

## Physical and biological controls on trace gas fluxes in semi-arid urban ephemeral waterways

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**Abstract** Rapid increases in human population and land transformation in arid and semi-arid regions are altering water, carbon (C) and nitrogen (N) cycles, yet little is known about how urban ephemeral stream channels in these regions affect biogeochemistry and trace gas fluxes. To address these knowledge gaps, we measured carbon dioxide (CO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), and methane (CH<sub>4</sub>) before and after soil wetting in 16 ephemeral stream channels that vary in soil texture and organic matter in Tucson, AZ. Fluxes of CO<sub>2</sub> and N<sub>2</sub>O immediately following wetting were among the highest ever published (up to 1,588 mg C m<sup>-2</sup> h<sup>-1</sup> and 3,121 μg N m<sup>-2</sup> h<sup>-1</sup>). Mean post-wetting CO<sub>2</sub> and N<sub>2</sub>O fluxes were significantly higher in the loam and sandy loam channels (286 and 194 mg C m<sup>-2</sup> h<sup>-1</sup>; 168 and 187 μg N m<sup>-2</sup> h<sup>-1</sup>) than in the sand channels

(45 mg C m<sup>-2</sup> h<sup>-1</sup> and 7 μg N m<sup>-2</sup> h<sup>-1</sup>). Factor analyses show that the effect of soil moisture, soil C and soil N on trace gas fluxes varied with soil texture. In the coarser sandy sites, trace gas fluxes were primarily controlled by soil moisture via physical displacement of soil gases and by organic soil C and N limitations on biotic processes. In the finer sandy loam sites trace gas fluxes and N-processing were primarily limited by soil moisture, soil organic C and soil N resources. In the loam sites, finer soil texture and higher soil organic C and N enhance soil moisture retention allowing for more biologically favorable antecedent conditions. Variable redox states appeared to develop in the finer textured soils resulting in wide ranging trace gas flux rates following wetting. These findings indicate that urban ephemeral channels are biogeochemical hotspots that can have a profound impact on urban C and N biogeochemical cycling

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pathways and subsequently alter the quality of localized water resources.

**Keywords** Urban stream · Trace gas flux · Semi-arid · Nitrogen · Carbon · Methane

## Introduction

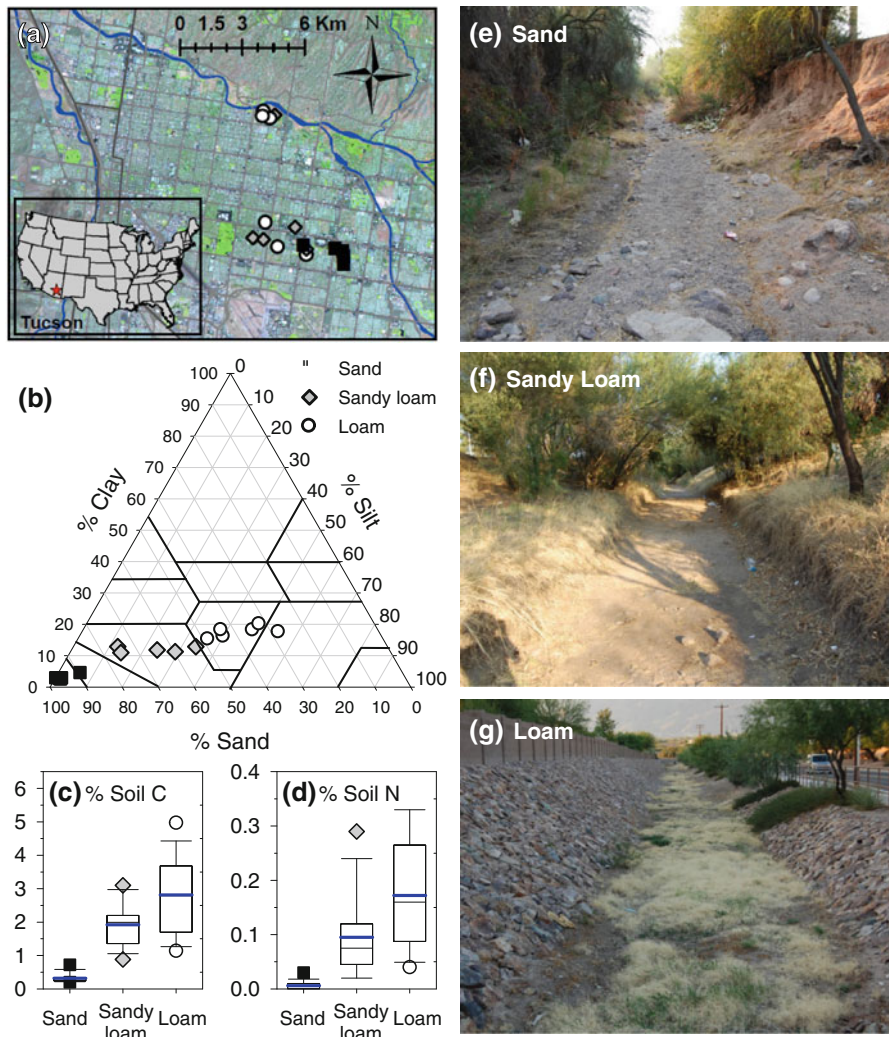
Arid and semi-arid ecosystems are experiencing disproportionate increases in human population and land transformation worldwide resulting in altered hydrosystems and biogeochemical cycles (Ezcurra 2006; Kaye et al. 2006; Grimm et al. 2008a). Numerous studies have focused on how urbanization alters the redistribution of water, nutrients and biogeochemical responses in upland arid and semi-arid ecosystems (Kaye et al. 2006; Kennedy 2007; McCrackin et al. 2008; Hall et al. 2009), as well as the consequences for runoff and the delivery of nutrients to areas of focused groundwater recharge (Lewis and Grimm 2007; Grimm et al. 2008a; Gallo et al. 2012a, 2013). However, little is known about how the morphology of urban streams, specifically ephemeral streams that dominate arid and semi-arid regions (Levick et al. 2008), alter N transformations and removal via trace gas fluxes and what controls those fluxes. Understanding water and materials fluxes in urban environments and the role that ephemeral streams play in controlling trace gas fluxes will be critical for developing science-based management strategies for the long term sustainability of urban ecosystems in water limited environments (Grimm et al. 2008a; Goddard et al. 2010). This is especially true in the rapidly urbanizing semi-arid Southwestern United States (Grimm et al. 2008a, b) where urban runoff is actively managed to augment a limited water supply, and reducing delivery of nitrate to focused areas of recharge is critical to sustaining groundwater quality (Carlson et al. 2011).

Recent research in the rapidly urbanizing Southwestern US indicates accelerated carbon (C) and nitrogen (N) cycling and gas losses in upland ecosystems owing to changes in the redistribution of water, carbon and nitrogen resulting from land use (Fenn et al. 2003; Lohse et al. 2008). Lohse et al. (2008), for example, show that urbanization in the Central Arizona Phoenix Long-term Ecological Research (CAP LTER) study area increases C and N loading to urban core ecosystems via dry and wet deposition

compared to desert ecosystems; and Hall et al. (2008) measured higher rates of nitrogen cycling and nitric oxide and nitrous oxide losses from grass lawns compared to xeric landscaped areas. Other studies show that downstream engineered lake and grass catch basins have higher C and N-cycling rates and thus higher potential for N loss via denitrification than xeric gravel basins (Zhu et al. 2005; Larson 2010; Roach and Grimm 2011).

Despite the prevalence of ephemeral streams (81 % of southwestern streams, Levick et al. 2008) and a projected doubling of urban land cover by 2,050 in the semi-arid southwest (Theobald et al. 2013), to our knowledge, no studies have measured trace gas losses in ephemeral stream channels, especially those undergoing urbanization. Findings from Gallo et al. (2012a, b, 2013) in Tucson, AZ indicate that drainage networks and the characteristics of urban ephemeral streams, such as substrate texture, play important roles in controlling nutrient load patterns in urban runoff and soil solute loads following a runoff event. These findings suggest that much of the nutrient processing and C and N gas flux occur within ephemeral channels between wetting events, subsequently altering urban runoff quality. Research in upland ecosystems show immediate biogeochemical and biological responses to rainfall following periods of soil water limitation (Cable and Huxman 2004; Reynolds et al. 2004; Schwinning and Sala 2004). In arid and semi-arid regions, rainfall pulses can sustain soil biological processes (Snyder and Williams 2000; Loik et al. 2004; Belnap et al. 2005) which under warmer spring and summer temperatures, can increase microbial activity and responses such as trace gas fluxes (Conant et al. 2004; Bowling et al. 2011).

The objective of this research was to examine how stream channel characteristics control summertime trace gas losses in response to soil wetting following an extensive dry period in ephemeral urban streams, or washes, in Tucson, Arizona, USA. We focus on summertime trace gas fluxes when warm temperatures and summer rainfall may enhance biogeochemical processes. We selected 16 sites in ephemeral stream channels that ranged in soil texture and organic matter and measured trace gas fluxes prior to and following soil wetting. We used linear regression and non-parametric statistical analyses to quantify relationships between site characteristics and flux and identify likely mechanisms controlling gas flux responses.



**Fig. 1** **a** Location of urban ephemeral washes in Tucson, Arizona included in this study, **b** soil texture properties of the study washes, percent soil **c** carbon (C) and **d** nitrogen (N) used to classify the study sites into 3 major categories: **e** sand washes,

**f** sandy loam washes and **g** loam washes. The thick *blue box plot lines* indicate means, the thin *black lines* indicate medians. (Color figure online)

## Study site description

This study was conducted in ephemeral washes across Tucson, Arizona (Fig. 1a) prior to the first summertime rainfall event, following an extensive period of dry conditions (3–4 months). The climate is semi-arid with a mean annual rainfall of 310 mm, mean annual evaporation of 270 mm and potential evaporation of 1,900 mm. Rainfall occurs during the summer and winter with summertime atmospheric convection resulting in intense rainfall of short duration (The North American Monsoon, Guido 2008), whereas moisture systems originating in the Pacific Ocean generate cool, protracted winter rainfall.

Stream flow in these urban Tucson washes is ephemeral and occurs only in response to rainfall (Gallo et al. 2012a, 2013). Similar to non-urban streams, significant stream channel transmission losses result in waterways that might experience repeated wetting due to rainfall during the summertime months, but that exhibit a small number of seasonal runoff events (Houser et al. 2000; Gallo 2011; Zhang et al. 2011). The majority of summertime rainfall events in this region tend to be less than 20 mm in magnitude (Cable and Huxman 2004; Loik et al. 2004; Bowling et al. 2011), with the average rainfall event at these sites being between 8 and 11 mm (Gallo et al. 2013).

**Table 1** Physical characteristics of the study ephemeral channels

Site	Class	Soil texture (%) <sup>a</sup>			Bulk density (g cm <sup>-3</sup> ) <sup>b</sup>	Fraction of fine earth <sup>c</sup>	% Soil organic matter <sup>d</sup>	% Soil C <sup>e</sup>	% Soil N <sup>e</sup>
		Sand	Silt	Clay					
1	Sand	96.9	0.1	3.0	1.6 (0.04)	0.41 (0.02)	0.4 (<0.1)	0.2 (<0.1)	<0.1 (<0.1)
2	Sand	95.8	1.6	2.6	1.67 (0.24)	0.50 (0.06)	0.2 (<0.1)	0.3 (<0.1)	<0.1 (<0.1)
3	Sand	96.0	1.3	2.7	1.86 (0.05)	0.52 (0.01)	0.4 (<0.1)	0.3 (<0.1)	<0.1 (<0.1)
4	Sand	95.3	1.7	3.0	1.91 (0.08)	0.60 (0.04)	0.5 (<0.1)	0.3 (<0.1)	<0.1 (<0.1)
5	Sand	89.4	6.0	4.6	1.9 (0.07)	0.72 (0.03)	0.5 (0.1)	0.6 (0.1)	<0.1 (<0.1)
6	Sandy loam	74.8	12.3	13.0	1.69 (0.11)	0.80 (0.01)	2.6 (0.5)	1.8 (0.3)	0.1 (<0.1)
7	Sandy loam	59.7	29.0	11.3	1.68 (0.25)	0.63 (0.06)	1.3 (0.1)	1.3 (0.1)	<0.1 (<0.1)
8	Sandy loam	74.9	14.1	11.0	1.32 (0.21)	0.74 (0.02)	2.2 (0.2)	1.8 (0.1)	0.1 (<0.1)
9	Sandy loam	64.4	23.8	11.8	1.09 (0.24)	0.89 (0.06)	2.7 (0.8)	2.0 (0.6)	0.1 (<0.1)
10	Sandy loam	53.2	34.0	12.9	1.38 (0.12)	0.86 (0.05)	6.3 (1.6)	2.5 (0.3)	0.2 (<0.1)
11	Loam	34.8	47.0	18.2	1.24 (0.23)	0.90 (0.05)	6.8 (1)	3.5 (0.1)	0.2 (<0.1)
12	Loam	48.7	36.0	15.3	1.21 (0.06)	0.77 (0.06)	2.5 (0.7)	1.5 (0.3)	0.1 (<0.1)
13	Loam	43.5	38.1	18.3	1.03 (0.12)	0.72 (0.05)	4.5 (0.1)	2.7 (0.1)	0.2 (<0.1)
14	Loam	27.9	54.5	17.6	0.73 (0.09)	0.94 (0.04)	7.5 (2.3)	3.6 (0.7)	0.2 (0.1)
15	Loam	43.9	39.9	16.2	1.21 (0.09)	0.95 (0.01)	2.3 (<0.1)	1.6 (0.1)	0.1 (<0.1)
16	Loam	32.0	47.8	20.2	0.85 (0.04)	0.98 (0.01)	8.5 (0.1)	4.0 (0.2)	0.3 (<0.1)

Values reported are means ( $\pm$ SE;  $n = 3$ ) with the exception of soil texture where  $n = 1$  and final soil moisture and water filled pore space which were modeled using Hydrus 1-D. Superscripts indicate the methodology used to characterize each physical or chemical soil parameter

<sup>a</sup> Soil texture (% sand, % silt and % clay) was determined using the modified pipette method for particle size analyses (Gee and Bauder 1986)

<sup>b</sup> Bulk density (g cm<sup>-3</sup>) was determined using a modified version of the excavation method (Grossman and Reinsch 2002)

<sup>c</sup> The fraction of fine earth was calculated as one minus the rock volume divided by the sample volume

<sup>d</sup> % soil organic matter was assumed to be equal to the mass lost on ignition (Gallo et al. 2012b)

<sup>e</sup> Percent soil carbon (% soil C) and soil nitrogen (% soil N) were determined on an Elemental Analyzer (ThermoElectron Corporation Bremen, Germany) at Idaho State University

We selected 16 locations in ephemeral stream reaches spanning a range of soil textures and soil C and N (Table 1; Fig. 1b–d). Based on soil texture, the study sites were grouped into 1 of 3 ephemeral channel substrate classes: (1) sandy, (2) sandy loam and (3) loam (Fig. 1e–g). Average sand content was  $94.7 \pm 1.3$  (standard error, SE),  $65.4 \pm 4.2$  and  $38.5 \pm 3.3$  % in the sand, sandy loam and loam washes, respectively. Average silt + clay content was  $5.3 \pm 1.3$ ,  $34.0 \pm 4.2$  and  $61.5 \pm 3.3$  % in the sand, sandy loam and loam washes, respectively. Bulk density was highest in the sand (1.60–1.91 g cm<sup>-3</sup>) followed by sandy loam (1.09–1.69 g cm<sup>-3</sup>) and loam washes (0.73–1.24 g cm<sup>-3</sup>). Percent SOM, determined by mass loss-on-ignition, was on average  $0.4 \pm <0.1$ ,  $3.0 \pm 0.9$  and  $5.4 \pm 1.1$  % in the sand, sandy loam and loam washes, respectively. Percent

soil C was on average  $0.3 \pm 0.1$ ,  $1.9 \pm 0.2$  and  $2.8 \pm 0.4$  % in the sand, sandy loam and loam washes, respectively, while % soil N was on average  $<0.1 \pm <0.1$ ,  $0.1 \pm <0.01$  and  $0.2 \pm <0.1$  % in the sand, sandy loam and loam washes, respectively (Table 1).

## Methods

### Experimental design for trace gas sampling

We conducted an artificial rainfall experiment and monitored trace gas fluxes prior to and after soil wetting following protocols described by Hall et al. (2008). In brief, gas fluxes were monitored using static gas chambers consisting of a polyvinyl chloride (PVC) chamber base and cap. Chamber bases were installed

at least 1 h prior to any gas monitoring, and trace gases were sampled before ( $t = -1$ ), immediately after ( $t = 0$ ) and for several hours ( $t = 0.5, 2$  and  $6$  h) after wetting. We evenly wetted the soil within the static chamber with an artificial rainstorm of depth of 10 mm applied over 15 min at a rate of  $40 \text{ mm h}^{-1}$ . This rainfall depth and intensity is well within the range of observations made elsewhere in the region (Mendez et al. 2003; Cable and Huxman 2004; Bowling et al. 2011) and within urban Tucson catchments (Gallo et al. 2013). Soil wetting was performed at 8 am across all our sites in order to facilitate the execution of the experiment and to ensure that field work was completed during daylight hours. We capped the chamber base and collected five gas samples, one every 15 min to calculate the gas flux rate for each monitoring period ( $t = -1, 0.5, 2$  and  $6$  h after wetting) using linear regression of gas concentration inside the chamber versus time. Gas samples were collected using a 20 ml syringe and 10 ml glass Wheaton bottle with inert grey butyl rubber crimp caps. Bottles were vented with needle and flushed with 20 ml of gas sample and then injected with a second 20 ml sample. At the end of each monitoring period ( $t = -1, 0.5, 2$  and  $6$  h after wetting), the gas chamber cap was removed and the air inside the chamber was allowed to equilibrate with the atmosphere. The first gas sample collected following soil wetting was considered the instantaneous abiotic gas flux ( $t = 0$ ). Soil temperature was monitored during every sampling period using a soil thermometer.

The gas samples were analyzed for carbon dioxide ( $\text{CO}_2$ ), nitrous oxide ( $\text{N}_2\text{O}$ ) and methane ( $\text{CH}_4$ ) on a gas chromatograph (GC) fitted with a thermal conductivity detector (TCD), an electron capture detector (ECD), and flame ionization detector (FID) (Agilent Technologies, Santa Clara, CA), respectively, in the Hall Laboratory at Arizona State University. The GC was calibrated using certified  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{CH}_4$  standards (Scott Specialty and Matheson Tri-Gas). We used temperature and barometric pressure data from AZMET (<http://ag.arizona.edu/azmet/>) and the chamber volume to determine the mass of  $\text{CO}_2$  as C in mg and  $\text{N}_2\text{O}$  as N and  $\text{CH}_4$  as C in  $\mu\text{g}$  during each monitoring event. Gas flux rates in  $\text{mg m}^{-2} \text{ h}^{-1}$  for  $\text{CO}_2$  as C,  $\mu\text{g m}^{-2} \text{ h}^{-1}$  for  $\text{N}_2\text{O}$  as N and  $\text{CH}_4$  as C during each monitoring period (time =  $-1, 0.5, 2$  and  $6$  h since wetting) were calculated via linear regression of gas concentrations versus number of minutes elapsed since the chamber cap placement and

divided by the chamber area. Total or cumulative  $\text{CO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{CH}_4$  flux over the monitoring period was calculated by integrating the flux rates over time from the onset of wetting to the end of the experiment.

#### Physical and biogeochemical processes explaining fluxes

To minimize disturbance to the soils and chambers, soils were only collected after the wetting experiment and analyzed for soil water content, N pools, and N cycling. Triplicate soil cores (0–5 cm deep) were collected adjacent to the gas monitoring area and brought back to the lab for immediate processing. Soils were sieved to 2 mm and initial gravimetric soil moisture (initial % soil moisture) was determined by drying a 25 g subsample at  $105^\circ\text{C}$ ; and we calculated the percent water filled pore space (%WFPS) by dividing soil moisture by the total porosity and multiplying by 100 (Sarrantonio et al. 1996). Nitrogen pools and transformation rates were measured using aerobic laboratory incubations on composite soil samples from each of the study reaches following methods modified from Hart et al. (1994). In brief, we extracted inorganic N from a soil subsample with 2 N potassium chloride (KCl, 1:5 soil to extract ratio) by shaking it on an orbital mixer for 1 h and then filtering it through a pre-leached Whatman 1 filter. Another subsample was incubated in the dark at room temperature ( $\sim 25^\circ\text{C}$ ) for 7 days after which inorganic N was extracted as described above. Soil extracts were analyzed for nitrite + nitrate nitrogen ( $\text{NO}_2 + \text{NO}_3$  as N,  $\text{NO}_3$  henceforth) and ammonium nitrogen ( $\text{NH}_4$  as N) in a SmartChem Discrete Analyzer (Westco Scientific Instruments, Brookfield, CT, limit of detection = 0.001).

We used HYDRUS-1D (Šimunek et al. 2005) to estimate % soil moisture and %WFPS over time at each of our sites, and estimate final % soil moisture and %WFPS. We used % sand, % silt, % clay and bulk density (Table 1) to parameterize the water characteristic curve at each site, and used evaporation flux data from AZMET (<http://ag.arizona.edu/azmet/>) to constrain evaporative soil water losses.

#### Statistical analyses

All statistical analyses were carried out with JMP 10.0.2 statistical software (SAS, Cary, NC). We used the Wilcoxon non-parametric comparison of means (Zar



1999) to identify significant ( $p \leq 0.05$ ) differences among the substrate groups on bulk density, % soil moisture, fraction of fine earth, %WFPS, % SOM, % soil C, % soil N, pre-wetting flux rates and cumulative  $\text{CO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{CH}_4$  fluxes; soil inorganic N ( $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N} + \text{NO}_2\text{-N}$ ), net mineralization and net nitrification. In addition, we used Wilcoxon non-parametric comparison of means to test for differences in pre-wetting trace gas flux rates ( $t = -1$ ) from instantaneous ( $t = 0$ ) and post-wetting ( $t \geq 0.5$ ) gas flux rates. We used linear regression to determine if flux rates in each soil category varied in response to soil temperature, % soil moisture, %WFPS, and to determine if cumulative flux, net mineralization and net nitrification varied in response to bulk density, initial and final % soil moisture, fraction of fine earth, initial and final %WFPS, % SOM, % soil C, % soil N to cumulative flux. We used factor analysis (Kaiser 1958; DeCoster 1998; Lehman et al. 2005) to identify patterns and potential mechanisms controlling stream channel biogeochemistry across all sites and within each soil category. Flux rates, net mineralization and nitrification, and all the aforementioned soil characteristics were included in these analyses. Only factors explaining more than 10 % of the data variance were retained for further analyses and interpretation. Variables with loadings greater than  $0.70 < -0.70$  were considered to heavily load onto that factor and were retained for analyses interpretation.

Finally, to put into a larger context the trace gas flux rates measured here, we compare our results to fluxes quantified in a number of studies in semi-arid, arid and humid climates in both, urbanized and non-developed landscapes. We report published values including flux rate mean and rate minimum and maximum. We have standardized all rates to mass of C (mg) or N ( $\mu\text{g}$ )  $\text{h}^{-1} \text{m}^{-2}$ .

## Results

### Soil temperature and moisture

Soil temperatures were lowest in the morning ( $34.7 \text{ }^\circ\text{C} \pm 0.5 \text{ SE}$ ) before soil wetting, were highest at mid-day, 2 h after soil wetting ( $45.7 \text{ }^\circ\text{C} \pm 0.6$ , Fig. 2a). Initial soil moisture was  $0.1 \pm <0.1 \%$  in the sandy sites,  $1.2 \pm 0.7 \%$  in the sandy loam sites and  $0.9 \pm 0.3 \%$  in the loam washes. Initial %WFPS was

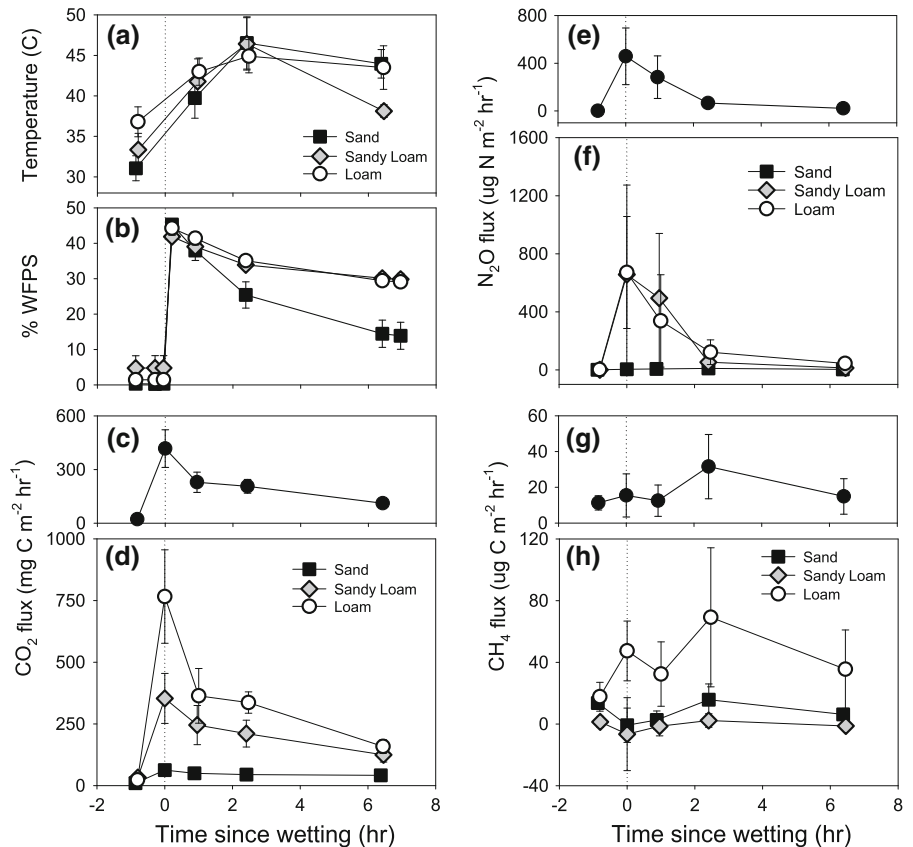
$0.4 \pm 0.2 \%$  in the sand washes,  $4.8 \pm 3.5 \%$  in the sandy loam and  $1.5 \pm 0.6 \%$  in the loam washes. Hydrus soil moisture modeling indicated that immediately after wetting ( $t = 0$ ), % soil moisture and %WFPS across sites were  $17.7 \pm 3.1$  and  $43.9 \pm 1.0 \%$ , respectively and decreased over time thereafter (Fig. 2b). At the end of the experiment % soil moisture was significantly higher in the loam ( $18.5 \pm 3.6 \%$ ) than in the sandy loam washes ( $9.9 \pm 1.5 \%$ ), and in the sandy loam washes than in the sand washes ( $2.3 \pm 0.5 \%$ ). Significant differences in final %WFPS occurred only between the loam and sand washes ( $29.1 \pm 1.2$  and  $13.9 \pm 3.9 \%$ , respectively).

### Trace gas fluxes and nitrogen processing

Fluxes of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  increased following soil wetting across sites and substrates (Fig. 2c–g). Pre-wetting fluxes of  $\text{CO}_2$  were significantly ( $p < 0.05$ ) higher in the sandy loam and loam sites than in the sand sites (Table 2), and across sites,  $\text{CO}_2$  fluxes significantly increased after wetting from  $21.9 \pm 4.2 \text{ (SE) mg C m}^{-2} \text{ h}^{-1}$  to  $240 \pm 34.0 \text{ (SE) mg C m}^{-2} \text{ h}^{-1}$ . Instantaneous ( $t = 0$ )  $\text{CO}_2$  fluxes across sites were surprisingly large ( $417.2 \pm 105.42 \text{ mg C m}^{-2} \text{ h}^{-1}$ ), significantly higher than fluxes at  $t = 0.5, 2$  and  $6 \text{ h}$  (Fig. 2c), and significantly higher and more variable in the loam than in the sand sites (Fig. 2d; Table 2). Fluxes of  $\text{CO}_2$  remained low and unchanged in the sand sites following wetting, whereas flux rates decreased over time in the sandy loam and loam sites (Fig. 2d).

Similarly, post-wetting  $\text{N}_2\text{O}$  fluxes ( $207.4 \pm 76.3 \text{ } \mu\text{g N m}^{-2} \text{ h}^{-1}$ ) were significantly higher than pre-wetting  $\text{N}_2\text{O}$  fluxes ( $1.5 \pm 0.7 \text{ } \mu\text{g N m}^{-2} \text{ h}^{-1}$ , Fig. 2e) and were significantly higher and more variable in the sandy loam and loam sites than in the sand sites (Fig. 2f; Table 2). Instantaneous  $\text{N}_2\text{O}$  fluxes across sites were also surprisingly large ( $458.6 \pm 237.7 \text{ } \mu\text{g N m}^{-2} \text{ h}^{-1}$ ) and significantly higher in the loam than in the sand sites (Table 2). Fluxes of  $\text{N}_2\text{O}$  remained elevated following wetting at the sandy loam and loam sites, and decreased significantly over time at the loam sites (Fig. 2f). Unlike  $\text{CO}_2$  and  $\text{N}_2\text{O}$  fluxes, there were no significant differences or temporal patterns in pre-wetting, instantaneous or post-wetting  $\text{CH}_4$  fluxes across sites (Fig. 2g), which averaged  $17.1 \pm 5.07 \text{ } \mu\text{g C m}^{-2} \text{ h}^{-1}$ . However, post-wetting  $\text{CH}_4$  fluxes were significantly

**Fig. 2** Variation in **a** soil temperature, **b** percent water filled pore space (%WFPS), fluxes of CO<sub>2</sub> carbon **c** across sites and **d** within each soil texture group, fluxes of N<sub>2</sub>O nitrogen **e** across sites and **f** within each soil texture group, fluxes of CH<sub>4</sub> carbon **g** across sites and **h** within each soil texture group over the duration of the 6 h monitoring period including pre-wetting fluxes. Symbols denote means ( $\pm$ SE)



higher in the sand and loam than in the sandy loam sites, and most variable at the loam sites (Table 2; Fig. 2h).

Cumulative CO<sub>2</sub> losses over the monitoring period were significantly greater in the loam than in the sandy loam sites (Fig. 3a; Table 2); and although N<sub>2</sub>O and CH<sub>4</sub> losses were not significantly different across substrates (Fig. 3b, c), cumulative N<sub>2</sub>O losses were highly variable in the sandy loam (SE = 789 mg C m<sup>-2</sup>) and loam sites (SE = 742  $\mu$ g N m<sup>-2</sup>), while CH<sub>4</sub> losses were highly variable in the loam sites (SE = 157 mg C m<sup>-2</sup>).

Initial soil NH<sub>4</sub> and NO<sub>2</sub> + NO<sub>3</sub> were significantly higher in the loam than in the sand or sandy loam washes (Fig. 4a, b; Table 2). Average net mineralization and nitrification rates were not significantly different across substrate categories, due primarily to highly variable responses in sandy loam and loam sites where both net production and net consumption occurred (Table 2; Fig. 4c, d).

### Correlations and factor analyses

Fluxes of CO<sub>2</sub> varied positively and significantly with soil temperature at the sand and sandy loam washes (coefficient of determination,  $r^2 = 0.38$  and  $0.27$ , respectively), and across sites with soil moisture conditions, with the strongest correlations being those of CO<sub>2</sub> flux versus % soil moisture at the sandy loam sites ( $r^2 = 0.62$ ) and %WFPS at the sand and loam sites ( $r^2 = 0.47$  and  $0.41$ , respectively). The only significant N<sub>2</sub>O flux correlation observed was of a significant N<sub>2</sub>O flux increase with %WFPS ( $r^2 = 0.17$ ) at the sand sites. Similarly, the only significant correlation observed for CH<sub>4</sub> fluxes was a positive one with soil temperature ( $r^2 = 0.25$ ) at the loam sites only.

Cumulative CO<sub>2</sub> flux varied significantly with soil texture and associated physical and biogeochemical variables across sites. Specifically, cumulative CO<sub>2</sub> fluxes exhibited significant linear, positive correlations with % clay ( $r^2 = 0.58$ ), % silt ( $r^2 = 0.59$ ), the

**Table 2** Mean ( $\pm$ SD) pre-wetting, instantaneous and post-wetting trace gas flux rates, and cumulative flux during the experimental period, initial pools of soil  $\text{NH}_4$  and  $\text{NO}_3$  and net mineralization and nitrification rates for each of the soil texture groups

	Sand	Sandy loam	Loam
<b>CO<sub>2</sub> flux (mg C m<sup>-2</sup> h<sup>-1</sup>)</b>			
Pre-wetting	9.8 (2) <sup>b</sup>	32.5 (26.4) <sup>a</sup>	23 (4.5) <sup>a</sup>
Instantaneous	62.6 (40.6) <sup>b</sup>	353.2 (226.9) <sup>ab</sup>	765.9 (463.9) <sup>a</sup>
Post-wetting	45.4 (33) <sup>b</sup>	193.5 (131.1) <sup>a</sup>	286.2 (187.3) <sup>a</sup>
Cumulative flux (mg m <sup>-2</sup> )	224.9 (220.8) <sup>b</sup>	1019.4 (677) <sup>ab</sup>	1691.1 (729) <sup>a</sup>
<b>N<sub>2</sub>O flux (ug N m<sup>-2</sup> h<sup>-1</sup>)</b>			
Pre-wetting	0.6 (0.8) <sup>a</sup>	0.9 (1.5) <sup>a</sup>	2.7 (4.4) <sup>a</sup>
Instantaneous	4.9 (6.1) <sup>b</sup>	656.9 (1378.5) <sup>ab</sup>	671.4 (944.4) <sup>a</sup>
Post-wetting	6.9 (12.6) <sup>b</sup>	187.1 (579.9) <sup>a</sup>	168.1 (457.3) <sup>a</sup>
Cumulative flux (ug m <sup>-2</sup> )	43 (85.4) <sup>a</sup>	973.2 (1765.4) <sup>a</sup>	957.2 (1817.2) <sup>a</sup>
<b>CH<sub>4</sub> flux (μg C m<sup>-2</sup> h<sup>-1</sup>)</b>			
Pre-wetting	13.6 (6.2) <sup>a</sup>	1.4 (8.1) <sup>b</sup>	17.7 (23) <sup>ab</sup>
Instantaneous	-0.8 (24.9) <sup>a</sup>	-6.6 (52.9) <sup>a</sup>	47.4 (47.5) <sup>a</sup>
Post-wetting	8.2 (15.3) <sup>a</sup>	-0.1 (9.5) <sup>b</sup>	45.7 (76.1) <sup>a</sup>
Cumulative flux (μg m <sup>-2</sup> )	-27.2 (79.2) <sup>a</sup>	-7.1 (14.6) <sup>a</sup>	201.4 (385.4) <sup>a</sup>
Initial $\text{NH}_4$ (μg N g <sup>-1</sup> soil)	0.9 (1.1) <sup>b</sup>	1.6 (1.1) <sup>b</sup>	5.5 (1.5) <sup>a</sup>
Initial $\text{NO}_3$ (μg N g <sup>-1</sup> soil)	6.8 (11.6) <sup>b</sup>	26.2 (31.2) <sup>b</sup>	177 (126.2) <sup>a</sup>
Net mineralization (μg N g <sup>-1</sup> day <sup>-1</sup> )	0 (0.1) <sup>a</sup>	0.6 (1.3) <sup>a</sup>	4.7 (12.8) <sup>a</sup>
Net nitrification (μg N g <sup>-1</sup> day <sup>-1</sup> )	0.1 (0.2) <sup>a</sup>	0.8 (1.4) <sup>a</sup>	4.9 (11.7) <sup>a</sup>

Means sharing the same superscripted letter across columns indicate values that are not significantly ( $p > 0.05$ ) different

fraction of fine earth ( $r^2 = 0.63$ ), % SOM ( $r^2 = 0.61$ ), % soil C ( $r^2 = 0.68$ ) and N ( $r^2 = 0.61$ ), soil  $\text{NH}_4$  ( $r^2 = 0.49$ ) and  $\text{NO}_2 + \text{NO}_3$  ( $r^2 = 0.39$ ), and final soil moisture ( $r^2 = 0.38$ ). Meanwhile, cumulative  $\text{CH}_4$  fluxes, net mineralization and net nitrification varied positively and significantly with soil  $\text{NH}_4$  ( $r^2 = 0.31$ ) and  $\text{NO}_2 + \text{NO}_3$  ( $r^2 = 0.65$ ). In contrast, cumulative  $\text{N}_2\text{O}$  fluxes were not significantly correlated to any measured soil variables.

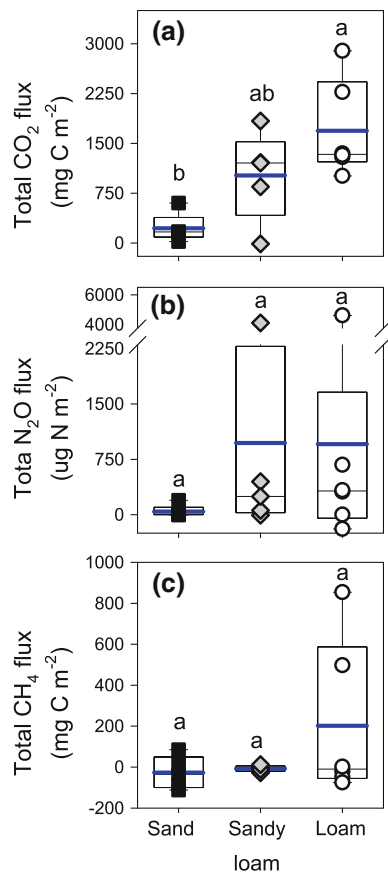
Because many of these site-specific soil characteristics covary, factor analysis provides a quantitative assessment of these joint variations and the resultant relationships with observed gas fluxes. Factor analyses including data from all sites did not identify any general relationships between soil characteristics and trace gas responses. In contrast however, factory analyses within each soil texture class showed clear relationships between gas fluxes and substrate physical and chemical characteristics. In the sand washes, 3 factors accounted for 95.3 % of the data variability, with most of the variance explained by Factor 1 (54.2 %), with cumulative  $\text{CO}_2$  and  $\text{N}_2\text{O}$  flux, soil  $\text{NO}_3$ , the fraction of fine earth, initial and final soil moisture and %WFPS, and % soil C and N loading positively onto Factor 1. Net mineralization, net nitrification and soil  $\text{NH}_4$  loaded positively onto

Factor 2, while pre-wetting  $\text{CH}_4$  flux loaded heavily and negatively onto Factor 2, which explained 22.7 % of the data variance (Fig. 5a). Pre-wetting  $\text{N}_2\text{O}$  flux and bulk density loaded positively, while cumulative  $\text{CH}_4$  flux and pre-wetting  $\text{CO}_2$  flux loaded negatively onto Factor 3, which explained 18.4 % of the data variance (Table 3).

At the sandy loam washes, 2 factors accounted for 80.9 % of the data variance (Table 3). Additional factors did not increase individual factor loadings or improve the interpretation of the factor analyses. Variables loading on Factor 1 were % SOM, % soil C and N, soil  $\text{NH}_4$  and  $\text{NO}_3$ , net nitrification and mineralization, and cumulative  $\text{N}_2\text{O}$  and  $\text{CH}_4$  flux, and explained 46.6 % of the data variance. Factor 2 explained 34.3 % of the data variance with fraction of fine earth, post-monitoring % soil moisture and %WFPS, and cumulative  $\text{CO}_2$  flux loading positively on Factor 2, and initial % soil moisture and %WFPS loading negatively (Fig. 5b).

Finally, at the loam washes, Factors 1, 2, 3 and 4 explained 29.1, 28.3, 21.8 and 15.7 % of the data variance, respectively (94.9 % total, Table 3). Cumulative  $\text{CH}_4$  flux, pre  $\text{CH}_4$  flux, net mineralization, net nitrification and soil  $\text{NO}_3$  loaded positively onto Factor 1, while pre-wetting  $\text{N}_2\text{O}$  loaded negatively.



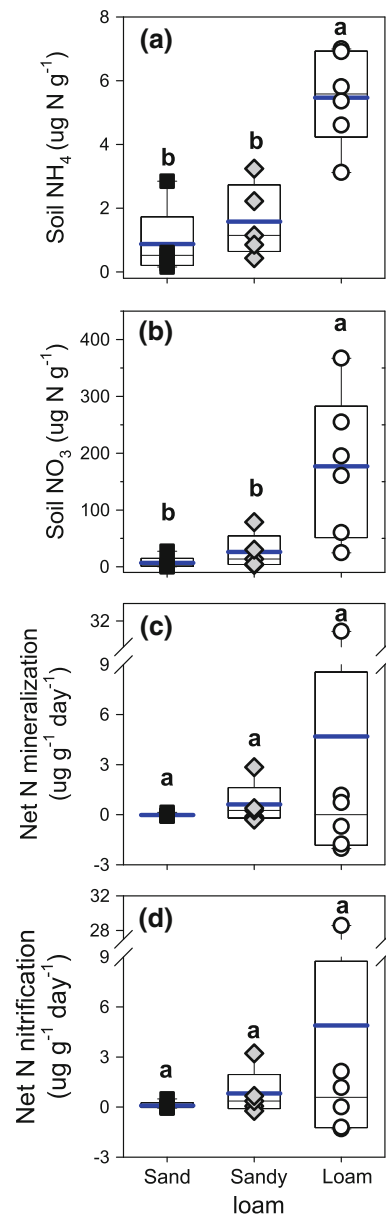


**Fig. 3** Total cumulative fluxes ( $\pm$ SE) over the 6 h of the experiment as **a** carbon dioxide (CO<sub>2</sub>), **b** nitrous oxide (N<sub>2</sub>O), and **c** methane (CH<sub>4</sub>) for sand, sandy loam, and loam substrates. The thick blue boxplot lines indicate means, the thin black lines indicate medians. Box plots not sharing the same letter are significantly ( $p < 0.05$ ) different. (Color figure online)

Final % soil moisture, %WFPS, % SOM and % soil C and N loaded positively onto Factor 2, while bulk density loaded negatively (Fig. 5c). Cumulative CO<sub>2</sub> flux, initial % soil moisture and %WFPS loaded positively onto Factor 3 while soil NH<sub>4</sub> and pre CO<sub>2</sub> flux loaded positively and cumulative N<sub>2</sub>O flux loaded negatively onto Factor 4 (Fig. 5d).

## Discussion

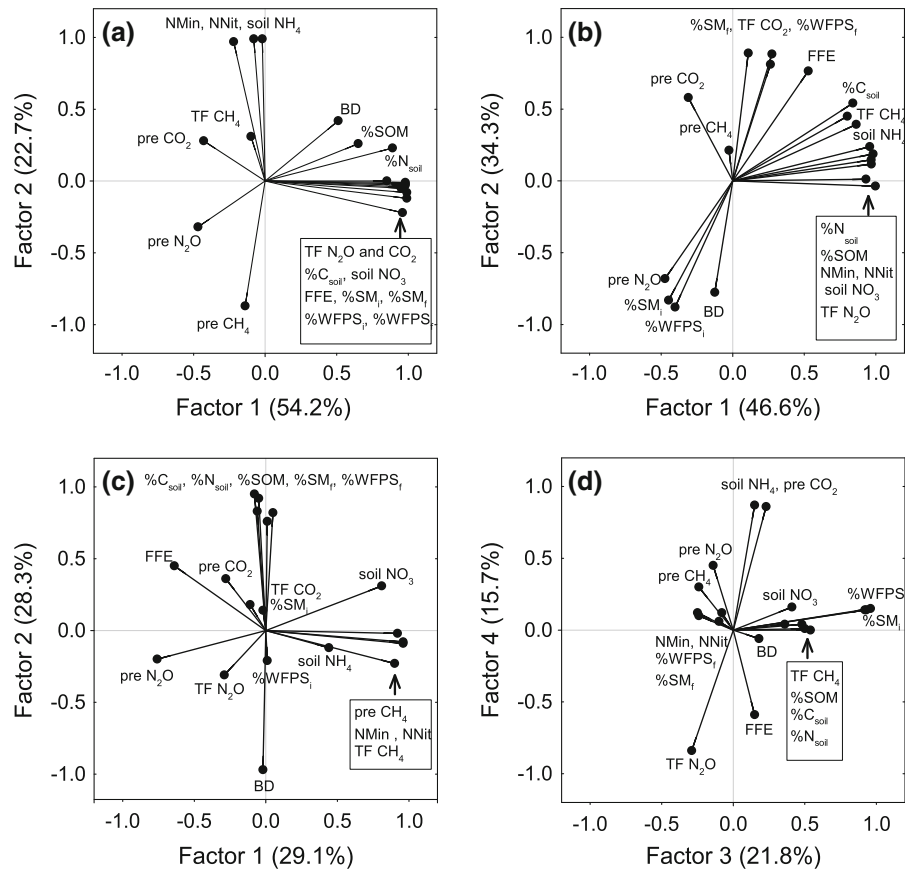
Few studies have examined how urbanization in water limited regions alters fluxes of C and N gases in hotspots such as ephemeral streams, although it is well established that urbanization alters C and N loading and nutrient cycling pathways (Pouyat et al. 2002;



**Fig. 4** Initial **a** soil ammonium-N (NH<sub>4</sub>), **b** nitrate-N (NO<sub>3</sub>), **c** net mineralization and **d** net nitrification for the sand, sandy loam and loam substrates. The thick blue boxplot lines indicate means, the thin black lines indicate medians. Box plots not sharing the same letter are significantly different ( $p < 0.05$ ). (Color figure online)

Kaye et al. 2006; Grimm et al. 2008a; Lorenz and Lal 2009; Pataki et al. 2011). Our results demonstrate that trace gas fluxes from these washes are among the largest gas fluxes observed (e.g. Sponseller 2007; Groffman and Pouyat 2009; Townsend-Small et al.

**Fig. 5** Variable loadings onto factors 1 and 2 at the **a** sandy **b** sandy loam and **c** loam sites, and **d** factors 3 and 4 at the loam sites



"pre" indicates pre-wetting  $\text{CO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{CH}_4$  fluxes.

TF  $\text{CO}_2$ , TF  $\text{N}_2\text{O}$ , TF  $\text{CH}_4$  indicate total (cumulative) trace gas flux.

%SM<sub>i</sub> and %SM<sub>f</sub> are percent soil moisture initial and final, respectively.

%WFPS<sub>i</sub> and %WFPS<sub>f</sub> are water filled pore space initial and final, respectively.

BD, FFE are bulk density and fraction of fine earth, respectively.

2011, Table 4) and that the magnitude, duration, and direction of these fluxes varies based on the stream channel substrate characteristics. These urban streams are areas of focused runoff that are disproportionately important in regulating water quality and potential nutrient loading to groundwater (Gallo et al. 2012a, b, 2013). The extremely high instantaneous fluxes we observe following wetting are indicative of physical displacement of soil gases that accumulated over time (Marañón-Jiménez et al. 2011; Kim et al. 2012) while sustained high fluxes over the 6 h observation period indicate rapid biological response to added moisture (e.g. McLain et al. 2008; Unger et al. 2010). Together, these data suggest that ephemeral channels are both hot spots of biogeochemical cycling on the landscape that also act as biogeochemical hot

spots following wetting (McClain et al. 2003; Harms and Grimm 2008).

#### Temporal patterns in trace gas fluxes

Not surprisingly, in a strongly water limited system all trace gas fluxes were low prior to wetting (Huxman et al. 2004; Belnap et al. 2005; Harms and Grimm 2012). Our pre-wetting  $\text{CO}_2$  fluxes were lower than fluxes observed in desert uplands and in more humid non-urban systems (Table 4, McLain and Martens 2006; McCrackin et al. 2008), but were similar to those observed in a more humid metropolitan area (Table 4, Raciti et al. 2011). Given the dry pre-wetting conditions in this study, it is likely that pre-wetting  $\text{CO}_2$  fluxes are driven in part by photodegradation of

**Table 3** Factor analysis summary

	Sand			Sandy loam		Loam			
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 1	Factor 2	Factor 3	Factor 4
Variance explained (%)	54.2	22.7	18.4	46.6	34.3	29.1	28.3	21.8	15.7
Cumulative variance (%)	54.2	76.9	95.3	46.6	80.9	29.1	57.4	79.2	94.9
Factor loadings									
Cumulative flux									
CO <sub>2</sub> (mg C m <sup>-2</sup> )	<b>0.98</b>	-0.01	0.17	0.27	<b>0.88</b>	-0.11	0.18	<b>0.93</b>	0.14
N <sub>2</sub> O (μg N m <sup>-2</sup> )	<b>0.99</b>	-0.08	-0.05	<b>1.00</b>	-0.04	-0.29	-0.31	-0.29	<b>-0.84</b>
CH <sub>4</sub> (μg C m <sup>-2</sup> )	-0.10	0.31	<b>-0.76</b>	<b>0.80</b>	0.45	<b>0.90</b>	-0.23	0.36	0.04
N-processing rates (μg N g <sup>-1</sup> soil day <sup>-1</sup> )									
Net mineralization	-0.22	<b>0.97</b>	0.01	<b>0.97</b>	0.12	<b>0.96</b>	-0.08	-0.24	0.10
Net nitrification	-0.08	<b>0.99</b>	-0.06	<b>0.97</b>	0.15	<b>0.96</b>	-0.09	-0.25	0.12
Pre-wetting fluxes									
CO <sub>2</sub> (mg C m <sup>-2</sup> h <sup>-1</sup> )	-0.43	0.28	<b>-0.86</b>	-0.31	0.58	-0.28	0.36	0.23	<b>0.86</b>
CH <sub>4</sub> (μg C m <sup>-2</sup> h <sup>-1</sup> )	-0.14	<b>-0.87</b>	0.39	-0.03	0.21	<b>0.92</b>	-0.02	-0.24	0.30
N <sub>2</sub> O (μg N m <sup>-2</sup> h <sup>-1</sup> )	-0.47	-0.32	<b>0.82</b>	-0.47	-0.68	<b>-0.76</b>	-0.2	-0.14	0.45
Bulk density (g/mL)	0.51	0.42	<b>0.75</b>	-0.13	<b>-0.78</b>	-0.02	<b>-0.97</b>	0.18	-0.06
Fraction of fine earth	<b>0.85</b>	0	0.53	0.53	<b>0.76</b>	-0.64	0.45	0.15	-0.59
Initial soil moisture (%)	<b>0.96</b>	-0.04	-0.12	-0.45	<b>-0.83</b>	-0.02	0.14	<b>0.92</b>	0.14
Initial WFPS (%)	<b>0.98</b>	-0.02	-0.1	-0.40	<b>-0.88</b>	0.01	-0.21	<b>0.96</b>	0.15
Final soil moisture (%)	<b>0.96</b>	-0.22	0.11	0.11	<b>0.89</b>	-0.08	<b>0.95</b>	-0.10	0.06
Final WFPS (%)	<b>0.95</b>	-0.05	0.30	0.26	<b>0.81</b>	-0.05	<b>0.92</b>	-0.08	0.12
Soil organic matter (%)	0.65	0.26	0.42	<b>0.98</b>	0.19	-0.06	<b>0.83</b>	0.48	0.04
% soil C	<b>0.98</b>	-0.03	0.15	<b>0.84</b>	0.54	0.05	<b>0.82</b>	0.50	0.01
% soil N	<b>0.89</b>	0.23	0.35	<b>0.96</b>	0.24	0.01	<b>0.76</b>	0.54	0
Soil NH <sub>4</sub> (mg N g <sup>-1</sup> soil)	-0.02	<b>0.99</b>	-0.16	<b>0.86</b>	0.39	0.44	-0.12	0.15	<b>0.87</b>
Soil NO <sub>3</sub> (mg N g <sup>-1</sup> soil)	<b>0.99</b>	-0.12	0.02	<b>0.93</b>	0.01	<b>0.81</b>	0.31	0.41	0.16

Loading values for variables that heavily load (variable loading >0.70 or <-0.70) onto a factor are noted in bold

WFPS water filled pore space

organic matter (Rutledge et al. 2010), particularly at the sandy sites where soils were driest. Pre-wetting N<sub>2</sub>O and CH<sub>4</sub> fluxes were similar to those observed in bare soils of undeveloped deserts (Billings et al. 2002; McLain et al. 2002, 2008), suggesting that in addition to soil moisture limitations, pre-wetting fluxes of CO<sub>2</sub> are also limited by soil C resources. Large, initial trace gas fluxes following wetting are consistent with previous work in arid and semi-arid regions (Austin et al. 2004; Cable and Huxman 2004; Huxman et al. 2004; Sponseller 2007; Sponseller and Fisher 2008). However, our instantaneous CO<sub>2</sub> and N<sub>2</sub>O fluxes are among the highest ever published (Fig. 2d, f; Table 2) and are most likely indicative of physical displacement

of gases that have accumulated within the soil following previous wetting events (Marañón-Jiménez et al. 2011; Kim et al. 2012). High variability in these instantaneous fluxes may be due to site differences in antecedent microbial activity, or possibly rapid increases in microbial metabolism (Sponseller 2007). Indeed, high fluxes following soil wetting have been described as the “Birch Effect”, a set of biogeochemical responses to a wetting pulse following a period of drought that include enhanced decomposition of labile soil organic matter, increased rates of nitrogen mineralization (Birch 1958) and high post-wetting CO<sub>2</sub> flux (Jarvis et al. 2007; McLain et al. 2008; Unger et al. 2010; Kim et al. 2012; Navarro-García et al. 2012).

Given the extremely dry soils it is likely that these fluxes result primarily from physical displacement of soil gasses, but further work is needed to evaluate the potential contribution of immediate microbial responses.

Surprisingly, temperature did not emerge as a major control on trace gas fluxes at these sites. Although the soil temperatures measured here are consistent with diel temperature fluctuations observed in other regional studies (McLain and Martens 2006; Hall et al. 2008), temperature explained a relatively small fraction of the trace gas flux patterns we observed, including 38 and 27 % of the CO<sub>2</sub> fluxes at the sand and sandy loam sites and 25 % of CH<sub>4</sub> fluxes at the loam sites. Consistent with the results of Conant et al. (2004), the effect of soil temperature on trace gas fluxes appears to be overshadowed by the release of early summer soil water limitations in these urban ephemeral streams, which facilitate the physical displacement soil gasses and stimulate microbial activity.

#### Magnitude of trace gas fluxes relative to previous studies

Overall, Fluxes of CO<sub>2</sub> and N<sub>2</sub>O from the sandy loam and loam washes were almost 30 times higher and more variable than in the sand washes, and overall higher than those measured in both, humid and water limited urban and non-urban environments (Table 4, Kaye et al. 2004; McLain and Martens 2006; Allaire et al. 2008; McCrackin et al. 2008; Groffman et al. 2009; Raciti et al. 2011); with the exception of CO<sub>2</sub> fluxes, which were similar to those in a non-urban ephemeral stream (Table 4, Sponseller 2007). Indeed, N<sub>2</sub>O fluxes at the sandy loam and loam washes were as much as 2 orders of magnitude greater than fluxes reported in a natural upland (Table 4, McLain et al. 2008), a floodplain ecosystem in southeastern Arizona (Table 4, Harms and Grimm 2012) and elsewhere (Table 4, Billings et al. 2002; Bijoor et al. 2008; Groffman et al. 2009, Table 4) under similar soil wetting conditions. In other arid urban studies such as Hall et al. (2008) and Townsend-Small et al. (2011), N<sub>2</sub>O fluxes from the finer textured washes were between 10 and 50 % of those observed at the sandy loam and loam washes in this study (Table 4). Finally, CH<sub>4</sub> fluxes were surprisingly larger and more variable than those reported in other arid and semi-arid studies

(Table 4, Kaye et al. 2004; McLain and Martens 2006) but were similar to fluxes in humid urban and non-urban environments (Table 4, Groffman et al. 2009; Groffman and Pouyat 2009).

#### Substrate characteristics and physical controls on trace gas fluxes

The primary control on trace gas flux in these sites was moisture availability, and secondarily how the artificial wetting interacted with wash substrate. Sites with coarser substrates had lower water filled pore space, lower water holding capacity (Saxton et al. 1986), and smaller trace gas responses to wetting. Of secondary importance across sites was soil carbon content. Previous work in non-urban arid and semi-arid environments show that soil organic matter content (Sponseller 2007), rainfall amount (Sponseller 2007; Cable et al. 2008; McLain et al. 2008), antecedent moisture conditions and soil texture (Cable et al. 2008) control CO<sub>2</sub> fluxes. While all of these factors emerged as CO<sub>2</sub> flux controls in the ephemeral urban waterways of this study, here we show that soil texture largely controls the extent of priming and subsequent magnitude of soil respiration, presumably due to the close association between soil water holding content and soil organic matter (Hudson 1994; Saxton and Rawls 2006). Additional factors such as the quality and photodegradation of litter and soil organic matter (Brandt et al. 2009; Austin and Ballare 2010; Rutledge et al. 2010), might be important controls for C cycling in urban arid and semi-arid streams given the high solar radiation influx in the region (Unland et al. 1996; NREL 2008), and warrant further study.

N<sub>2</sub>O fluxes were similarly controlled first by water availability, and secondarily by the rate of nitrogen cycling, net mineralization and nitrification rates and stocks of soil C and N, consistent with the “leaky pipe” model (Firestone et al. 1989). The higher variability in N<sub>2</sub>O fluxes, mineralization and nitrification rates in the finer textured washes, coupled with simultaneous production of CO<sub>2</sub> and CH<sub>4</sub> gases indicate that as particle size decreases, the likelihood of variable redox states within the soil matrix increases. Simultaneous increases of CO<sub>2</sub> and N<sub>2</sub>O fluxes in both instantaneous and post wetting responses, may not seem in harmony with our conceptual understanding as aerobic respiration, the process responsible for CO<sub>2</sub> production, depends on

**Table 4** Trace gas losses from natural and urban arid and semi-arid ecosystems

Study	Location	Climate and biome (Koppen)	Habitat/soil type	Mean flux (min, max mass m <sup>-2</sup> h <sup>-1</sup> )		
				mg CO <sub>2</sub> -C	µg N <sub>2</sub> O-N	µg CH <sub>4</sub> -C
This study	Tucson, AZ	Subtropical dry arid (Sonoran desert)	Sandy ephemeral streams <sup>a</sup>	41.8 (7.4, 126)	5.3 (0, 45.4)	7.5 (-44.1, 56.1)
			Sandy loam ephemeral stream <sup>a</sup>	193.3 (2.4, 613.2)	243.9 (-0.4, 3,122)	-1.1 (-95.2, 37)
			Loam ephemeral stream <sup>a</sup>	329.5 (15.2-1,588.5)	235.6 (-250.6, 2540)	40.4 (-11.5, 266.2)
Allaire et al. (2008)	Quebec city, Canada		Urban turf grass lawns	60 (-59, 655)		
Bijoor et al. (2008)	Irvine, CA	Coastal mediterranean	Urban fescue and crabgrass lawn		(0, 21 <sup>b</sup> )	
			Urban fescue and crab grass lawn—artificially warmed		(0, 83.3)	
Billings et al. (2002)	Mercury, NV	Mid-latitude dry arid (Mohave desert)	Desert soils—under plants		(1.0, 1.8)	
			Desert soils—interspaces		0.7	
Bremer (2006)	Rocky Ford, KS		Perennial ryegrass turf grass fertilized		(-22, 407)	
Galbally et al. (2008)	Victoria, AU	Semiarid	Native Scrub		2.16	13.7
Groffman et al. (2009)	White mountain national forest, NH		Forest soil	(-10, 160)	(-80, 60)	(-167, 33)
Groffman and Pouyat (2009)	Baltimore LTER, MD		Urban grass			-7.3 (-31.9, 63.7)
			Urban and non-urban forest			-50.3 (-191.2, 286.8)
Hall et al. (2008)	Phoenix, AZ	Subtropical dry arid (desert)	Urban xeric landscapes		(<30)	
			Undeveloped desert		<20	
Harms and Grimm (2012)		Subtropical dry arid (Sonoran desert)	Urbanized lawns		(18, 80)	
Kaye et al. (2004)	Fort Collins, CO	Mid-latitude dry semiarid (steppe)	Floodplain soils		0.7 (<95)	
			Urban lawns		27.4	(-17.1)
			Corn fields		<10 (<50)	(>-20)
			Native grass and wheat		(<4, 19)	-0.30 (-25, -55)
McCrackin et al. (2008)	Maricopa, AZ	Subtropical dry arid (desert)	Remnant non-developed urban soils—under plant	(~8, 462)		
			Remnant non-developed urban soils interspaces	(~8, 173)		



Table 4 continued

Study	Location	Climate and biome (Koppen)	Habitat/soil type	Mean flux (min, max mass m <sup>-2</sup> h <sup>-1</sup> )		
				mg CO <sub>2</sub> -C	µg N <sub>2</sub> O-N	µg CH <sub>4</sub> -C
McLain and Martens (2006)	San pedro river, AZ	Subtropical dry arid (Sonoran desert)	Soils under mesquite	(12, 121)	~(0, 15)	(-28, 0)
			Soils under sacaton	(7, 118)	~(0, 5)	(-27, >65)
McLain et al. (2008)	Santa rita experimental range, AZ	Subtropical dry arid (Sonoran desert)	Soil between plants	(6, 113)	~(0, 5)	(-38, 0)
				(<6, >116)	(<-6, >37)	(-31, >76)
Raciti et al. (2011)	Baltimore, MD, BES		Suburban lawn, not fertilized	23.2	-0.07	
Sponseller (2007)	Sycamore creek, phoenix, AZ	Subtropical dry arid (desert)	Suburban lawn, fertilized	43.4	2.0	
			Ephemeral stream—soil beneath plants	(50, 2,200)		
			Ephemeral stream—plant interspaces	(30, 690)		
Townsend-Small et al. (2011)	Pomona and irvine, CA	Coastal Mediterranean	Row crops		13.7	
			Corn fields		25.1	
			Urban turf lawn		26.3	
			Urban athletic fields		20.5	
Townsend-Small and Czimczik (2010)	Irvine, CA	Coastal Mediterranean	Park turf		92.9 (0, 720)	

<sup>a</sup> Mean includes pre-wetting fluxes

the presence of oxygen ( $O_2$ ) to act as a terminal electron acceptor whereas  $N_2O$  production via denitrification is an anaerobic process. As McLain et al. (2008) suggest, high rates of respiration and or gas diffusional limitations may create localized anaerobic microsites where denitrification can occur (Parkin 1987). Production of  $N_2O$  may also be derived from organic N nitrification and subsequent nitrifier denitrification, an aerobic process, and thus not be dependent on the formation of anaerobic microsites (McLain and Martens 2005; Kool et al. 2011). In addition,  $N_2O$  production may be derived from activity of heterotrophic fungi, which are more adapted to lower soil moisture than bacteria and have been shown to generate substantial fluxes in this region (Jensen and Hauggaard-Nielsen 2003; Pietikäinen et al. 2005; McLain and Martens 2006). Finally, recent studies suggest that DNRA is more ubiquitous than previously thought and may also produce  $N_2O$  gases as nitrate is being reduced to ammonium (Bagges 2011).

We observed enhanced  $CH_4$  uptake in the sand and sandy loam washes suggesting methanotrophic conditions in these coarser, drier and more C and N limited soils; while in the loam washes, we observed enhanced  $CH_4$  production (Figs. 2h, 3c) suggesting methanogenic conditions in these finer textured, wetter and less nutrient limited soils (Angel 2010; Kim et al. 2012). Despite these patterns, the high variability in  $CH_4$  fluxes over time (Fig. 2h), particularly in the loam washes, indicate the possibility of concurrent methanotrophy and methanogenesis. While the co-occurrence of these processes may seem contradictory, studies point to chemical pathways for oxic  $CH_4$  production in soils (Hurkuck et al. 2012; Jugold et al. 2012) as well as aerobic  $CH_4$  production in plant and animal tissues (Keppler et al. 2009). Although exact chemical pathways for oxic  $CH_4$  production in soils remain to be identified, Hurkuck et al. (2012) and Jugold et al. (2012) demonstrate that abiotic oxic  $CH_4$  production varies with UV radiation, temperature, soil organic matter quality and quantity, and soil moisture regime. A study by McLain et al. (2008) in a semi-arid rangeland ecosystem near Tucson, AZ observed similarly high  $CH_4$  production as we document here, which was linked to the activity of methanogens residing in the guts of soil invertebrates and termites, a biotic process that may, in part, explain the patterns we observed. In addition, Angel (2010) documents the co-existence of

methanogenic and methanotrophic bacteria within oxic biological soil crusts of Israeli desert soils. While the activity of methanogens was reduced under aerobic conditions, the rapid development of anoxic micro sites following soil wetting allowed for a significant, albeit somewhat depressed flux of  $CH_4$  during prevailing oxic conditions. It is plausible that the rapid development of anoxic micro-sites, coupled with an enhanced availability of labile carbon following wetting (Kim et al. 2012) may allow for the co-occurrence of methanogenesis and methanotrophy in the loam washes, and might enhance  $CH_4$  production between rainfall events.

#### Implications of ephemeral stream channel biogeochemistry to management

Our data indicates that ephemeral urban channels provide ecosystem services beyond those of a flow through stormwater management system; they are hot spots where disproportionately high rates of biogeochemical cycling occur during hot moments that have potentially large effects on basin scale N balances. For example, in their study of the Central Arizona Phoenix (CAP) LTER, Baker et al. (2001) found that more than 50 % of the N loss from arid urban ecosystems occurs via denitrification. Preliminary estimates for catchment wide N-budgets in the Tucson basin made using findings from this study and coupled with our previous work (Gallo et al. 2012a, b, 2013) indicate that as much as  $500 \text{ mg m}^{-2}$  of N may be lost via  $N_2O$  gas flux from ephemeral streams to the atmosphere in response to summertime rainfall events of 15 mm in depth or less. Thus, these small and often non-runoff producing events can jump start biogeochemical processes by releasing soil moisture limitations, particularly in sites like the sandy loam washes which are primarily water limited.

The temporal distribution of biogeochemical hot moments in ephemeral waterways remains to be quantified over an entire season. Our previous work indicates that following a wetting event, soil moisture quickly resets to pre-wetting conditions (Gallo et al. 2012a, b); and here we show that trace gas fluxes vary primarily with soil moisture, and that antecedent moisture conditions result in variable redox states and nutrient cycling pathways. Combined, our work suggests that mid and late summer trace gas fluxes in response to wetting might approximate early season

trace gas flux rates as soil moisture decreases and the intervening period between rainfall events increases.

Because urban runoff is increasingly managed to augment limited water supplies in arid and semi-arid regions, reducing delivery of nitrate areas of focused recharge is critical to sustaining groundwater resources (Carlson et al. 2011). Our previous work suggest that larger rainfall events produce runoff for potential recharge and transport N out of urban catchments (Gallo et al. 2012a, 2013), while this study indicates that small rainfall events, like that simulated here, have the potential to remove N from ephemeral channels that serve as primary recharge zones (Pool 2005; Blasch et al. 2010). Through removal of N via trace gas losses, these urban biogeochemical hotspots, which include pervious streams and green storm water management infrastructure, may improve downstream water quality by reducing the delivery of NO<sub>3</sub> to areas of groundwater recharge. However, tradeoffs related to greenhouse gas production warrant further evaluation.

## Conclusions

In this study we show that trace gas losses in response to a rainfall event are largely controlled by the textural characteristics of ephemeral stream substrate which alter how soil water, carbon and nitrogen interact and flux through the soil system between wetting events. We observed shifts in trace gas flux controls, from soil moisture, soil C and soil N limitations on trace gas production in coarser stream soils, to biologically favorable antecedent conditions due to higher soil C and N availability, soil organic matter and subsequent soil moisture retention in the finer textured stream soils. The patterns in trace gas fluxes over the soil texture gradient suggest that redox states within the stream channel substrate become more variable as particle size decreases. Surprisingly, here we document extremely high fluxes of CO<sub>2</sub> and N<sub>2</sub>O in response to stream channel wetting, indicating that ephemeral urban streams have the potential to process large loads of C and N following non-runoff producing rainfall pulses. The fluxes we document are elevated in comparison to undeveloped deserts, urbanized uplands and more humid systems. Collectively, our study suggests that the urban ephemeral stream channels examined here comprise urban

biogeochemical hot spots that have short, pronounced hot moments when a rainfall pulse follows an extensive period of drought; and that urban streams have the potential to significantly alter C and N fluxes and pathways of urban environments.

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