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## Nitrous oxide emissions and isotopic composition in urban and agricultural systems in southern California

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[1] Nitrous oxide (N<sub>2</sub>O) is a powerful greenhouse gas increasing in atmospheric mixing ratio and linked to increasing amounts of reactive N in the environment, particularly fertilizer use in agriculture. The consequences of urbanization of agricultural land for global and regional N<sub>2</sub>O emissions are unclear, due to high spatial and temporal variability of fluxes from different ecosystems and relatively few studies of urban ecosystems. We measured fluxes and the stable isotope composition ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) of N<sub>2</sub>O over 1 year in urban (ornamental lawns and athletic fields) and agricultural (corn and vegetable fields) ecosystems near Los Angeles, California, United States. We found that urban landscapes (lawns and athletic fields) have annual N<sub>2</sub>O fluxes equal to or greater than agricultural fields. Fertilization rates of urban landscapes were equal to or greater than agricultural fields, with comparable N<sub>2</sub>O emissions factors.  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of N<sub>2</sub>O varied widely in all ecosystems, and were not consistent with ecosystem type, season, soil moisture, or temperature. There was, however, a consistent response of  $\delta^{15}\text{N}$ -N<sub>2</sub>O to pulses of N<sub>2</sub>O emission following fertilization, with an initial depletion in  $\delta^{15}\text{N}$  relative to prefertilization values, then gradual enrichment to background values within about 1 week. Preliminary scaling calculations indicated that N<sub>2</sub>O emissions from urban landscapes are approximately equal to or greater than agricultural emissions in urbanized areas of southern California, which further implies that current estimates of regional N<sub>2</sub>O emissions (based on agricultural land area) may be too low.

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### 1. Introduction

[2] Increases in atmospheric greenhouse gas concentrations are linked to human activities and alter the radiative forcing of the Earth's atmosphere, causing changes in climate on a global scale [Forster *et al.*, 2007]. Nitrous oxide (N<sub>2</sub>O) is produced during microbial nitrification and denitrification [Pérez *et al.*, 2001, 2006] and has a global warming potential that is 298 times greater than carbon dioxide (CO<sub>2</sub>) on a 100 year timescale, making it a very important greenhouse gas [Forster *et al.*, 2007]. Nitrous oxide is also a major ozone-depleting gas [Ravishankara *et al.*, 2009]. Over the past ~150 years, the atmospheric inventory of N<sub>2</sub>O has increased from about 270 parts per billion (ppb) at a rate (for the past few decades) of about 0.7 ppb yr<sup>-1</sup> [Smith *et al.*,

2010] to current levels of about 323 ppb [National Oceanic and Atmospheric Administration, 2010]. This increase is usually attributed generally to an increase in the amount of reactive N in the environment [Kroeze *et al.*, 1999], and specifically to increased production and use of fertilizer in agriculture [Mosier *et al.*, 1998]. Most previous estimates of global and regional N<sub>2</sub>O emissions have not considered urban emissions, despite the widespread use of N fertilizers in lawn and landscape maintenance. Total nonfarm fertilizer use in the United States is around 10% [Qian *et al.*, 2003], and in 1999 the U.S. Environmental Protection Agency (EPA) estimated that, in California, about 20% of total fertilizer use was for purposes other than agriculture, including residential, recreational, and public landscaping [EPA, 1999]. In addition, previous studies have shown that fertilized urban ecosystems such as turfgrasses may also be significant sources of N<sub>2</sub>O at least regionally [Guilbault and Matthias, 1998; Kaye *et al.*, 2004; Bijoor *et al.*, 2008]. This is of special concern in warm temperate climates, where lawns may be cultivated over the entire year while agricultural fields are fallow in winter. Because of the high global warming potential of N<sub>2</sub>O, such emissions may also reduce the ability of urban and agricultural ecosystems to act as net greenhouse gas sinks [Robertson *et al.*, 2000; Liu and Greaver, 2009].

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[3] Given the high global warming potential, N<sub>2</sub>O emissions are a critical component of greenhouse gas emissions reduction targets. However, contributions of individual sources to regional N<sub>2</sub>O budgets are difficult to estimate because of large spatial and temporal variability in fluxes [e.g., Turner *et al.*, 2008]. Stable isotopes are useful indicators of urban versus agricultural sources of CO<sub>2</sub> and CH<sub>4</sub> [Tyler, 1986; Pataki *et al.*, 2007; Whiticar and Schaeffer, 2007], and some previous studies have suggested that the same may be true for N<sub>2</sub>O [Pérez *et al.*, 2001; Wrage *et al.*, 2004].

[4] The  $\delta^{15}\text{N}$  of N<sub>2</sub>O depends on the isotopic composition of the initial substrate and the fractionation factor of the microbial process responsible for N<sub>2</sub>O production: nitrification (conversion of NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup>) or denitrification (conversion of NO<sub>3</sub><sup>-</sup> to N<sub>2</sub>) [Pérez, 2005]. Both pathways produce N<sub>2</sub>O depleted in <sup>15</sup>N relative to the initial substrate: this enrichment factor ( $\epsilon$ ) can be calculated as  $\epsilon = \delta^{15}\text{N-N}_2\text{O}_{\text{emitted}} - \delta^{15}\text{N}_{\text{substrate}}$ . Nitrification <sup>15</sup>N enrichment factors are about  $-50 \pm 10\%$ , whereas denitrification enrichment factors are higher, about  $-25 \pm 10\%$  [Pérez *et al.*, 2006; Baggs, 2008]. Partial consumption of N<sub>2</sub>O by denitrifiers (usually only in very waterlogged soils) can further enrich <sup>15</sup>N in N<sub>2</sub>O by about 13‰ [Pérez, 2005]. In managed soils,  $\delta^{15}\text{N-N}_2\text{O}$  can be a useful proxy for distinguishing between the two N<sub>2</sub>O production pathways, since most fertilizers are made from atmospheric N<sub>2</sub> and therefore have a  $\delta^{15}\text{N}$  near 0‰. Some studies have tried to use  $\delta^{18}\text{O}$  of N<sub>2</sub>O as a proxy for N<sub>2</sub>O production pathways [Wrage *et al.*, 2005; Menyailo and Hungate, 2006], but interpreting the  $\delta^{18}\text{O}$  of N<sub>2</sub>O is complicated. In nitrification, N<sub>2</sub>O-O can be derived from soil H<sub>2</sub>O, O<sub>2</sub> in soil air, and hydroxylamine (NH<sub>2</sub>OH; the initial product of nitrification). In denitrification, N<sub>2</sub>O-O is derived from NO<sub>3</sub><sup>-</sup>, but in both reaction pathways  $\delta^{18}\text{O}$  of N<sub>2</sub>O can also be affected by exchange with H<sub>2</sub>O or other intermediate products of such as NO<sub>2</sub><sup>-</sup> [Kool *et al.*, 2007, 2009; Snider *et al.*, 2009], which may in turn be altered isotopically by other physical and biological processes such as evaporation or microbial respiration. N<sub>2</sub>O can also be produced abiotically in soils during chemodenitrification, the chemical decomposition of NO<sub>3</sub><sup>-</sup>, or via other chemical reactions consuming hydroxylamine, an intermediary of nitrification: however, these processes are at most negligible contributors to N<sub>2</sub>O emissions from soils [Bremner, 1997]. One study of N<sub>2</sub>O produced during chemodenitrification showed that the process had a <sup>15</sup>N fractionation factor of  $-38\%$ , with no major difference ( $<2\%$ ) between  $\delta^{18}\text{O}$  of the NO<sub>3</sub><sup>-</sup> substrate and N<sub>2</sub>O emitted [Samarkin *et al.*, 2010].

[5] Here we present the results of an investigation of N<sub>2</sub>O fluxes and isotope composition from both urban and agricultural land cover in southern California, United States. Los Angeles is one of the world's largest cities, and human settlement has spread in recent years, replacing agricultural land with residential areas. The region is seasonally very dry, but turfgrass lawns are widespread due to irrigation from groundwater extraction and water imports from northern California and the Colorado River [Fitzhugh and Richter, 2004]. We measured emission rates and isotopic composition ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) of N<sub>2</sub>O emitted from urban ornamental lawns and athletic fields (N<sub>2</sub>O flux data from some of these urban sites are also summarized by Townsend-Small and Czimczik [2010]), as well as corn fields and other vegetable fields in order to address our two main research

questions: How do urban and agricultural soils compare as regional N<sub>2</sub>O sources, and can stable isotopes be used as tracers of regional N<sub>2</sub>O sources?

## 2. Methods

[6] The study was conducted in the Los Angeles basin, California, United States, a coastal plain surrounded by peninsular and transverse mountain ranges. The basin is highly urbanized and includes the city of Los Angeles as well as portions of Los Angeles, Riverside, and San Bernardino Counties and all of Orange County. The climate is Mediterranean with an average annual air temperature of about 18.5°C and about 350 mm of precipitation, occurring mostly in winter [Bijoor *et al.*, 2008].

[7] N<sub>2</sub>O emissions from urban soils were measured in four city parks in Irvine, CA (33°41'N, 117°47'W), that were established in different decades ranging from the 1960s to the current decade. There were two types of turfgrass sampled in the study: ornamental lawns ("lawns"), similar in use and maintenance to residential lawns; and baseball fields ("athletic fields"). There were four different ornamental lawns sampled and four different baseball fields sampled. At each field, the N<sub>2</sub>O flux for each day was calculated as the average of three flux chambers. In this region, athletic fields are managed more intensively than ornamental lawns to maintain a consistent appearance, including resodding to replace dead portions of grass twice annually (ornamental lawns are reseeded occasionally if needed), regular aeration (12 times per year as opposed to 3 times per year for ornamental lawns), and a greater fertilization rate (Table 1). Grass species included *Fescue* L., *Lolium perenne* L., and *Cynodon* RICH. The fields sampled ranged in age from 3 to 35 years, with organic matter content of soils in ornamental lawns ranging from 0.6% to 8.7% organic C and, on average, increasing with age [Townsend-Small and Czimczik, 2010]. In athletic fields, organic C content of surface soils ranged from 1.8% to 9.1% and there was no relationship of organic C content with field age. Soil types varied from well drained upland soils to poorly drained silty soils and clays [U.S. Department of Agriculture (USDA), 1978]. More details about these parks can be found in [Townsend-Small and Czimczik, 2010]. In both the athletic fields and ornamental lawns, fertilizer was applied about four times per year (once per season) by sprinkling dry fertilizer directly onto the turf. In the ornamental lawns, one type of fertilizer was used year-round (Table 1), whereas in athletic fields, the fertilizer applied varied depending on season (Table 1). Total fertilization rates are shown in Table 1. Both ornamental lawns and athletic fields were watered approximately daily based on local estimates of evapotranspiration. We observed two fertilization events in the athletic fields (Figure 1a) and one fertilization event in the lawn sites (Figure 1b).

[8] We also measured N<sub>2</sub>O fluxes from agricultural soils at two farms. One farm was also located in Irvine, CA, at the University of California South Coast Research and Extension Center (33°4'17"N, 117°43'18"W). The soil type in this field is Sorrento loam and Sorrento clay loam, with 0 to 2 percent slopes [USDA, 1978]. Here, we investigated N<sub>2</sub>O emissions from five vegetable crops rotated throughout the year including celery (*Apium* L.), tomatoes (*Solanum lycopersicum* L.), carrots (*Daucus carota* L.), beans (*Pha-*

**Table 1.** Fertilization Types and Reported Rates for the Four Soil Types Sampled in This Study<sup>a</sup>

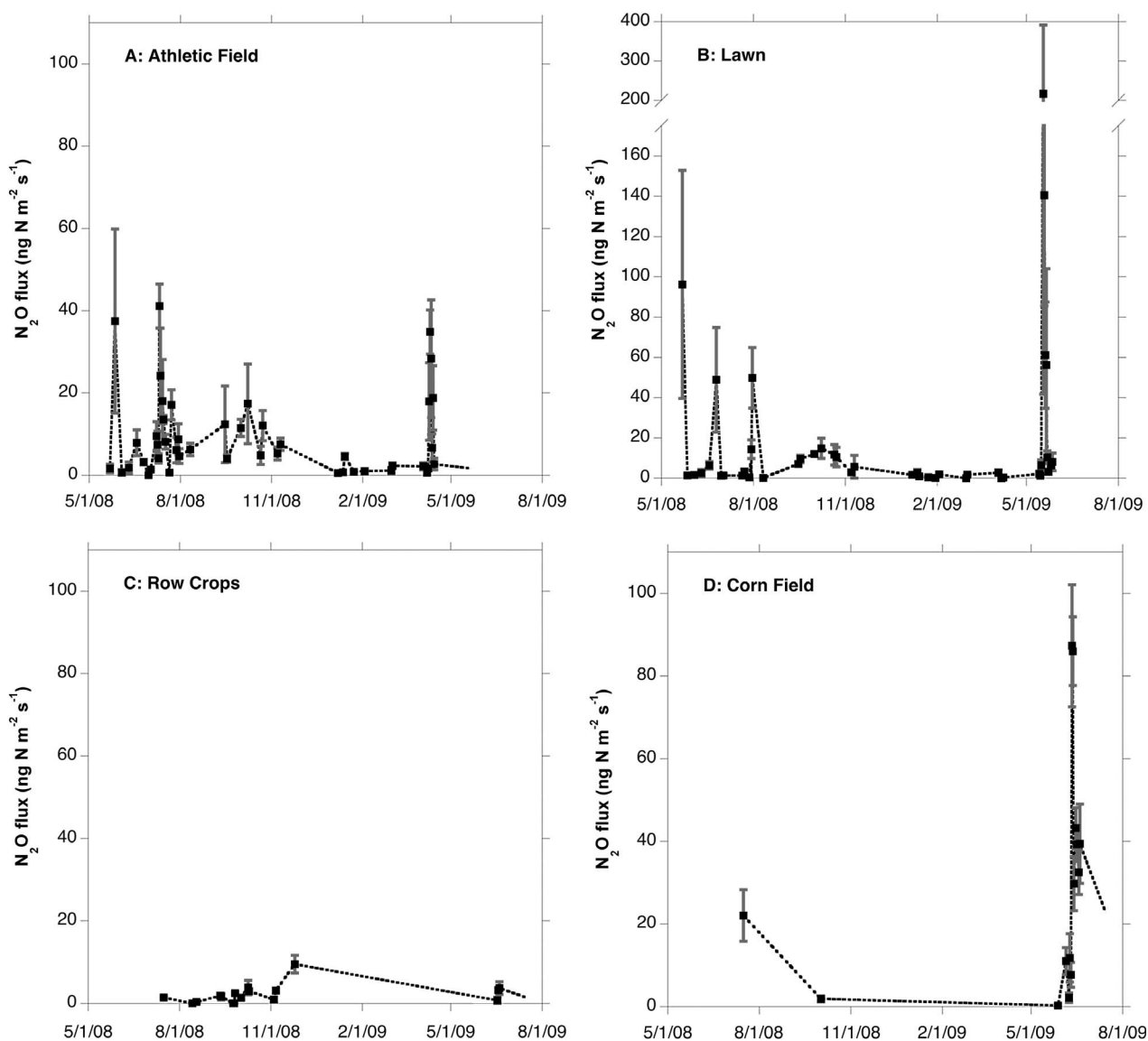
Land Cover Type	Fertilizer Type	Fertilization Rate (g N m <sup>-2</sup> yr <sup>-1</sup> )	δ <sup>15</sup> N (‰)	Note
Lawn	“Turf Supreme” NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	10	-1.0	Dry fertilizer application on turf surface
Athletic field	Fall and summer: sulfur-coated urea (NH <sub>2</sub> ) <sub>2</sub> CO	30	-2.3	Dry fertilizer application on turf surface
	Spring and winter: “Nitra-King” (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + Ca(NO <sub>3</sub> ) <sub>2</sub> ·NH <sub>4</sub> NO <sub>3</sub>	30	1.2	Dry fertilizer application on turf surface
Corn	(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + Ca(NO <sub>3</sub> ) <sub>2</sub> ·NH <sub>4</sub> NO <sub>3</sub> (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	16	-2.4	Dry fertilizer application under crop rows during planting
Row crops	NH <sub>4</sub> NO <sub>3</sub>	7	1.3	Dissolved in drip irrigation water

<sup>a</sup>Here we report fertilization rates directly observed in the field. Timing of fertilization and number of events is shown in Figure 1.

*seolus vulgaris* L.), and alfalfa (*Medicago sativa* L.). The crops were fertilized and irrigated identically and so have been lumped together as “row crops” in the succeeding analysis. At this farm, fertilizer was dissolved in irrigation

water regularly throughout the year. We observed four distinct fertilization events at this farm (Figure 1c).

[9] At the second farm, located at California State Polytechnic University in Pomona, CA (34°2'41"N, 117°48'47"W),



**Figure 1.** Nitrous oxide fluxes from the four land cover types sampled in this study, presented versus time. The points represent actual measurements of N<sub>2</sub>O flux; n = 3 or 4; ± standard error. Lines are linear interpolations between flux measurements.

we measured N<sub>2</sub>O emissions from two separate corn fields (*Zea mays* L.). There is no information available on the soil type at this field, as the USDA has not surveyed this part of southeastern Los Angeles County. The corn fields were irrigated weekly and were fallow during the winter months. Fertilizer was applied once annually in the spring (Figure 1d).

[10] We collected samples of the fertilizers used at all of these fields for analysis of  $\delta^{15}\text{N}$  (Table 1). More details on fertilization rates and types for the four land cover types are provided in Table 1. Although, in some cases, the site managers reported fertilization rates over the entire year that were greater than what we observed in the field, here we report only the fertilization events and amounts (in Table 1) directly observed. The experimental sites represented actual land cover and not controlled experiments; as a result, the fertilizer application rates for each event are self-reported by park and farm managers.

[11] The study was conducted during June 2008 to June 2009. Sampling was daily during fertilization events when we hoped to capture the major source of N<sub>2</sub>O to the atmosphere. We also sampled less frequently during nonfertilizer, or “baseline” periods, about once per month in the lawn sites, and less during fallow periods in the agricultural fields. Sampling was generally conducted in the early morning (~7 A.M. local time) to avoid windy conditions. However, we also conducted two overnight sampling campaigns to determine the effects of changing atmospheric conditions. Nitrous oxide fluxes were measured using static soil chambers (25 cm diameter). Headspace samples from soil chambers were taken every 7 min using 30 mL nylon syringes and immediately transferred to evacuated glass vials sealed with gray butyl rubber septa and aluminum crimps. Air and soil temperature were measured at 5 cm depth at each flux chamber using a Fisher Scientific digital thermometer with stainless steel temperature probe. Soil moisture at approximately 5 cm was also measured at each chamber using a Dynamax TH<sub>2</sub>O portable soil moisture meter (Houston, TX, United States).

[12] Fluxes are presented as the average of several chambers sampled simultaneously. There were multiple fields for each type of land cover (see above). If we sampled only one field on a given day, the flux was calculated as the average of three chambers. If we sampled two fields of the same type (i.e., two different ornamental lawns) on a given day, the flux was calculated as the average of six chambers; if we sampled three fields, the flux is the average of nine chambers, etc.

[13] Air samples were analyzed within 24 h on a gas chromatograph with an electron capture detector (GC-2014 Nitrous Oxide Analyzer, Shimadzu Scientific Instruments). Samples were analyzed with a series of calibrated reference gases that bracketed the expected concentration of the samples. The precision of this method is within 1% of expected N<sub>2</sub>O concentration in parts per billion (ppb). N<sub>2</sub>O fluxes were calculated from the slope of the line of N<sub>2</sub>O concentration in each chamber versus time. Regressions with  $r^2 < 0.9$  were assumed to represent negligible fluxes. Fluxes of N<sub>2</sub>O on nonmeasurement days were estimated by linear interpolation between measurement days, and the resulting daily fluxes were summed to estimate annual N<sub>2</sub>O emissions from each land cover type [Kaye *et al.*, 2004].

Multiple sampling events per day did not show a consistent change in N<sub>2</sub>O flux with temperature or time of day (Figure 4).

[14] Samples for analysis of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of N<sub>2</sub>O emitted from soils were taken from a larger (L 39 cm × W 26 cm × H 22 cm) flux chamber (one sample for each set of 3 flux measurements). The chamber was placed on the soil surface for 20–30 min to allow N<sub>2</sub>O to accumulate, and then the headspace was withdrawn slowly through a 23-gauge needle (~100 mL/min) with a vacuum pump into an evacuated 1.5 mL stainless steel gas canister. We also sampled air from outside the chamber using the same method to correct for N<sub>2</sub>O already present in background air.

[15] Isotope measurements were made by continuous flow isotope ratio mass spectrometry at the University of California, Irvine Stable Isotope Facility. Whole air samples were injected into a preconcentration device that was continuously flushed with helium. Air passed through a CO<sub>2</sub> and water trap (Ascarite and magnesium perchlorate) and then a series of liquid N<sub>2</sub> cryotrap that retain N<sub>2</sub>O (and any remaining CO<sub>2</sub> and H<sub>2</sub>O) and allow other components of air to pass through. After the cryofocusing steps, the gas was thawed and passed through a GC column, separating residual CO<sub>2</sub> from N<sub>2</sub>O, and then measured with an isotope ratio mass spectrometer (Delta Plus XP, Thermo Finnigan). The instrument was calibrated daily with two N<sub>2</sub>O standards of known isotopic composition. The precision of this method was within 0.2‰ for  $\delta^{15}\text{N}$  and within 0.5‰ for  $\delta^{18}\text{O}$ , and internal standards of N<sub>2</sub>O analyzed daily were replicated from day to day within 0.5‰ for  $^{15}\text{N}$  and 1‰ for  $^{18}\text{O}$ . Fertilizers were analyzed in duplicate on an elemental analyzer coupled to an isotope ratio mass spectrometer (Delta Plus, Thermo Finnigan). Isotope data are presented as  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  versus Air-N<sub>2</sub> and Vienna Standard Mean Ocean Water (VSMOW), respectively, using conventional  $\delta$  notation.

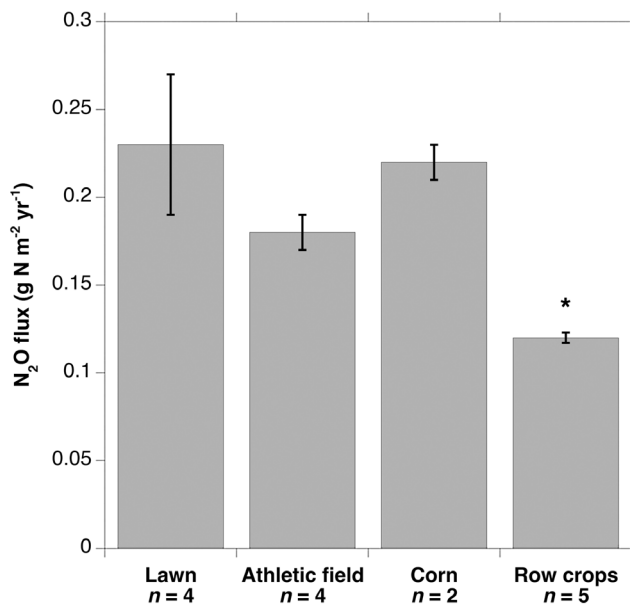
[16] The isotopic composition of N<sub>2</sub>O extracted from a flux chamber (“total N<sub>2</sub>O”) represents N<sub>2</sub>O emitted from soils during the chamber incubation (“soil N<sub>2</sub>O”) as well as N<sub>2</sub>O present in the air before chamber placement (“background N<sub>2</sub>O”).  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values presented in this paper represent soil N<sub>2</sub>O emissions only, calculated according to the following equation:

$$\begin{aligned} (\text{total } \delta)^* (\text{total N}_2\text{O concentration}) \\ = (\text{soil } \delta)^* (\text{soil N}_2\text{O concentration}) \\ + (\text{background } \delta)^* (\text{background N}_2\text{O concentration}) \end{aligned}$$

For accurate point source characterization, N<sub>2</sub>O isotope measurements were conducted only on samples with concentrations more than 30 ppb higher than background air (~320 ppb). Differences in annual fluxes and average annual isotope ratios were assessed using ANOVA and *t* tests, with significance assigned at  $p < 0.05$ .

### 3. Results

[17] The athletic fields, lawns, and corn fields showed a general pattern of rapid increases in N<sub>2</sub>O fluxes following fertilization and low (but not necessarily zero) emissions between fertilization events (Figure 1). Time since fertilization was the major driver of N<sub>2</sub>O fluxes in these sites: at



**Figure 2.** Annual fluxes of N<sub>2</sub>O (±SE) from each land cover type. The replicate number of sites of each type of land cover (n) is also shown. Row crops had significantly lower N<sub>2</sub>O emissions than other types of land cover (\*;  $p < 0.0001$ ).

each site, there was no relationship between soil moisture or temperature and N<sub>2</sub>O fluxes ( $p > 0.05$ ). In the row crops, N<sub>2</sub>O flux did not significantly increase after fertilization (Figure 1c). Data from all urban parks were combined as lawn age or organic matter content did not significantly influence N<sub>2</sub>O emissions ( $p > 0.05$ ). There was no statistical difference between annual N<sub>2</sub>O fluxes from lawns ( $0.23 \pm 0.04$  g N m<sup>-2</sup> yr<sup>-1</sup>), athletic fields ( $0.18 \pm 0.01$  g N m<sup>-2</sup> yr<sup>-1</sup>), and corn ( $0.22 \pm 0.01$  g N m<sup>-2</sup> yr<sup>-1</sup>) (Figure 2). Row crops had about 50% lower annual N<sub>2</sub>O emissions ( $0.12 \pm 0.003$  g N m<sup>-2</sup> yr<sup>-1</sup>) than the other three land cover types ( $p \leq 0.0001$ ). Increased sampling or continuous monitoring of N<sub>2</sub>O emissions, including during fallow periods in agricultural fields, would likely improve these annual flux estimates. Lawns and athletic fields had the highest soil moisture content overall ( $34.7 \pm 0.6\%$  and  $36.2 \pm 0.7\%$ , respectively), with row crops ( $29.2 \pm 0.8\%$ ) and corn fields ( $15.5 \pm 0.7\%$ ) drier overall. The method used here to estimate total annual N<sub>2</sub>O flux from lawns and athletic fields (linear interpolation between measurement days) gives a similar result to the method used in our previous work ( $0.1$  to  $0.3$  g N m<sup>-2</sup> yr<sup>-1</sup>), where we determined the average response of N<sub>2</sub>O emission to fertilization and multiplied it by a range of potential fertilization rates [Townsend-Small and Czimczik, 2010]. We are not certain that we captured all fertilization events, such that our annual fluxes may be underestimated.

[18] The isotopic composition of N<sub>2</sub>O was highly variable for both N and O and there were no consistent differences by land cover type when all samples were averaged.  $\delta^{15}\text{N}$  of N<sub>2</sub>O ranged from  $-48.2\%$  to  $-2.3\%$ , and  $\delta^{18}\text{O}$  ranged from  $7.2\%$  to  $39.1\%$ . For reference, the average concentration (± standard error) of N<sub>2</sub>O in our “background air” samples was  $321 \pm 2$  ppb with a  $\delta^{15}\text{N}$  of  $5.1 \pm 0.2\%$  and a  $\delta^{18}\text{O}$  of

$41.0 \pm 1.3\%$  ( $n = 21$ ). In order to determine whether the isotopic composition of N<sub>2</sub>O was related to fertilization, we separated our N<sub>2</sub>O isotope data into two categories: samples taken during baseline flux rates (i.e., when fluxes were low between fertilization events), and samples taken following fertilizer application (within 2 weeks after fertilization). There was no consistent difference in  $\delta^{15}\text{N}$  of N<sub>2</sub>O with sampling time. In athletic fields, the average  $\delta^{15}\text{N}$  of N<sub>2</sub>O sampled during fertilizer pulses was significantly lower than  $\delta^{15}\text{N}$  of N<sub>2</sub>O sampled during baseline fluxes (Figure 3). In row crops, there was a nonsignificant trend of lower  $\delta^{15}\text{N}$  of N<sub>2</sub>O during baseline conditions than during fertilizer pulses (Figure 3). There was no difference in  $\delta^{18}\text{O}$  of N<sub>2</sub>O in these same comparisons (Figure 3).

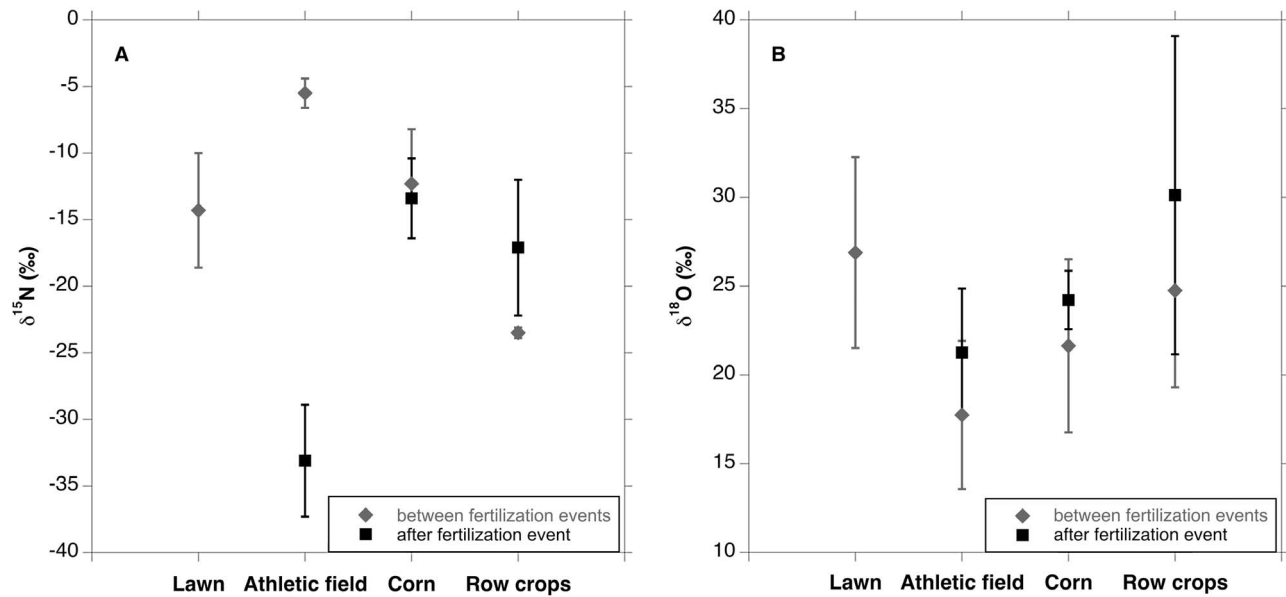
[19] A closer examination of N<sub>2</sub>O fluxes and isotopic composition for shorter time periods reveals that fluxes may be highly variable even within small spatial and temporal scales. Figure 4a shows flux measurements taken over a single 24 h period in athletic fields and ornamental lawns in the same park. Fluxes in the ornamental lawn varied between 50 and 5 ng N m<sup>-2</sup> s<sup>-1</sup> while fluxes in the athletic field were generally constant over the measurement period at about 5–10 ng N m<sup>-2</sup> s<sup>-1</sup>. As with fluxes,  $\delta^{15}\text{N}$  of N<sub>2</sub>O was highly variable in the lawn and less so in the athletic field (Figure 4b), but the variation in  $\delta^{15}\text{N}$  in the lawn was not correlated to the flux rates.  $\delta^{18}\text{O}$  of N<sub>2</sub>O was highly variable in both sites over the 24 h period (Figure 4c).

[20] We conducted several high-intensity sampling campaigns aimed at analyzing the effect of the fertilizer pulse of N<sub>2</sub>O emitted after fertilization on the isotopic composition of N<sub>2</sub>O. Figure 5 shows the results from a corn field following fertilization with ammonium phosphate (16 g N m<sup>-2</sup>; Table 1), and Figure 6 shows the results for two athletic fields fertilized with Nitra-King (Table 1) at approximately the same reported rate (15 g N m<sup>-2</sup>) on the same day. All three sites show an increase in N<sub>2</sub>O fluxes following fertilization (on day 0) that remain elevated for up to 10 days (Figures 5a and 6a). The two athletic fields had vastly different responses of N<sub>2</sub>O fluxes to fertilization (Figure 6a). In both the corn field and the athletic fields,  $\delta^{15}\text{N}$  of N<sub>2</sub>O became much more depleted relative to pretreatment levels following fertilization, and then returned to enriched values over the next several days (Figures 5b and 6b). Based on our measurements of  $\delta^{15}\text{N}$  of fertilizers, we calculated enrichment factors of  $-22.8\%$  and  $-49.4\%$  for the initial N<sub>2</sub>O produced in the corn fields and athletic fields, respectively. In the corn field,  $\delta^{18}\text{O}$  of N<sub>2</sub>O became more enriched following fertilization, remained enriched for a few days, and then became more depleted to pretreatment levels (Figure 5c). In the athletic fields, the response of  $\delta^{18}\text{O}$  of N<sub>2</sub>O to fertilization was similar to the response in  $\delta^{15}\text{N}$ : an initial depletion following fertilization and enrichment thereafter (Figure 6c).

## 4. Discussion

### 4.1. N<sub>2</sub>O Fluxes From Urban and Agricultural Ecosystems

[21] Our work clearly shows that urban ecosystems can emit N<sub>2</sub>O at rates comparable to highly managed agricultural fields. This is similar to results found in Colorado, United States, where urban lawns and corn fields emitted N<sub>2</sub>O at  $0.2$  g N m<sup>-2</sup> yr<sup>-1</sup>, about 10 times greater than unirrigated and



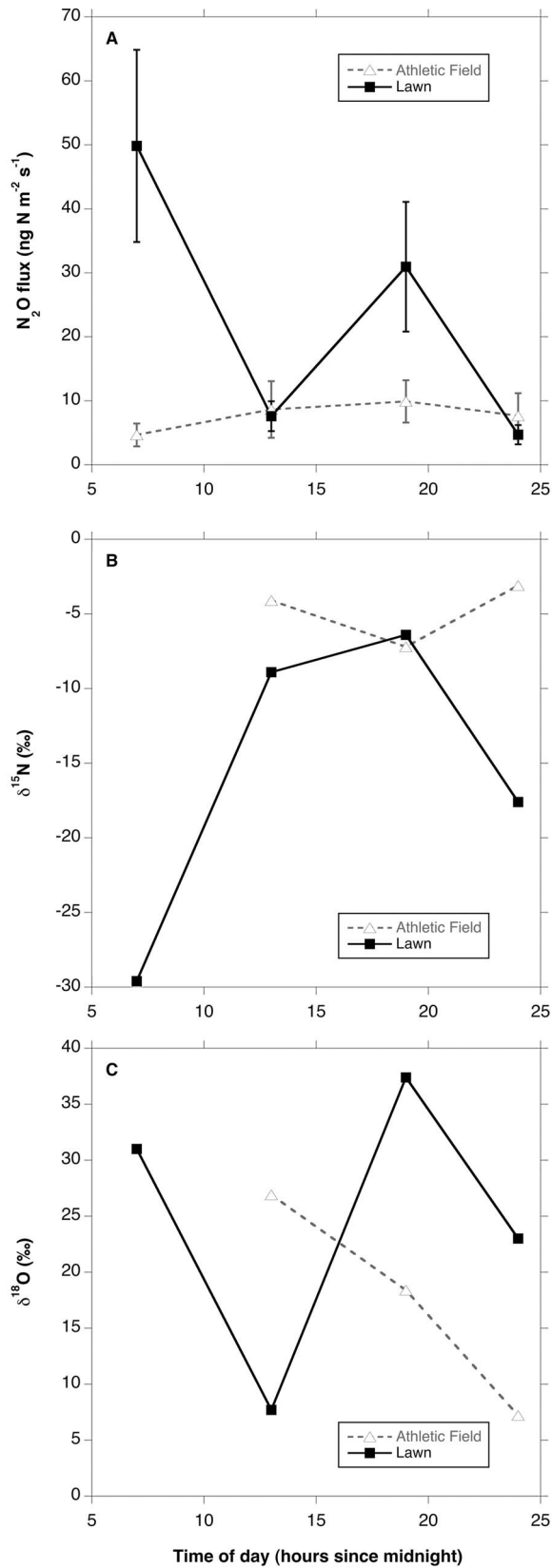
**Figure 3.** The (a) nitrogen and (b) oxygen isotope ratio ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) of N<sub>2</sub>O of each crop separated by sampling period. “Between fertilization events” is isotopic composition of N<sub>2</sub>O emitted from soil during baseline fluxes before or after a fertilizer pulse. “After fertilization event” is isotopic composition during the increased N<sub>2</sub>O flux following fertilization. Note that there were no “fertilizer” samples for the ornamental lawns. The difference between the two sample types was only statistically significant for  $\delta^{15}\text{N}$  in athletic fields ( $p > 0.0001$ ). Error bars show the standard error.

unfertilized grasslands or wheat fields [Kaye *et al.*, 2004]. In Phoenix, Arizona, United States, irrigated and fertilized urban lawns emitted N<sub>2</sub>O at rates about 5 times higher than unirrigated urban soils [Hall *et al.*, 2008]. Another study found similar rates of N<sub>2</sub>O emission in urban lawns and suburban forests in the northeastern United States [Groffman *et al.*, 2009]. In southern California, urban ecosystems may be a larger source of N<sub>2</sub>O than agriculture. Agricultural soils account for only 1% of total land cover in the South Coast Air Basin, which encompasses the Los Angeles basin [Jacobson, 2008]. In a recent study of vertically averaged greenhouse gas concentrations in the troposphere above Los Angeles, N<sub>2</sub>O emissions were 2 to 8 times larger than estimated by agricultural land cover alone [Wunch *et al.*, 2009]. Besides urban landscaping, other potential sources of N<sub>2</sub>O in the region include sewage treatment plants, marine denitrification and nitrification, and fossil fuel combustion [Wunch *et al.*, 2009].

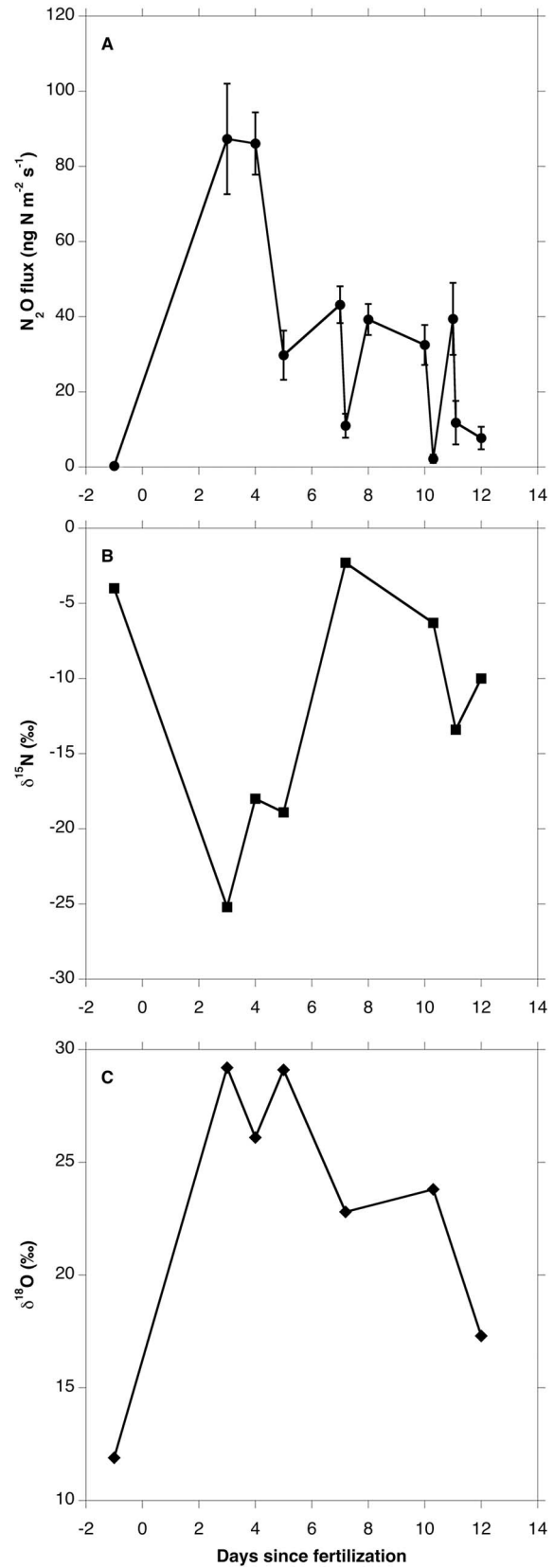
[22] We did not find a direct relationship between fertilization rate and annual N<sub>2</sub>O emissions ( $r^2 = 0.0304$ ) in our study (Table 1 and Figure 2), possibly because we do not know the exact amount of fertilizer applied in each type of ecosystem. Future studies would benefit from careful measurements of fertilization rate in conjunction with site managers. Besides fertilization rate, there are several other factors that have been shown to affect soil N<sub>2</sub>O emissions, including soil moisture, temperature, and organic matter levels [Weitz *et al.*, 2001; Schindlbacher *et al.*, 2004; Ruser *et al.*, 2006], although these factors do not always covary with N<sub>2</sub>O flux in situ [Flessa *et al.*, 1995]. In the present study, soil temperature did not vary between sites, and soil temperatures were relatively constant throughout the study period due to the mild, Mediterranean climate, so temperature variations

do not explain the differences in overall N<sub>2</sub>O flux between land cover types. The relationship between soil organic matter content and N<sub>2</sub>O emission is the subject of considerable debate, as some studies have shown that a shift from conventional tillage to no-till agriculture to increase soil carbon sequestration can also lead to increased emission of N<sub>2</sub>O, thereby negating the positive effects of reduced tillage [Six *et al.*, 2004; Behedyt *et al.*, 2008]. However, this finding is not universal, as other studies have shown that changes in tillage leading to an increase in soil organic matter do not increase N<sub>2</sub>O emissions [Helgason *et al.*, 2005; Bavin *et al.*, 2009]. Here we show that N<sub>2</sub>O emissions do not differ between untilled soils (lawns) and soils that are regularly tilled (athletic fields, corn) (Figure 2), and we also found no overall difference in N<sub>2</sub>O emissions from older lawns with high soil organic C content and newer lawns with less total organic matter. Nonetheless, if the row crop fields contain significantly less organic matter than the other three land cover types, this may explain the drastically lower N<sub>2</sub>O emission rate from these fields. Soil moisture is a common driver of N<sub>2</sub>O flux, but, in this study, there was no clear relationship between soil moisture and annual N<sub>2</sub>O emissions. In fact, the corn fields, which had the lowest soil moisture overall, had equivalent annual N<sub>2</sub>O fluxes to the athletic fields (which were fertilized more than the corn fields) and ornamental lawns (which had higher soil moisture than the corn fields).

[23] Using our measurements of annual N<sub>2</sub>O emissions from the four study areas and estimates of fertilization rates from managers, we can calculate fertilizer-induced direct emissions factors for urban and agricultural soils in southern California. The Intergovernmental Panel on Climate Change (IPCC) estimates that 1% of applied fertilizer is released as

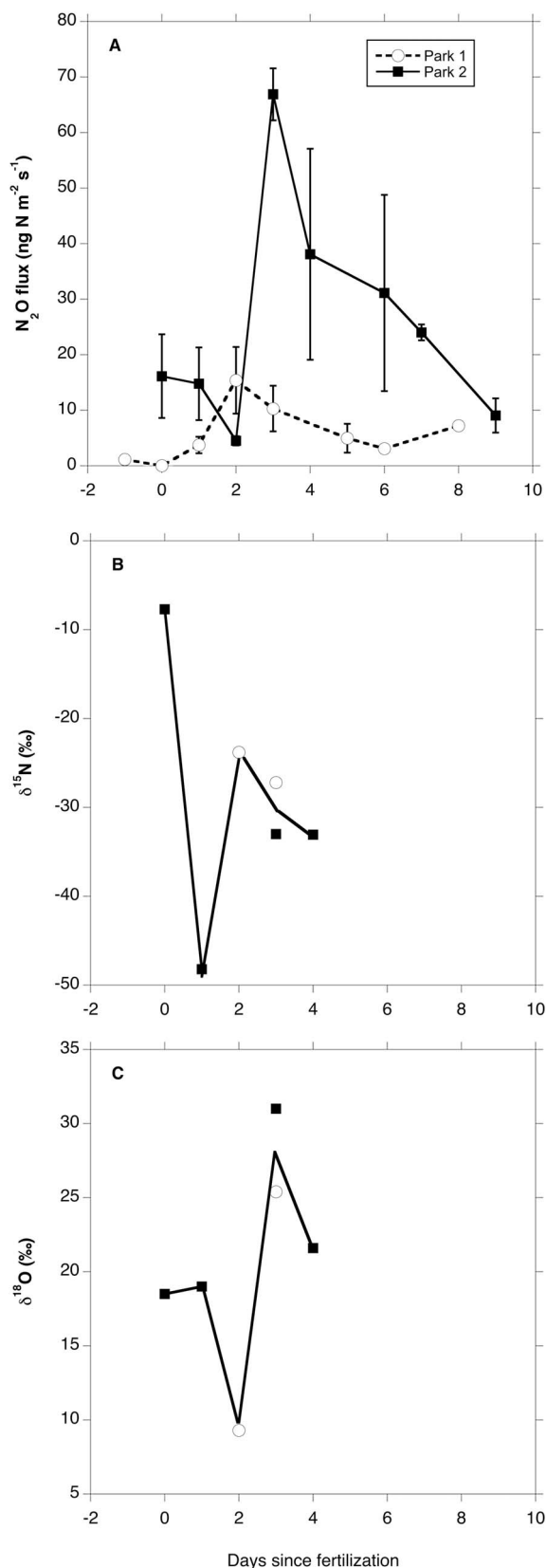


**Figure 4.** (a) N<sub>2</sub>O flux, (b) nitrogen isotope composition ( $\delta^{15}\text{N}$ ), and (c) oxygen isotope composition ( $\delta^{18}\text{O}$ ) of N<sub>2</sub>O sampled during a single 24 h period within an urban lawn site. Error bars show the standard error.



**Figure 5.** (a) N<sub>2</sub>O flux, (b) nitrogen isotope composition ( $\delta^{15}\text{N}$ ), and (c) oxygen isotope composition ( $\delta^{18}\text{O}$ ) of N<sub>2</sub>O produced following fertilization at a corn field. Error bars show the standard error.





**Figure 6.** (a) N<sub>2</sub>O flux, (b) nitrogen isotope composition (δ<sup>15</sup>N), and (c) oxygen isotope composition (δ<sup>18</sup>O) of N<sub>2</sub>O produced following fertilization at similar rates on the same day at two athletic fields. Error bars show the standard error.

N<sub>2</sub>O in agricultural fields [IPCC, 2006]. In the current study, we have found direct emissions factors for urban and agricultural ecosystems that are comparable to those calculated by the IPCC: N<sub>2</sub>O emissions accounted for 2.3% (lawns), 0.6% (athletic fields), 1.4% (corn), and 1.7% (row crops) of reported amounts of applied fertilizer N. IPCC emissions factors are used in California to estimate annual N<sub>2</sub>O emissions based on agricultural land area [California Air Resources Board, 2006], but do not include irrigated and fertilized urban landscapes, despite similar and in some cases higher emissions factors and fertilizer use in urban as opposed to agricultural soils (Table 1). Indirect N<sub>2</sub>O emissions (such as those associated with leaching and runoff of N fertilizers) associated with urban landscaping and agricultural cultivation are in need of further study and quantification, as these may be of great importance to regional N and N<sub>2</sub>O budgets [Seitzinger et al., 2000; IPCC, 2006]. In particular, if direct N<sub>2</sub>O emissions are tempered by large losses of N through leaching, this may resolve some of the discrepancies we have seen between fertilization events and N<sub>2</sub>O efflux. Revised emissions inventories that include urban land cover are possible, although there are still far less data for urban than agricultural land cover, and the appropriate emission factors remain uncertain. Our results highlight the inherent variability of N<sub>2</sub>O fluxes after fertilization, as ornamental lawns and athletic fields showed very different results.

[24] Our results show a large range in response of N<sub>2</sub>O emissions to fertilizer application. Figure 6 shows the response of N<sub>2</sub>O emission to fertilization with “Nitra-King” (Table 1) at the same reported rate in two baseball fields on the same day. N<sub>2</sub>O emissions following fertilization in Park 1 were more than 3 times higher than in Park 2, which have the same grass species and underlying soil parent material. In addition, multiple sampling events per day in slightly different locations showed that N<sub>2</sub>O flux may be very heterogeneous even within the same field (Figure 4). Such high spatial and temporal variability in soil N<sub>2</sub>O flux is common and often generally attributed to underlying soil microbial populations, N and organic matter availability, and O<sub>2</sub> levels [Parkin, 1987; Röver et al., 1999; Grant and Pattey, 2003; Helgason et al., 2005; Turner et al., 2008]. In particular, intrasite or intersite differences in moisture and O<sub>2</sub> availability can cause changes in the proportion of N<sub>2</sub>O:N<sub>2</sub> emitted during denitrification [Pérez, 2005].

#### 4.2. Stable Isotope Constraints on N<sub>2</sub>O Sources

[25] The high spatial and temporal variability in N<sub>2</sub>O fluxes reported here and in previous studies creates a need for alternative methods for estimating fluxes and sources. Stable and radioactive isotopes have proved to be excellent tracers of various sources of CO<sub>2</sub> due to consistent differences in the isotopic composition of sources [Pataki et al., 2003a, 2003b, 2007]. Unfortunately, the isotopic composition of N<sub>2</sub>O from soils appears to be highly variable due to factors other than land cover type. In fact, both δ<sup>15</sup>N and δ<sup>18</sup>O appeared to vary greatly even within the same ecosystem and the same day (Figure 4).

[26] The isotopic composition of N<sub>2</sub>O showed depletion in δ<sup>15</sup>N following fertilization for up to 48 h and then returned to pre-fertilization levels (Figures 5 and 6). It is difficult to explain these changes by shifts in the ratio of nitrification

to denitrification without measurements of the  $\delta^{15}\text{N}$  of substrates ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ , respectively). Fertilization dramatically increases the pool of available inorganic N for nitrification and denitrification, and this increased availability may lead to greater isotopic fractionation by microbes. Previous studies incorporating measurements of N<sub>2</sub>O isotopes and microbial rate measurements have shown that depletion of  $\delta^{15}\text{N}$  of N<sub>2</sub>O emitted directly following fertilization may be due to an initial pulse of nitrification, which declines with declining availability of  $\text{NH}_4^+$  from fertilizer [Pérez *et al.*, 2001]. This may be followed by an increase in denitrification that takes advantage of increased  $\text{NO}_3^-$  availability from nitrification, resulting in emission of  $^{15}\text{N}$ -enriched N<sub>2</sub>O. After the added  $\text{NH}_4^+$  and  $\text{NO}_3^-$  are depleted, denitrification of N<sub>2</sub>O to N<sub>2</sub> may further reduce N<sub>2</sub>O emissions. Nitrification is thought to be the dominant source of N<sub>2</sub>O in moderately moist soils such as in the current study (range 4.5–58.6% by volume; average equal to  $32.9\% \pm 0.4$  [s.e.]) [Pérez, 2005]. In studies with higher soil moisture content following fertilization, denitrification can dominate soil N<sub>2</sub>O fluxes [Panek *et al.*, 2000].

[27] The initial depletion in  $^{15}\text{N}$  of N<sub>2</sub>O following fertilization may also be due to a change in  $\delta^{15}\text{N}$  of the substrate, rather than a shift in the dominance of one microbial process over another. Assuming that fertilizer is the main substrate and that it has a  $\delta^{15}\text{N}$  of approximately 0‰ (Table 1), the initial depletion in  $\delta^{15}\text{N}$  of N<sub>2</sub>O may be due microbial fractionation. As time progresses and the substrate is isotopically enriched by microbial and plant uptake, this is reflected in progressive enrichment of  $\delta^{15}\text{N}$  of N<sub>2</sub>O. In addition, enrichment in  $\delta^{15}\text{N}$  of N<sub>2</sub>O throughout the time series of fertilization may also reflect a decrease in total substrate availability, so that denitrifiers are eventually forced to reduce N<sub>2</sub>O to N<sub>2</sub>, thereby reducing the total N<sub>2</sub>O flux and increasing the  $\delta^{15}\text{N}$  of N<sub>2</sub>O. In order to better understand the exact mechanisms by which fertilization increases the flux of N<sub>2</sub>O, future studies would benefit from combining N<sub>2</sub>O isotope measurements with analyses of substrate isotope ratios [e.g., Pérez *et al.*, 2001], measurements of denitrification and nitrification rates [Davidson *et al.*, 1993], and/or genetic or molecular indicators of each process [Casciotti *et al.*, 2003; Sutka *et al.*, 2006]. The use of isotopically labeled fertilizers may also help to identify microbial N<sub>2</sub>O production pathways [Panek *et al.*, 2000; Baggs, 2008]. These types of detailed studies are difficult to conduct in a survey of multiple land cover types, but may be conducted in specific locations.

[28] It should be noted that for sampling periods between fertilization events, both agricultural and urban N<sub>2</sub>O fluxes (including other nonsoil sources such as vehicle emissions) were generally too small to cause a sufficient increase in atmospheric N<sub>2</sub>O concentrations for an accurate isotope measurement. At each sampling time in this study, two types of air samples were taken for isotope analysis: one from inside an N<sub>2</sub>O flux chamber, and one from just outside the soil chamber (but still on the lawn, corn field, etc.) to correct for the presence of background air. Because of the small fluxes between fertilization events, our isotope data set was biased toward fertilization events. In addition, the concentration of measured “background” air outside of the chambers did not vary more than 5 ppb above 320 ppb, the approximate concentration of clean air in 2008. Thus, emissions of

N<sub>2</sub>O in the study region did not appear to have a large influence on the local atmospheric concentrations of N<sub>2</sub>O, in contrast to the reported elevated urban concentrations of other gases such as CO<sub>2</sub> and CH<sub>4</sub> [Blake *et al.*, 1984; Pataki *et al.*, 2003a; Wunch *et al.*, 2009]. These low local concentrations complicate monitoring of N<sub>2</sub>O isotopes as a means of tracing regional sources.

[29] A continuous time series of N<sub>2</sub>O fluxes and isotope composition following fertilization might allow for isotope-based source monitoring while further elucidating microbial sources and providing a more robust flux estimate. This is especially true for the first 24–48 h following fertilizer application: our discrete sample periods potentially miss some of the largest changes in  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of N<sub>2</sub>O. A few studies have successfully used micrometeorological methods to monitor N<sub>2</sub>O emissions [Edwards *et al.*, 2003; Scanlon and Kiely, 2003], and this technology will likely soon be widely commercially available. A continuous record of atmospheric N<sub>2</sub>O concentrations could greatly aid in timing of sampling for isotope analyses, perhaps even revealing a greater increase in ambient air N<sub>2</sub>O concentration following fertilization than we have shown here and a significant impact on local N<sub>2</sub>O isotopic composition. If fertilization produces a short-term change in atmospheric N<sub>2</sub>O concentration that is characteristically depleted, these measurements could be used to distinguish soil from other local sources such as sewage treatment plants, animal manure, or aquatic and marine emissions.

## 5. Conclusions and Implications

[30] We have shown that urban landscapes can contribute a significant portion of total N<sub>2</sub>O emissions, at least on regional scales. For example, Orange County, California, has approximately 160 km<sup>2</sup> of parks and 223 km<sup>2</sup> of agricultural land [County of Orange, 2009]. Assuming annual N<sub>2</sub>O emission rates from urban and agricultural land cover that are intermediate of the two types of each we studied (0.21 and 0.17 g N m<sup>-2</sup> yr<sup>-1</sup>, respectively), parks contribute about 34 tons N<sub>2</sub>O-N per year, and farms about 38 tons N<sub>2</sub>O-N per year. The county does not collect data on residential turf area, but previous studies have shown that turfgrass can account for about 40 to 50% of urban and suburban areas and are probably fertilized about 60 to 90% less than golf courses and athletic fields [Milesi *et al.*, 2005, and references therein]. Let us assume that residential lawns emit 50% less N<sub>2</sub>O than parks, due to more conservative irrigation and fertilization. If we assume that just 20% of the approximately 600 km<sup>2</sup> total residential land in Orange County is turfgrass managed in this way, urban lawns become the dominant soil source of N<sub>2</sub>O in the region. The additional consideration of indirect N<sub>2</sub>O emissions from urban landscaping activities may further emphasize the importance of these activities in regional greenhouse gas budgets. The omission of urban landscapes in models of N<sub>2</sub>O emissions in California may explain why measured N<sub>2</sub>O emissions in the Los Angeles area are so much higher than the estimate in the statewide greenhouse gas inventory [Wunch *et al.*, 2009]. Clearly, more research is needed on lawn fertilization and irrigation rates, especially in residential areas, in order to gain a complete picture of the impacts of turfgrass on regional N<sub>2</sub>O budgets.

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