volatile organic compounds (VOCs) to produce nitric acid and other organic nitrates, respectively, that enter ecosystems via atmospheric deposition and alter N cycling due to acidification or enrichment [*Aber et al.*, 1998; *Monson and Holland*, 2001]. In addition, high concentrations of NO_x typical of the continental United States can lead to the net production of tropospheric O_3, and these compounds are partially responsible for exceedance of the national O_3 standard by 455 counties in 31 states in 2006 [*Crutzen*, 1970; *Finlayson-Pitts and Pitts*, 2000; U.S. Environmental Protection Agency (EPA), Green Book Non Attainment Areas for Criteria Pollutants, online database, 2007]. In addition to operating as a greenhouse gas in the troposphere, O_3 is highly regulated because of its contribution to photochemical smog and its capacity to significantly damage downwind vegetation [*Gregg et al.*, 2003; *Kangasjarvi et al.*, 1994].

[3] Microbial processes in soil produce N oxides through various transformations of N species including nitrification and denitrification [*Firestone and Davidson*, 1989]. Additionally, some abiotic pathways lead to NO emissions from soil, including decomposition of nitrous acid under acidic conditions [*Allison*, 1963]. Both biotic and abiotic mechanisms of N oxide production are stimulated by increased inorganic N pools in soils [*Davidson et al.*, 2000; *Venterea et al.*, 2005]. As a result, anthropogenic N inputs have significantly increased soil N_2O and NO fluxes through direct fertilization of managed agricultural soils and through atmospheric deposition that indirectly fertilizes soils downwind of agricultural and urbanizing regions [*Fenn et al.*, 1998; *Hall et al.*, 1996; *Ineson et al.*, 1998; *Mosier et al.*, 1998; *Venterea et al.*, 2003].

[4] Although soils are the primary source of N_2O in the atmosphere, they produce only a fraction of the total atmospheric NO_x compared to annual fossil fuel combustion in most ecosystems [*Davidson et al.*, 1998]. However, because of the bidirectional nature of NO_2 flux, soils may play significant roles in net atmospheric transfer of NO_x compounds. Among other loss pathways, NO_2 is removed from the atmosphere through deposition to soil and uptake by plant surfaces [*Sparks et al.*, 2001], and this downward flux is controlled by ambient concentrations and various surface resistance factors, including soil moisture and plant cover [*Gut et al.*, 2002]. However, during the spring and

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summer when warm temperatures can stimulate microbial nitrification and denitrification processes, significant NO fluxes from moist, N-rich soils can offset rates of NO_2 deposition, rendering the soil a net source of NO_x rather than a sink during a time when potential O_3 production is at its largest [*Fowler et al.*, 1998].

[5] Like agriculture, urban and suburban ecosystems such as residential yards, streams, municipal parks, and roadsides are also highly managed and rich in N compared to surrounding natural areas [*Groffman et al.*, 2004; *Hope et al.*, 2005; *Zhu et al.*, 2004]. Moreover, although urban ecosystems currently comprise <2% of the global land area, they are increasingly prevalent components of land use worldwide. For example, turfgrass lawns are now the largest irrigated crop in the United States, and in support of these lush landscapes, land owners use on average 700–900 L of water per person per day and up to 500 kg N ha^{-1} as fertilizer per year, rates comparable to the most intensively managed agricultural fields globally [*Milesi et al.*, 2005]. Urban landscaping alternatives to lawns, such as xeriscape, are increasingly common in the U.S. Southwest and promoted for their water-conserving benefits. However, these yards are also highly managed with irrigation, raking, and pruning, and often planted with N-fixing trees that may increase soil fertility and alter gas fluxes to the atmosphere [*Martin*, 2001; *Martin et al.*, 2003a]. Despite their similarities to agriculture and their growing importance on the landscape, few studies have quantified the contribution of urban soils to regional atmospheric composition or air quality [*Aneja and Roelle*, 1997; *Kaye et al.*, 2004; *Thornton and Shurpali*, 1996].

[6] Phoenix, Arizona is the fifth largest city in the United States, and at 3.5% a^{-1}, population growth in the greater metropolitan area is the fastest in the country (Greater Phoenix Economic Council, online information, 2007). Much of the urban growth up to 1975 replaced former agricultural lands, but recently, development is occurring on the outside fringes of the city where lawns and managed xeric yards are replacing native Sonoran Desert ecosystems [*Keys et al.*, 2007]. In this study, we explore the impact of urban land uses on soil N cycling and emissions of N_2O and NO from soils. Because lawns are high in organic matter and irrigated/fertilized much like agricultural crops, we expected these sites to support high N oxide fluxes compared to native landscapes. Furthermore, although the biogeochemistry of xeriscaped yards has not been well studied, we hypothesized that these managed ecosystems would be the largest soil sources of NO_x due to a combination of warm temperatures, coarse soil textures, periodic irrigation, and large N pools, all factors that are known to promote nitrification and emissions of NO_x to the atmosphere.

2. Methods

2.1. Site Description

[7] Our study sites included three different land-use types in Phoenix, Arizona: lawn, managed xeric landscapes, and protected Sonoran Desert lands within the urban core. Sampling occurred at two different times of year, during spring when temperatures were mild (March 2001) and during summer when temperatures were high (May/June 2006). All sites were within the boundaries of the Central Arizona–Phoenix Long Term Ecological Research site (CAP-LTER) that covers 6,400 km^2 of central Arizona, including the Phoenix metropolitan area [*Grimm and Redman*, 2004] (Figure 1). All sites were relatively flat (<2°) and located on geological substrates of mixed alluvium. Furthermore, all xeric and lawn landscapes were predated by former agriculture. Vegetation in lawn sites was dominated by bermuda grass (*Cynodon dactylon*), while xeriscaped sites were diverse, composed of common shrubs (e.g., *Leucophyllum* spp), cacti, and some annuals (e.g., *Kallstroemia* spp.). Additionally, two of the xeriscaped sites contained N-fixing mesquite (*Prosopis* spp). Vegetation in the Sonoran desert remnant sites was dominated by the shrubs *Larrea tridentata* and *Ambrosia deltoidea*, and included cacti (saguaro, *Carnegiea gigantean,* and cholla, *Opuntia spp.*) and various herbaceous species (*Poa* sp., and *Boraginacea* sp.). All samples in desert and xeriscaped sites were taken in the spaces between plants. Land cover in the CAP ecosystem is composed of Sonoran Desert vegetation (36%), lawn (11%; residential, municipal/industrial, golf courses), managed xeric landscapes (13%; residential, municipal/industrial, transportation corridors), agriculture (8%), bare ground (9%; vacant lots, dirt roads), water (1%; canals, streams), and impervious surface (22%).

[8] Mean annual temperature in the Phoenix metropolitan area is 23°C and ranges from 12°C in winter to 34°C in summer [*NOAA*, 2006]. Mean annual precipitation is 210 mm a^{-1}, with most rain falling in summer (33%) and winter (35%). No rain fell over the sampling period in March 2001, and trace precipitation (0.4 cm) fell on one day during the May/June field campaign in 2006 (Figure 2).

2.2. Diel Fluxes

[9] In March 2001, we sampled soil N oxide fluxes from two urban land-use types five times over the course of 24 hours to determine the effect of temperature on gas fluxes. The first site was composed of residential lawn and the second was a nearby xeriscaped side yard. Four closed top chambers were located on soil anchors >1 m apart from one another and were used to measure fluxes of N_2O and NO. Surface soil temperature (0–3 cm) in the shade was recorded at the time of gas flux measurements. Soil and air temperature, and soil N_2O and NO fluxes were measured at 1700 and 2300 LT on 18 March 2001, and at 0700, 1100, and 1500 LT the following day. In addition, we collected five soil cores (0–10 cm) randomly within the plot in order to measure soil moisture, inorganic N concentrations, and potential N transformations.

2.3. Background and Postwatering Soil N Cycling and Gas Fluxes

[10] Over both seasons, we measured background soil N cycling and N oxide emissions from replicate sites of lawns, managed xeric landscapes, and remnant Sonoran Desert sites within the urban airshed (n = 3 in 2001; n = 4 in 2006; Figure 1). All background measurements were taken between 1100 and 1700 LT to minimize temperature differ-

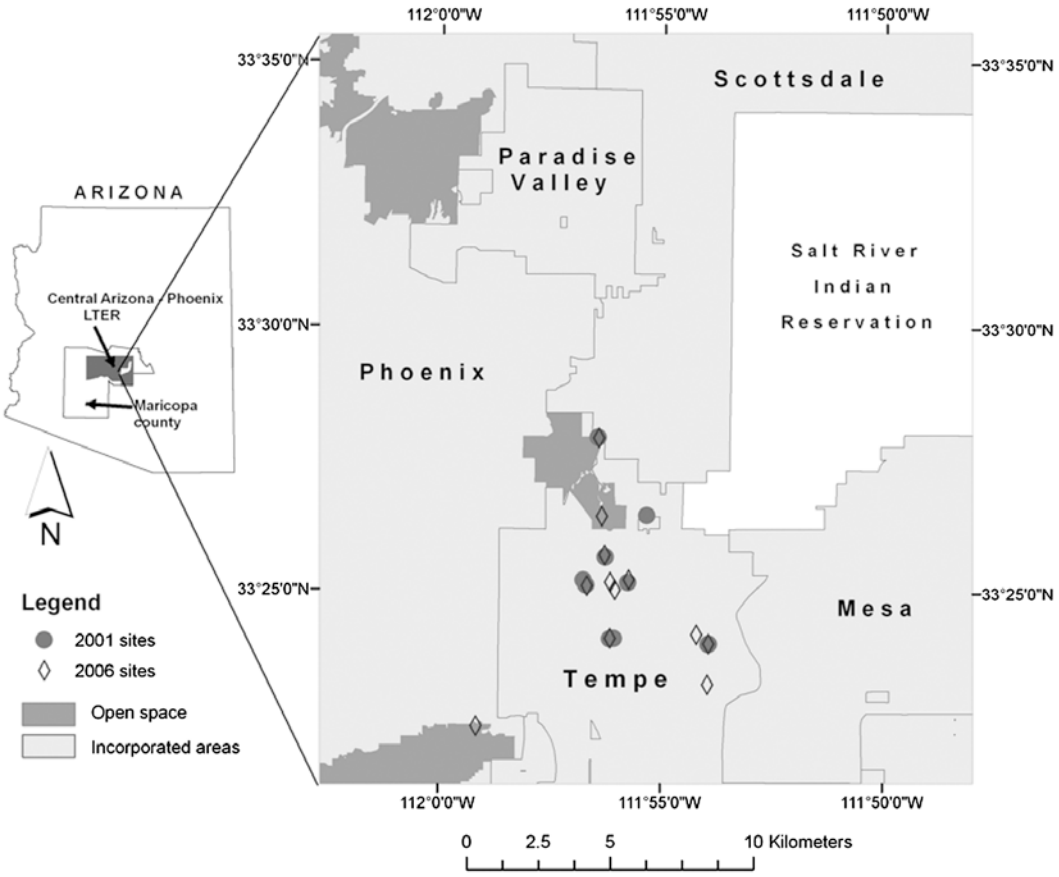

Figure 1. Map of study sites within the Phoenix metropolitan area. Sites used in spring 2001 and summer 2006 are indicated by solid circles and open diamonds, respectively.

ences between sites. To assess the effects of rainfall, we measured gas emissions at all sites before and 2–3 h after a simulated 5 mm rainstorm. Rain was simulated by sprinkling 500 mL of deionized water (in 2001) or water with 0.1N MgCl (in 2006, to simulate the electrical conductivity of rainfall) evenly over the measurement area. Prior to watering, we collected five soil cores (0–10 cm) randomly across each plot.

2.4. Gas Collection and Analysis

[11] Soil N_2O was measured using a closed chamber technique [*Hall and Matson*, 2003]. Four beveled PVC

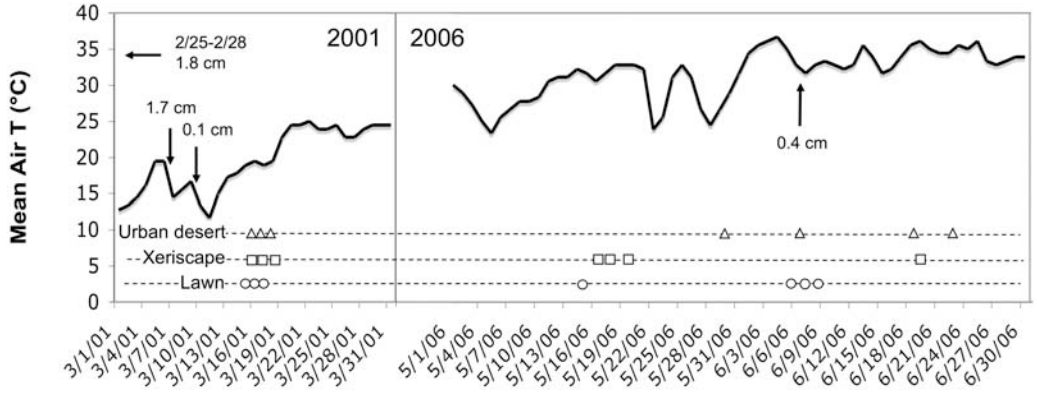

Figure 2. Mean air temperatures (°C, black line) and precipitation events (arrow, cm rainfall) in the sampling area over period of data collection. Temperature and rainfall data were taken from a weather station monitored by the Flood Control District of Maricopa County at South Mountain Park, located in the same urban open space area as one of our study sites (sensor 6525). Sampling dates for each site and landscape type are indicated. (For more information, see http://www.fcd.maricopa.gov/home/sitemap.aspx.)

rings were inserted several cm into the soil at random locations in each site. Each ring was >1 m away from the others and served as an anchor for a white, opaque chamber. Molded PVC chambers were placed over each ring, and air was sampled from the chamber four times over a 30-min period. Twenty milliliters of chamber air were collected in plastic syringes and immediately placed in preevacuated, silicone-sealed, 10 mL glass Wheaton vials with inert stoppers (black butyl rubber, Geo-microbial Technologies, Inc., Oklahoma). Samples and certified N_2O standards were collected and treated in the same way. Samples were analyzed using a gas chromatograph (GC) fitted with an electron capture detector (SRI, Torrance, California, and Varian, Palo Alto, California). The GC was calibrated in the laboratory using certified N_2O standards (Scott Specialty Gases and Matheson Tri-Gas). Gas fluxes were calculated as the increase in concentration within each chamber over a 30-min period corrected for chamber volume and air temperature. All fluxes are expressed in μg N m^{-2} h^{-1}.

[12] Nitric oxide was measured in situ at each site within 1 h of N_2O measurements within a Teflon-coated, white, opaque soil chamber using a portable chemiluminescent detector (LMA-3 in 2001 and LMA-3D in 2006, Unisearch Associates, Ltd., Canada) fitted with a CrO_3 filter that converts all NO to NO_2. The custom-made chamber top was fitted to each of the PVC rings immediately before or after measurement of N_2O fluxes. Nitrogen dioxide concentrations were estimated photochemically after their reaction with Luminol II solution. Several factors are known to interfere with the detection of NO_2 by the LMA instrument, including O_3, humidity, and peroxyacetyl nitrate (PAN) [*Drummond et al.*, 1990; *Hutchinson et al.*, 1999; *Kelly et al.*, 1990; *Schmidt et al.*, 1995]. For example, O_3 interferes with Luminol solution in conditions of "clean, background air" when ambient NO_2 mixing ratios are <1 ppb, resulting in a 0.003 ppb increase in signal for every 1 ppb of O_3 [*Drummond et al.*, 1990; *Kelly et al.*, 1990]. Average NO_2 concentrations and maximum 8-h O_3 concentrations measured near our sites in 2006 were 20 ppb NO_2 (maximum 79 ppb), and 86 ppb O_3 [*Arizona Department of Environmental Quality*, 2006]; thus we assume minimal impact of O_3 on the reactivity of the Luminol reaction in 2001 (LMA-3 with no O_3 filter) and none in 2006 (LMA-3D with O_3 filter). Humidity of the sample air also interferes with NO detection by reducing the efficiency of the NO to NO_2 conversion [*Hutchinson et al.*, 1999]. To eliminate inference of humid air coming from soil surface, we ran the LMA-3 at a 5:1 ratio of dry ambient air (scrubbed free of water vapor with anhydrous calcium sulfate) to chamber air according to methods developed for this instrument in [*Davidson et al.*, 1991; *Matson et al.*, 1996]. The LMA-3D used in 2006 was predesigned to dry humid samples by using an anhydrous calcium sulfate column to dehumidfy the shell air surrounding a nafion drier system [*Hutchinson et al.*, 1999]. Finally, PAN was not measured during our field campaigns but may increase the NO_2 signal by up to 25% if present [*Drummond et al.*, 1990]. Measurements of PAN from other studies in the Phoenix metropolitan area show that its concentration is generally low (<1 ppb), in part due to warm atmospheric temperatures in the city [*Gaffney et al.*, 2002]. However, in order to correct all chamber fluxes for any possible interferences that may have affected the reactivity of the Luminol solution or CrO_3 converter over the course of the day (including O_3, PAN, etc.), standard curves were performed in the field at each site immediately before, during, and after gas sampling using a known concentration of NO standard gas (Scott-Marrin Inc., Riverside, California). The standard curve was corrected for changes in O_2 mixing ratios caused by mixing of scrubbed air with O_2-free standard gas, and all chamber fluxes were calculated using the linear fit between instrument output (mV) and standard gas concentrations (ppb) over the range of expected values.

2.5. Estimation of Soil NO Fluxes

[13] Measurement of NO fluxes from soils using chamber techniques introduces a number of artifacts that affect emissions estimates [*Hutchinson and Livingston*, 2001]. In addition to reducing the diffusion gradient between soils and the atmosphere, high NO concentrations in chambers or in the atmosphere can decrease soil emissions because NO is both a reactant and product in microbial processes [*Conrad*, 1994]. However, in order to measure relatively small NO fluxes from soils where ambient NO concentrations are either large or variable, NO is commonly removed from the ambient air stream that flushes soil enclosures [e.g., *Williams et al.*, 1987; *Yamulki et al.*, 1995]. Consequently, fluxes measured under "zero-air" conditions likely estimate "potential" emissions but may not be representative of actual NO emissions from soils under normal field conditions. On the other hand, fluxes calculated using a linear model with ambient concentrations in the chamber headspace may underestimate fluxes due to decreases in the diffusion gradient between soils and the atmosphere within the chamber over the sampling period [*Livingston et al.*, 2005].

[14] In order to estimate soil NO fluxes from the Phoenix urban ecosystem where ambient NO_x is substantial, we calculate "minimum" and "maximum" soil NO_x flux estimates based on two different techniques used during different parts of the year when air temperatures were cool (minimum estimate, spring) and warm (maximum estimate, summer). For the minimum flux estimate, we measured soil fluxes from chambers without scrubbing ambient NO entering the chamber in the incoming air stream. A small 0.9 mm hole in the chamber pulled in air from outside during measurement and prevented a vacuum on the soil surface. In the diel experiment, NO fluxes were calculated as the difference between independent measurements of NO_x and NO_2 fluxes within the same chamber (measurements of each gas were taken one after the other with the chamber aired out between samples). In the background flux experiment, combined NO_x fluxes (NO + NO_2) were measured over the course of 6–8 min after the chamber was placed on the ring. The diel experiment showed that the majority of ambient NO_2 is consumed inside the chamber within the first 4 minutes after closure. Thus NO flux was calculated as the change in NO_x concentration between 4 and 8 min of sampling. Because ambient concentrations of NO_x were relatively high and the rate of airflow through the 5-L chamber was low (150 mL min^{-1}), a dilution factor was not used in flux calculations.

[15] For the maximum estimate made during the summer, ultrahigh-purity NO-free air was injected into the chamber

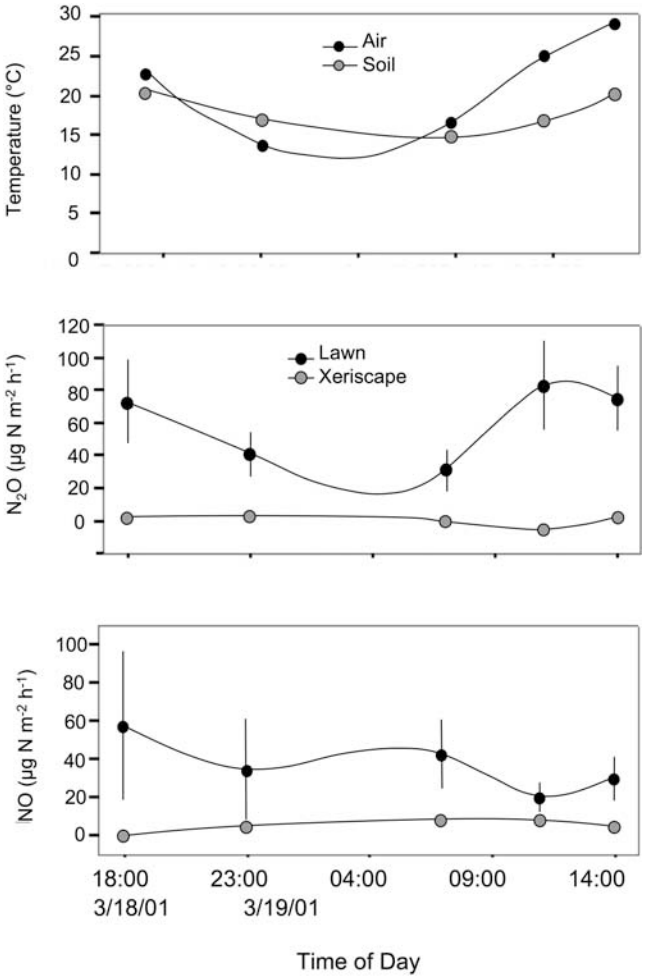

Figure 3. (a) Average air and soil temperatures, (b) N_2O, and (c) NO fluxes from a lawn and xeriscaped yard over the course of a day and night (18 March 2001 to 19 March 2001). Error bars represent ±1 SE from four replicate chambers per site.

for 30 s at 2 psi and allowed to vent until initial NO_2 concentrations at the soil surface were near zero. Chambers were then sealed, and the incoming air was scrubbed with a Purafil column to remove NO_x (granular Purafil® Select CP Blend; Purafil, Inc., Doraville, Georgia). Checks at the beginning and end of chamber measurement showed that NO_2 concentrations within each chamber remained low, and any detected increase in NO_2 concentration was subtracted from the combined NO_x signal. Because NO_x-free incoming air was introduced to the chamber at a relatively high flow rate, 900–1050 mL min^{-1}, all fluxes were corrected for the dilution of the sample from NO_x-free air using the following equation [*Martin et al.*, 2003b; *Venterea et al.*, 2003]:

$$F_{NO} = \frac{dC}{dt}\frac{V}{A} + C_A\frac{Q}{A}$$

where F_{NO} is the flux of nitric oxide (μg N m^{-2} h^{-1}), dC/dt is the rate of change of NO concentration (μg N m^{-3}) within the chamber over time (h) determined by linear regression, V is the chamber volume corrected for the ring height (m^3), A is the soil surface area (m^2), C_A is the average NO concentration during the time interval of regression, and Q is the air flow rate through the chamber (m^3 h^{-1}).

2.6. Soil Properties and Processes

[16] Once for each site during each season, we measured inorganic N concentrations in soil and potential rates of net N mineralization and nitrification using 2N KCl extraction and aerobic laboratory incubation methods. Collected soils were homogenized and sieved in the laboratory. One 10-g subsample from each sample was immediately shaken for 1 min in 50 mL 2N KCl, set aside for 18–36 h, filtered through preleached Whatman 42 filters, and then frozen immediately for later analysis. Another 10-g subsample was placed in a small, capped cup and its water content was raised to field capacity with deionized water. These subsamples were placed in the dark for 30–50 d at 22°C and moistened weekly to field capacity with DI water. After the incubation, soils were extracted as described above. All KCl extracts were analyzed colorimetrically for NH_4^+-N and NO_3- using a Lachat Quikchem 8000 autoanalyzer. Net N mineralization was calculated as the difference between the sum of NH_4^+ and NO_3- concentrations before and after each incubation. Net nitrification was calculated as the difference between NO_3- concentrations before and after each incubation. Gravimetric soil water was determined by drying soil subsamples for 24 h at 105°C.

2.7. Statistical Analyses

[17] All statistical tests were performed using SPSS 11.0 (SPSS 11.0 for Macintosh, 2005, SPSS, Inc., Chicago, Illinois) software. For the background flux experiment, fluxes from subsamples (gas chambers and soil samples) were averaged within a site, and data from replicate sites were used in all ANOVA and linear regression analyses. For the diel experiment, repeated measures ANOVA analyses were used to test differences in gas fluxes over time. All data with unequal variances were transformed (log, square root, reciprocal, or reciprocal root) prior to ANOVA and regression analyses to satisfy linear model assumptions. In cases where model assumptions could not be met, nonparametric statistics were used.

3. Results

3.1. Diel N_2O and NO Fluxes

[18] Fluxes of N_2O and NO were largest from lawn compared to xeriscape over the course of the day and night, but time of day did not exert a strong effect on emissions (Figure 3; repeated measures ANOVA, lower-bound test, time of day × N_2O or NO fluxes in each landscape type, $p > 0.05$). However, large N_2O from turf soils were significantly and positively related to temperature over the course of the day (N_2O × air temperature: $r^2 = 0.80$, $p = 0.04$). Temperature was not related to N_2O emissions from xeriscape or to NO emissions in either land-use category.

3.2. Soil Properties and N Cycling in Urban Landscapes

3.2.1. Soil Properties and Processes

[19] Soil moisture and temperatures were not significantly different between land-use types in March when soils were

Table 1. Soil Properties and N Cycling in Three Common Land Use Types Across Phoenix[a]

Soil Moisture, % of Dry Soil		Water-Holding Capacity, %		Soil Temperature, °C		Soil NH_4^+, mg N kg^{-1}		Soil NO_3^-, mg N kg^{-1}		Net N Mineralization, mg N kg^{-1} d^{-1}		Net Nitrification, mg N kg^{-1} d^{-1}	
Mar 2001	Jun 2006	Mar 2001	Jun 2006	Mar 2001	Jun 2006	Mar 2001	Jun 2006	Mar 2001	Jun 2006	Mar 2001	Jun 2006	Mar 2001	Jun 2006
Urban Desert													
4.4(a) (1.2)	1.1(a) (0.2)	ND	27.7(a) (2.4)	20.7(a) (2.6)	43.8(c) (1.0)	2.7(a) (0.8)	2.9(a) (0.3)	4.9(a) (1.2)	6.5(ab) (1.5)	0.28(a) (0.07)	0.07[b] (0.04)	0.32(a) (0.03)	0.08[b] (0.02)
Xeriscape													
7.4(a) (2.4)	3.2(b) (0.5)	ND	28.4(a) (3.0)	16.6(a) (0.9)	39.1(b) (1.5)	2.4(a) (0.8)	1.3(a) (0.6)	2.1(a) (1.0)	37.1(b) (22.4)	0.46(a) (0.21)	−0.30[b] (0.19)	0.48(a) (0.21)	−0.28[b] (0.18)
Lawn													
21.9(b) (1.2)	18.4(c) (3.6)	ND	65.4(b) (3.8)	17.7(a) (1.2)	31(a) (1.1)	2.4(a) (0.5)	1.6(a) (0.4)	2.4(a) (0.8)	3.4(a) (0.8)	0.50(a) (0.15)	0.60[b] (0.07)	0.52(a) (0.16)	0.58[b] (0.08)

[a]Lowercase letters in parentheses indicate significant differences between landscape types within columns (one−way ANOVA, soil variable × land use type, $p \leq 0.05$). ND, no data. Values in parentheses are standard errors.
[b]Net N mineralization × land use, $p = 0.01$; net nitrification × land use, $p = 0.01$; nonparametric (Kruskal−Wallis) test.

relatively cool, but during summer, when average air temperatures reached 37°C, urban desert soils were significantly drier and warmer than those of xeriscapes, which were also drier and warmer than lawn soils (Table 1). Soil moisture in summer was over twice as high in xeric compared to desert remnant sites, and > 5 times higher in lawns compared to xeriscaped yards and urban desert. These summer patterns in soil moisture were not explained by differences in water-holding capacity, as xeriscape soils could retain similar amounts of water as deserts (~28% by weight), which was far lower than what could be retained by organic matter-rich lawns (65%) (Table 1). Soil moisture was inversely correlated to soil temperature in urban deserts ($r = -0.84$, $p < 0.001$) and xeriscaped soils ($r = -0.72$, $p = 0.01$). In contrast, soil moisture and temperature were not related in lawns ($r = -0.12$, $p = 0.68$).

[20] Soil N cycling followed seasonal patterns in temperature and moisture. Land use had no significant effect on total soil inorganic N concentrations and net N transformations in spring, but in summer, soil NO_3- was highest, and most variable, in managed xeric landscapes. Furthermore, land use had significant effects on rates of net N transformations in summer, with xeriscaped soils consuming inorganic N in laboratory incubations compared to positive rates in urban deserts or lawns. In all sites and across all seasons, potential rates of net N mineralization were equivalent to rates of net nitrification. Similarly, when data were grouped together (excluding one outlier of NO_3- > 5 SD away from mean), net rates of nitrification and N mineralization were negatively related to soil NO_3- concentrations ($r^2 = 0.62$, $p < 0.001$ and $r^2 = 0.64$, $p < 0.001$, respectively).

3.2.2. Soil N Oxide Emissions

[21] Similar to patterns in soil properties and N cycling, the impact of land use on soil N oxide emissions differed by season (Figure 4). In spring, N_2O and NO fluxes prior to watering were not significantly different between land-use types, in part due to high variability between replicate xeric and lawn sites. However, in summer when temperatures were high, both N_2O emissions and NO emissions varied significantly among land uses. Additionally, experimental rainfall exposed differences between land use types, but this pattern also depended upon season. Rainfall had no effect on N_2O in any land-use type in spring, but emissions were stimulated by watering across all land uses in summer (no interaction of land use × water addition, $p = 0.4$) and showed a pattern between land-use types similar to prewater fluxes. In both seasons, rainfall affected NO fluxes differently in dry soils compared to lawns (Spring: urban desert > lawns; land use × water addition, $p = 0.03$; Summer: xeriscapes = urban desert > lawns; land use × water addition, $p < 0.001$). For example, watering increased NO fluxes in desert remnant patches by 3 times in spring and up to 36 times in summer, but fluxes in lawn, where soil moisture levels were already high, were unaffected by watering in either season. NO fluxes after watering were also elevated in xeriscaped yards, but not as much as in urban deserts (xeriscape post-rain fluxes = 21 × pre-rain fluxes).

[22] Ratios of N_2O/NO during summer were affected by land use and watering (two-way ANOVA on transformed data, land use, watering, and interaction, $p < 0.001$, $p = 0.04$, and $p < 0.01$, respectively). N_2O/NO ratios from lawns were near 1 prior to watering (0.9 ± 0.6) but increased after, to 3.5 ± 1.5. In contrast, ratios of N_2O/NO were near 1 or lower in xericaped (0.66 ± 0.28) and desert soils (0.11 ± 0.03), and significantly declined following watering, to 0.12 ± 0.03 and 0.02 ± 0.003, respectively.

4. Discussion

4.1. Urbanization and the Dynamics of Soil N Oxide Emissions

[23] Over the last several decades, development of urban and suburban landscapes has exceeded agricultural expansion as the dominant driver of land cover change in the United States and other developed countries [*Lambin et al.*, 2001; *United Nations Environment Program*, 2006]. In particular, the extent of residential development in the Phoenix metropolitan area has increased exponentially over the last 80 years while agricultural land has diminished, significantly altering climate, ecological processes, and ecosystem structure [*Hope et al.*, 2005; *Jenerette and Wu*, 2001]. In this study, we show that urbanization also alters fluxes of nitrogen trace gases from soils to the atmosphere,

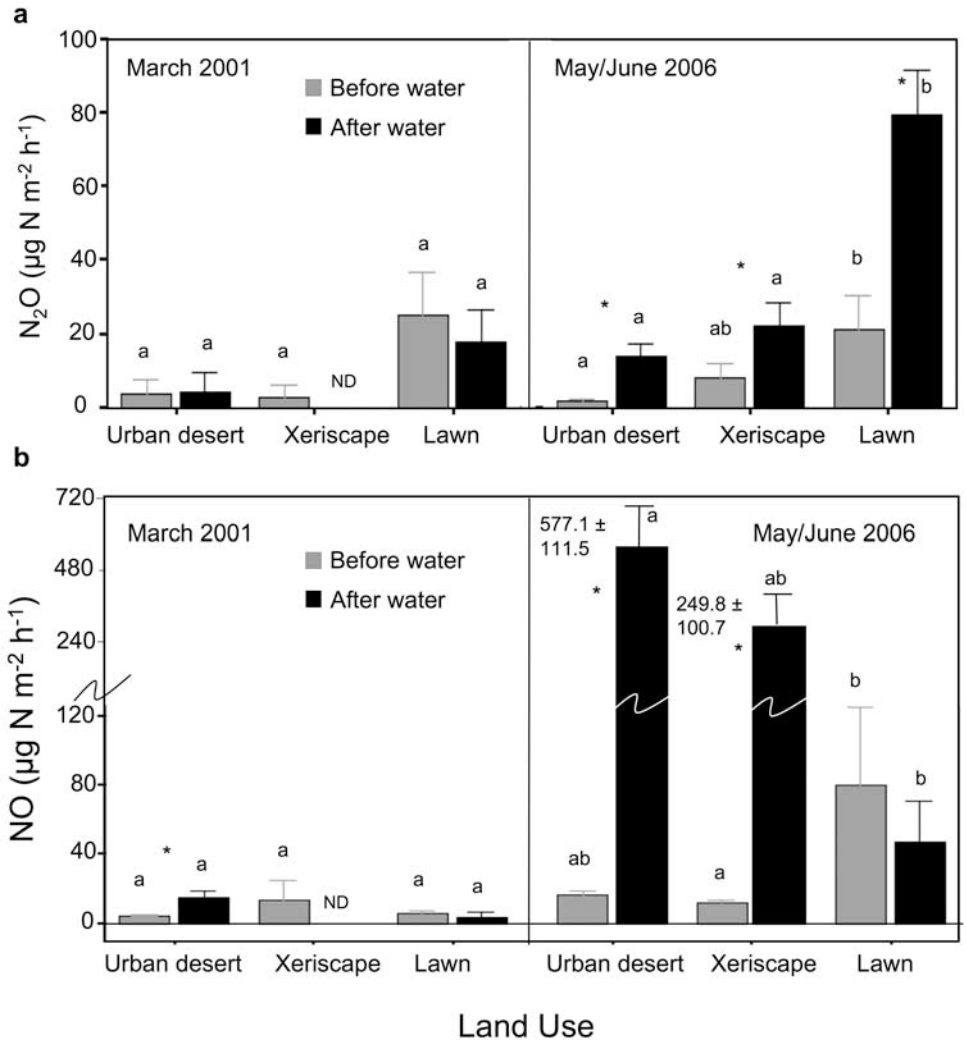

Figure 4. (a) Soil N_2O and (b) NO fluxes from urban desert, managed xeric landscapes, and lawns before and after an experimental rainstorm (±SE); ND, no data (xeric sites were not watered in 2001). Lowercase letters represent significant differences between land-use types (one-way ANOVA analyses performed within each season, before and after watering, N oxide emissions × land use). Asterisk indicates significant effect of rainfall within each land-use category (two-way ANOVA performed within each season, N oxide emissions: land use × water addition).

and that these fluxes are controlled largely by season, rates of N cycling, and the timing of water supply.

[24] We hypothesized that lawns would be the largest source of N_2O of the three land use types studied, where increased organic matter, high water availability, and consistent N fertilization likely support active microbial populations and high rates of denitrification. Prior to artificial wetting, N_2O fluxes from lawns in the Phoenix metropolitan area ranged from 21 to 25 μg N m^{-2} h^{-1}, higher than both xeriscapes (3–8 μg N m^{-2} h^{-1}) and urban desert (2–4 μg N m^{-2} h^{-1}), and comparable to residential lawns in Colorado [*Bremer*, 2006; *Kaye et al.*, 2004]), and N-saturated temperate forests [*Magill et al.*, 1997; *Tietema et al.*, 1998]). After irrigation, differences between land-use types were exaggerated, with fluxes of N_2O from lawns ranging from 18 to 80 μg N m^{-2} h^{-1}, four to six times larger than arid land use types. Home lawn care recommendations in Arizona and across the United States suggest application of fertilizer at the rate of ~150 kg N ha^{-1} a^{-1}, split between three seasonal applications of 49 kg N ha^{-1} (1000 pounds N/1000 square feet of lawn (University of Arizona Cooperative Extension, online information, 2005; University of Illinois Extension, online information, 2007). If we assume that lawn soils are frequently irrigated and wet for a third of the year (City of Phoenix, online information, 2007), that nighttime fluxes are half those of daytime (based on our diel flux experiment), and they are fertilized at recommended rates, Phoenix lawns would emit approximately 1.0% and 1.8% of fertilizer N inputs as N_2O in the spring and summer, respectively, comparable to managed agricultural ecosystems worldwide [*Mosier*, 1993; *Stehfest and Bouwman*, 2006]. N_2O emissions from lawns in this study were smaller than from effluent-treated golf courses in Arizona, which generally receive greater N and water inputs (145 ± 175 μg N m^{-2} h^{-1} [*Guilbault and Matthias*, 1998]).

Thus, with approximately 90 km^2 of golf courses in the Phoenix metropolitan area (~200 golf courses × 0.4 km^2 each, it is possible that our estimates are low (J. Passov, Escapes: Phoenix and Scottsdale, online information, 2007; U.S. EPA, Golf course adjustment factors, online information, 2006). However, if urban land uses replace fertilized agriculture instead of desert as occurred during the first phase of urban growth, the expansion of residential development (especially impervious surface and low-fertility xeric landscapes) may have decreased regional N_2O emissions relative to when agricultural land area was at its peak.

[25] In contrast, lawns emitted approximately the same rates of NO prior to irrigation as urban deserts, although the temporal dynamics differed substantially between land-use types. In particular, NO fluxes from lawns appeared to be "turned on" at a moderate level for most of the year and thus were responsive to other environmental factors such as seasonal temperature, while emissions from desert or xeric sites occurred primarily as pulses after water addition. For example, the highest NO fluxes from lawns occurred prior to irrigation/precipitation events, especially during summer when temperatures were high but soils were still moist enough to support active nitrifying populations (~20% moisture). Estimated NO emissions from lawns over the year ranged from 4 to 80 μg NO-N m^{-2} h^{-1}, comparable to the only other estimates in the literature for urban landscapes, summer lawns in Raleigh, North Carolina (20 μg NO-N m^{-2} h^{-1} [*Aneja and Roelle*, 1997]), and Nashville, Tennessee (1–8 μg NO-N m^{-2} h^{-1} [*Thornton and Shurpali*, 1996]).

[26] The timing and frequency of irrigation also appears to control the balance between N_2O and NO emissions from fertilized lawns, similar to patterns shown in agricultural ecosystems, while emissions are dominated year-round by NO in desert and managed xeric landscapes. Irrigation of already moist soil can increase water-filled pore spaces and reduce NO emissions while stimulating N_2O and N_2 emissions through denitrification [*Hall et al.*, 1996; *Matson et al.*, 1996]. As soils dry, nitrification resumes and aerobic pore spaces allow NO to escape to the atmosphere. Thus the ratio of N_2O/NO emissions from soil can be used as an index of the importance of reductive (N_2O/NO > 1) versus oxidative (N_2O/NO < 1) microbial processes [*Davidson et al.*, 2000]. Using this model, lawn irrigation appeared to switch the source of N oxide emissions from nitrification prior to watering to denitrification after, while emissions remained a product of nitrification in coarse-textured xeric and desert soils irrespective of water additions.

[27] While NO emissions from lawns were relatively constant over the year with respect to irrigation, they responded in pulses to water additions in managed xeric landscapes and deserts. For example, fluxes were relatively low when soils were dry (1–7% soil moisture) but increased over an order of magnitude within several hours of wetting during the warm summer. The pulsed temporal dynamics of NO emissions in response to water, lasting from hours to days, is well documented in arid soils and may be caused by stimulation of both chemical (reduction of accumulated soil nitrite) and microbial processes [*Hutchinson et al.*, 1997] (see *Davidson and Kingerlee* [1997] and *Hall et al.* [1996] for reviews). Dry desert soils are characterized by large inorganic N pools that may accumulate from atmospheric deposition and N mineralization in surface soils over long periods between rain, and these stores are likely mobilized quickly by nitrifying microorganisms after rainfall [*Stark and Firestone*, 1995; *Welter et al.*, 2005]. Furthermore, arid and semiarid ecosystems tend to be warm for much of the year, and temperature is an important modulator of microbial activity in these systems when population growth is first stimulated by precipitation events [*Conant et al.*, 2004]. Warm, arid and semiarid ecosystems emit the most biogenic NO_x globally, twice that of cultivated land [*Davidson and Kingerlee*, 1997]. Fluxes from desert soils in the Phoenix ecosystem ranged over 2 orders of magnitude, from 5 μg N m^{-2} h^{-1} in dry soils at ambient NO_x concentrations during the cool winter/spring to a potential of 577 μg N m^{-2} h^{-1} after wetting in summer, similar to the range of rates from tropical savanna and fertilized agricultural soils [*Davidson and Kingerlee*, 1997; *Hall et al.*, 1996].

[28] Contrary to our expectations, managed xeric landscapes function quite similarly to native deserts despite active management of resources within these ecosystems. Intentionally designed xeric landscapes are increasingly common components of arid cities in the U.S. Southwest. Since 1960, air conditioning has allowed residents to use yards less for cooling than for aesthetics, and most Phoenix area homeowners now prefer "oasis" designs that incorporate both colorful desert and mesic vegetation rather than simple lawn landscapes alone [*Harlan et al.*, 2006; *Martin*, 2001]. Furthermore, as water scarcity has become a concern, many municipalities within the Phoenix area use xeriscape designs along roadways and within commercial developments, and they encourage conversion of residential lawns to managed xeriscape with monetary rebate programs. Although they are often designed to mimic desert ecosystems, these landscapes are carefully planned and managed prior to installation with soil preparation (tilling, loosening) and plant selection, and afterward with organic or inorganic mulches, drip irrigation, pruning, raking, and occasional fertilization (Arizona Municipal Water Users Association, online information, 2007).

[29] Managed xeric landscapes in the Phoenix metropolitan area released approximately the same amount of N_2O and NO per unit land area as unmanaged deserts, and they were also similar to native landscapes with respect to seasonal and pulsed, postwatering dynamics. Water additions stimulated N oxide emissions in both land use categories, and NO dominated N oxide fluxes both before and after wetting. Furthermore, although managed xeric soils were significantly cooler and wetter than deserts, both supported relatively low rates of N transformations compared to lawns during summer, likely due in part to low water-holding capacities and small carbon pools that limited water retention and heterotrophic activity. However, our results also elucidate the subtle ways in which these managed "residential deserts" are more similar lawns than their native analogues. For example, for most of the year when soils are dry, mean N_2O fluxes from xeric landscapes fall between deserts and lawns in magnitude, statistically similar to both, perhaps due to higher soil carbon reserves in xeric landscapes from densely spaced vegetation and inorganic mulches that trap soil moisture. Cooler soils in xeric landscapes may also constrain biological activity compared to deserts when air temperatures are high.

For example, after summer wetting, mean NO fluxes from xeric soils are higher than from lawns but lower than from deserts, and statistically similar to both. *Martin* [2001] has shown that homeowners generally apply more water to xeric landscapes than plants require, and that regular pruning of drought-tolerant species can reinforce excessive irrigation by residents as water-use efficiency declines. Perhaps these and other factors such as plant selection (generally high productivity species), canopy cover, or microclimate are responsible for the biogeochemical similarities we observed between xeriscapes and lawns.

4.2. Urban Landscapes and Air Quality

[30] Several studies in mesic ecosystems have estimated that urban soils, primarily lawns, contribute ~1% of anthropogenic NO_x sources, although they may be responsible for up to 20% of the atmospheric pool in rural areas away from vehicle traffic [*Aneja and Roelle*, 1997; *Davidson et al.*, 1998; *Thornton and Shurpali*, 1996]. However, this study suggests that pulsed temporal dynamics of soil emissions after wetting of warm, arid soils may add a significant amount of NO_x to the Phoenix atmosphere over short timescales. For example, our data suggest that the largest soil emissions of NO_x occur after wetting of long-dry desert soils during summer. In a comprehensive N budget for the Phoenix metropolitan ecosystem, [*Baker et al.*, 2001] estimated that 33.8 Gg N a^{-1} were emitted to the atmosphere as NO_x from combustion (primarily vehicle) across a 12,384 km^2 region within and around the city. Assuming most of this combustion-derived NO_x is located within the CAP boundaries (6400 km^2) and that vehicle usage is similar across the year and equally distributed across the city, approximately 0.145 kg N ha^{-1} d^{-1} is emitted to the atmosphere from anthropogenic activities. If postwetting, summer fluxes from desert soils measured in this study represent the highest, potential estimates from this ecosystem (577 μg N m^{-2} h^{-1}), soil NO_x emissions after the first summer monsoon storms may reach rates equivalent to anthropogenic emissions, up to 0.138 kg N ha^{-1} d^{-1}. Assuming 40% of the CAP ecosystem that is composed of desert functions similarly to desert remnant sites used in this study, soils in the Phoenix metropolitan area may produce up to 0.034 Gg N d^{-1} after the first monsoon storms, roughly 35% of anthropogenic emissions over the same time period (0.093 Gg NO_x-N d^{-1} [*Baker et al.*, 2001]). Soils would likely contribute less to regional atmospheric chemistry over time, as pulsed gaseous fluxes from long-dry soils are known to attenuate quickly after subsequent wetting events [*Hall et al.*, 1996; *Sponseller*, 2007].

[31] Nitric oxide from soils can be converted to a number of different nitrogen oxides (NO_y) depending on ambient photochemistry and air temperatures, and these compounds have various lifetimes and affinifsties for surfaces that interact to regulate their deposition and impact on air quality [*Andreae et al.*, 2002; *Jacob and Wofsy*, 1990]. If soil emissions are immediately deposited to plant or soil surfaces, they are effectively recycled in the ecosystem before entering the greater atmospheric pool. Plant leaf area in upland Sonoran deserts is low on a landscape scale due to physiological adaptations that limit water loss and excessive heating. While these strategies promote water conservation, they also prevent gas exchange at the leaf surface, including N uptake. Thus soil NO_x fluxes of significant magnitude are more likely to influence atmospheric chemistry beyond the vegetation boundary layer in deserts compared to more mesic, productive ecosystems.

[32] Tropospheric O_3 production depends on a suite of physical factors and chemical precursors in addition to NO_x, including UV radiation and sufficient concentrations of carbon monoxide and VOCs. Under most rural atmospheric conditions outside of cities, low NO_x/VOC ratios make O_3 production sensitive to NO_x compounds that are produced by soil or are transported from nearby urban areas. In cities, however, NO_x emissions from combustion are usually high enough that O_3 production is limited by VOCs and thus is significantly influenced by emissions from local vegetation [*Finlayson-Pitts and Pitts*, 2000]. While VOC emissions from native plants are low in the U.S. Southwest [*Geron et al.*, 2006], imported plants within the urban area are often high producers (e.g., *Eucalyptus* and *Citrus* spp. [*Karlik and Winer*, 2001]). Additionally, VOC emissions from urban landscapes in the U.S. Southwest are sensitive to temperature and pulsed temporal dynamics of rainfall, and high VOC emissions during summer monsoons contribute significantly to O_3 episodes that are common during these time periods [*Diem and Comrie*, 2000]. Furthermore, recent work suggests that high VOC concentrations after summer rains in Tucson, Arizona, may be large enough to switch the balance of O_3 formation from VOC-sensitive to NO_x-sensitive conditions during the long, warm summer days when O_3 production capacity is at its highest [*Diem and Comrie*, 2001]. If soil NO_x emissions in the Phoenix area peak at the same time the NO_x/VOC ratio declines after the first summer rains, they may significantly contribute to regional O_3 episodes that regulate air quality.

5. Conclusion

[33] Seventy-five percent of people in the United States now live in urban areas, and over half of these live outside of the city center [*U.S. Census Bureau*, 2000], where ample land area allows space for single-family homes, lawns, and gardens. However, relatively little is known about soil-atmosphere biogeochemical exchange in urban and suburban ecosystems despite their increasing importance on the landscape. Phoenix is growing at 3.5% per year, in part due to its dependence on water import from a region forty times the area defined by city boundaries [*Luck et al.*, 2001]. Land conversion from native ecosystems to lawn may have relatively small impacts in mesic, forested regions where soil organic matter and nutrient pools are substantial; however, urbanization in arid and semiarid ecosystems of the western United States involves substantial water and N import and thus dramatically alters native soil properties and processes [*Lewis et al.*, 2006].

[34] This study suggests that land conversion from desert to lawn will significantly increase soil N_2O emissions and speed N cycling. Alternative urban landscaping practices such as xeriscape will reduce N_2O emissions compared to lawns in addition to promoting water conservation, but these designed ecosystems still retain important ecological differences from their native predecessors. In contrast, native desert ecosystems within the urban core released the highest rate of NO per land area, concentrated in pulses

after water addition during the warm, dry summer. Soils within the Phoenix ecosystem have the potential to emit substantial quantities of NO_x within hours after summer rains in magnitudes that constitute a significant fraction of anthropogenic combustion, and these pulses likely occur during times of the year most favorable for O_3 production. The potential for large pulses of biogenic NO_x emissions to coincide with NO_x-sensitive conditions during the summer monsoon season warrants further study of the role of soils in regional oxidant inventories.

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