ABSTRACT

Variability in seasonal soil moisture (SM) and temperature (T) can alter ecosystem/atmosphere exchange of the trace gases carbon dioxide (CO₂), nitrous oxide (N₂O), and methane (CH₄). This study reports the impact of year-round SM status on trace gas fluxes in three semiarid vegetation zones, mesquite (30 g organic C kg⁻¹ soil), open/forb (6 g organic C kg⁻¹ soil), and sacaton (18 g organic C kg⁻¹ soil) from July 2002–September 2003 in southeastern Arizona. Carbon dioxide and N₂O emissions were highly dependent on available SM and T. During the heavy rains of the 2002 monsoon (238 mm total rainfall), large differences in soil C content did not correlate with variations in CO₂ production, as efflux averaged 235.6 ± 39.5 mg CO₂ m⁻² h⁻¹ over all sites. In 2003, limited monsoon rain (95 mm total rainfall) reduced CO₂ emissions by 19% (mesquite), 40% (open), and 30% (sacaton), compared with 2002. Nitrous oxide emissions averaged 21.1 ± 13.4 (mesquite), 2.1 ± 4.4 (open), and 3.9 ± 5.2 μg N₂O m⁻² h⁻¹ (sacaton) during the 2002 monsoon. Limited monsoon 2003 rainfall reduced N₂O emissions by 47% in the mesquite, but N₂O production increased in the open (55%) and sacaton (5%) sites. Following a dry winter and spring 2002 (15 mm total rainfall), premonsoon CH₄ consumption at all sites was close to zero, but following monsoon moisture input, the CH₄ sink averaged 26.1 ± 6.3 μg CH₄ m⁻² h⁻¹ through April 2003. Laboratory incubations showed potentials for CH₄ oxidation from 0 to 45 cm, suggesting that as the soil surface dried, CH₄ oxidation activity shifted downward in the sandy soils. Predicted climate change shifts in annual precipitation from one dominated by summer monsoon rainfall to one with higher winter precipitation may reduce soil CO₂ and N₂O emissions while promoting CH₄ oxidation rates in semiarid riparian soils of the Southwest, potentially acting as a negative feedback for future global warming.

Increasing atmospheric concentrations of the trace gases CO₂, N₂O, and CH₄ are a major focus of current studies on global climate change. Atmospheric CO₂ has risen from 280 to 370 μL L⁻¹ since the beginning of the Industrial Revolution and in the same time period atmospheric CH₄ has risen from 0.75 to 1.8 μL L⁻¹ (Khalil, 1999). Atmospheric CH₄ has a lifetime of 12 to 17 yr and is responsible for approximately 25% of anticipated global warming (Intergovernmental Panel on Climate Change IPCC, 1995). Preindustrial N₂O levels in the atmosphere were 285 nL L⁻¹, and have risen to 311 nL L⁻¹ today (Khalil, 1999). With an atmospheric lifetime of 120 yr, the increase in atmospheric concentrations of N₂O could have significant implications for future climate change (Schlesinger, 1997).

Arid and semiarid lands cover as much as 30% of the earth’s surface (Potter et al., 1996) and may be increasing in response to global change (Emanuel et al., 1985). Although researchers have estimated the contribution of world soils to the atmospheric budgets of CO₂, N₂O, and CH₄, flux data for semiarid life zones are extremely sparse. Semiarid ecosystems are characterized by frequent drought stress, daily and seasonal T extremes, low organic matter content, and low nutrient reserves (Skujins, 1981; Lal, 2001), leading researchers to believe that semiarid soils are not significant consumers or producers of trace gases. As a result, arid and semiarid life zones were, until recently, largely overlooked in greenhouse gas (GHG) inventories (Bowden, 1986; Potter et al., 1996).

RID AND SEMIARID LANDS cover as much as 30% of the earth’s surface (Potter et al., 1996) and may be increasing in response to global change (Emanuel et al., 1985). Although researchers have estimated the contribution of world soils to the atmospheric budgets of CO₂, N₂O, and CH₄, flux data for semiarid life zones are extremely sparse. Semiarid ecosystems are characterized by frequent drought stress, daily and seasonal T extremes, low organic matter content, and low nutrient reserves (Skujins, 1981; Lal, 2001), leading researchers to believe that semiarid soils are not significant consumers or producers of trace gases. As a result, arid and semiarid life zones were, until recently, largely overlooked in greenhouse gas (GHG) inventories (Bowden, 1986; Potter et al., 1996).

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At present, Southwestern semiarid soils receive precipitation in a bimodal distribution consisting of intense, highly variable convective precipitation during the mid-summer months with longer duration, low intensity precipitation during the winter. Some climate change models, while controversial, suggest that global warming may shift the region’s precipitation distribution (currently 60% summer and 40% winter) to higher winter rainfall percentages (Magaña et al., 1997). Because organic C mineralization increases with higher soil T (Peterjohn et al., 1994), shifts in precipitation to one dominated by winter moisture may be expected to reduce annual CO₂ emissions. However, semiarid monitoring studies often limit sampling periods only to warm seasons and long-term studies of trace gas fluxes across different seasons are largely lacking (Potter et al., 1996).

Here we report the results of a continuous, 15-month study conducted in three vegetation communities in southeastern Arizona, where fluxes of CO₂, N₂O, and CH₄, as well as SM and T at the soil surface and at several depths were monitored. The first year of the study (2002) was characterized by an extremely dry winter and spring, followed by heavy monsoon rainfalls in July through September. Winter rainfall was more abundant during the cool season of the study (fall 2002–winter 2003), but the 2003 monsoon rainfall was 60% lower than 2002, allowing us to examine microbial responses to a range in monsoon precipitation. The environmental data collected enabled us to develop predictive models to quantify the impacts of SM and T on fluxes of CO₂, N₂O, and CH₄ across a range of soils and vegetation types.

**MATERIALS AND METHODS**

**Study Site: San Pedro Riparian National Conservation Area**

Our study sites were in the San Pedro Riparian National Conservation Area (SPRNCA), a federally managed preserve in southeastern Arizona, USA (31°40’ N, 110°11’ W; 1190 m elevation). Although riparian communities comprise just 60% summer and 40% winter) to higher winter rainfall percentages (Magaña et al., 1997). Because organic C mineralization increases with higher soil T (Peterjohn et al., 1994), shifts in precipitation to one dominated by winter moisture may be expected to reduce annual CO₂ emissions. However, semiarid monitoring studies often limit sampling periods only to warm seasons and long-term studies of trace gas fluxes across different seasons are largely lacking (Potter et al., 1996).

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**Trace Gas Flux Measurements**

Trace gas monitoring in the SPRNCA began in July 2002 before the first monsoon precipitation. Monitoring was done once or twice weekly during the summer monsoon period, and monthly or bimonthly in the fall and winter. Gas fluxes were measured by the static chamber technique using 22-cm diam. PVC chambers permanently installed at the soil surface. On sampling dates, lids were firmly affixed to the chamber surface and subsamples of the chamber atmosphere were removed, using gas tight syringes, every 15 min for 1 h. Gas samples were analyzed in the laboratory using a Shimadzu GC14-A Gas Chromatograph (Shimadzu Scientific Instruments, Columbia, MD) fitted with flame ionization and electron capture detectors for measurement of CH₄ and N₂O concentrations, respectively. The column was an 80/100 mesh HayeSep-Q, 2 m × 3 mm ID (Supelco, Inc., Bellefonte, PA) set at 45°C, using N₂ as a carrier gas (flow rate, 40 mL min⁻¹). The injector and detector were maintained at 110 and 250°C, respectively. Certified CH₄ and N₂O standards (Praxair Technology, Sa Ramon, CA) were used for calibration. Net fluxes were calculated from the exponential regression of the time series of trace gas concentrations.

Carbon dioxide efflux from soils beneath each flux chamber was determined following removal of the final (1 h) samples for CH₄ and N₂O analysis. Headspace gas from each chamber was pulled through an S151 Infra-Red Gas Analyzer (IRGA) at 500 mL min⁻¹ (Qubit Systems, Kingston, ON) while columns containing soda lime, affixed to a second port on the chamber lid, prevented introduction of ambient CO₂. The peak gas concentrations from the IRGA were used to calculate net fluxes of CO₂ from the soil surface. After passage through the IRGA, headspace gas from each chamber was bubbled into a flask containing a mixture of 2 mL of saturated SrCl₂ (Sigma Chemical Co., St. Louis, MO) and 20 mL of 250 mM NaOH, trapping CO₂ as SrCO₃ (Harris et al., 1997). Following repeated washings of the precipitate with distilled water to remove excess NaOH, dried carbonate samples were analyzed for 1³C isotope composition by dry combustion with a Europa Hydra 20/20 IRMS (Europa Scientific, Crewe, UK).

**Plant and Soil Analyses**

Soils at the SPRNCA sites are well-drained Typic Torricerels of the Pima series (fine-silty, mixed, superactive, calcareous, thermic Typic Torriferels). Before the start of the study, samples from the 0- to 45-cm soil depth were collected using a 5-cm soil core sampler. In the laboratory, soils were sifted through a 2-mm sieve and refrigerated at 4°C until analysis. Soil texture was determined using the hydrometer method (Gee and Bauder, 1986) and pH was measured in 1:5 (soil/water) dilutions using the method of Van Lierop (1990) with an Orion Model 310 m (Thermo Orion, Beverly, MA) and an Orion electrode. C and N content and isotope composition of both the vegetation collected during the growing season and the soils (O-horizon to 45 cm) were determined, following acid pretreatment to eliminate carbonates, by a dry combustion analyzer interfaced with a Europa Hydra 20/20 IRMS.

Soil NO₃⁻ concentrations were determined by deionized water (5 mL) extraction of 1.0 g of air-dried soil (shaken for 30 min), followed by centrifugation at 2000 × g (RSF) for 10 min. The supernatant was decanted into a clean vial, diluted...
to 10 mL, and analyzed for anions using a Dionex DX-500 ion chromatograph (Dionex Corp., Sunnyvale, CA) equipped with an AS-11 anion exchange column. Anions were separated with an isocratic 10 mM NaOH gradient and detected with a Dionex ED-40 electrochemical detector set in the conductivity mode.

**Measurement of Environmental Variables**

During the first 10 mo of monitoring, environmental variables known to impact trace gas fluxes were measured on each sampling date. Soil T, at the surface and at 5 cm below the surface, was measured using a digital stem thermometer (Indoor Health Products, Layton, UT). Soil moisture was measured at 0 to 5 and 5 to 10 cm using permanently installed gypsum soil blocks and a KS-D1 Soil Moisture Tester (Delmhorst Instrument Co., Towaco, NJ). Rainfall data was collected using a TR-525 Rain Gauge (Texas Electronics, Dallas, TX).

In May 2003, collection of environmental variables was expanded using weather stations equipped with data loggers installed at each of the monitoring sites. Every 5 min, these stations measured air and dew point T at 60 cm above the soil surface using HOBO ProTemp/RH Data Loggers (Onset Computer Corp., Pocasset, MA); soil T at the 15- and 30-cm depths using TMC6-HA Wide Range Temperature Sensors (Onset Computer Corp.); SM at 5 to 10 cm using a Watermark Irrrometer Soil Moisture Sensor (Spectrum Technologies, Inc., Plainfield, IL); and ambient CO2 concentrations at 15 cm above the soil surface using Vernier CO2-BTA CO2 Gas Sensors (Vernier Software and Technology, Beaverton, OR). All data stored in a HOBO H8 4-Channel External Data Logger (Onset Computer Corp.). On sampling dates, the data were downloaded into a HOBO data shuttle while SM values at 15 and 30 cm were collected from the gypsum blocks. Rainfall at the each site was measured on each sampling date with Tru-Chek Direct Reading Rain Gauges (Edwards Manufacturing Co., Albert Lea, MN) that contained an overlying film of mineral oil to minimize evaporation.

**Laboratory Incubations**

Laboratory incubations to quantify CH4 consumption were performed using open area soils collected in 5-cm increments to 45 cm. Twenty grams of soil from each depth were placed in duplicate 250-mL flasks, sealed, and incubated under near-optimum conditions for methanotroph activity (T = 20°C; SM = −34 kPa) for 5 d. Gas samples were collected from the incubation flasks every 24 h and analyzed for CH4 concentrations using GC/FID. Following each gas sampling, flasks were flushed with ambient air and resealed. Daily CH4 consumption was calculated from the decrease in headspace CH4 over the 24-h incubation period.

**Calculations and Statistical Analyses**

On sampling dates, the average CO2, N2O, and CH4 flux for each vegetation zone was calculated from fluxes measured at two or three chambers permanently installed at each site. Seasonal fluxes of CO2, N2O, and CH4 were calculated from the daily average of all samplings during that season, multiplied by the number of days in the season. Global warming potentials (GWP) were calculated by adding the total seasonal emission of N2O normalized to a CO2 equivalent (g N2O × 310), to the seasonal emission of CO2 (g CO2), and subtracting the total seasonal CH4 oxidation, normalized to a CO2 equivalent (g CH4 × 26) (IPCC, 1995).

Stepwise linear regression models were used to determine impacts of environmental variables on fluxes of trace gas. Models that revealed strong controls on trace gas fluxes by SM and T allowed the estimation of total annual trace gas fluxes using environmental data collected by other researchers in periods during which the above-described monitoring equipment was not installed (Jan–May 2002 and Oct–Dec 2003). Comparisons between vegetation sites across multiple measurement dates were performed using repeated-measures balanced analysis of variance. All statistical analyses were done using Minitab 13.32 Statistical Software (Minitab, Inc., State College, PA). A significance level of α = 0.05 was used for all statistical tests.

Isootope composition of the SrCO3 collected from headspace gas and concentrations of respired CO2 in the chamber headspace were used to calculate the contribution of C3 vs. C4 plants to net CO2 respired. These calculations used a mixing equation (Gerring, 1991):

\[ (X + Y)(\delta^{13}C_{\text{min}}) = (X)(\delta^{13}C_3) + (Y)(\delta^{13}C_4) \]

solving simultaneously for X and Y, where, \( X + Y = \text{total amount (mg) of C respired into chamber headspace; } \delta^{13}C_{\text{min}} = \text{isotope ratio of total headspace CO2; } \delta^{13}C_3 = \text{isotope ratio of CO2 derived from C3 plants (−27%o); } \delta^{13}C_4 = \text{isotope ratio of CO2 derived from C4 plants (−13%o).} \)

**RESULTS**

**Vegetation and Soils**

Analyses of the soil physical properties showed slight variations between the three vegetation sites, as pH in the 0- to 5-cm soil layer ranged from 6.05 (sacaton) and 6.55 (mesquite) to 7.35 (open). All surface (0–10 cm) soils were highly sandy in texture, with sacaton soils having 75% sand, while open and mesquite soils were 83% sand.

The results of the C and N analyses of the vegetation, surface litter, and soils from each vegetation zone are presented in Table 1. The vegetation isotopic signatures clearly defined the C4 sacaton grass (\( \delta^{13}C = −13.5\%o \)) and the C3 mesquite (\( \delta^{13}C = −27.1\%o \)), while the signature of the open/forb vegetation (\( \delta^{13}C = −19.9\%o \)) indicated C input from both C3 and C4 plants (Table 1). The

<table>
<thead>
<tr>
<th>Soil Depth</th>
<th>Organic C</th>
<th>( \delta^{13}C )</th>
<th>Total N</th>
<th>C/N</th>
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</thead>
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<td>9.7</td>
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<td>O-H</td>
<td>0-5 cm</td>
<td>29.9</td>
<td>−20.2</td>
<td>3.08</td>
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<td>12.7</td>
<td>−18.9</td>
<td>1.36</td>
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<tr>
<td></td>
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<td>7.2</td>
<td>−17.2</td>
<td>0.71</td>
</tr>
<tr>
<td>Open</td>
<td>Plant</td>
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<td>−18.4</td>
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</tr>
<tr>
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<td>0-5 cm</td>
<td>5.8</td>
<td>−18.3</td>
<td>0.63</td>
</tr>
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<td></td>
<td>5-10 cm</td>
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<td>−14.8</td>
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<td>−13.4</td>
<td>9.7</td>
</tr>
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</tr>
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<td></td>
<td>20-50 cm</td>
<td>6.5</td>
<td>−12.7</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Table 1. Soil C and N in three vegetation sites of the San Pedro Riparian National Conservation Area.
The soil C content in the top 20 cm was 1.3-fold higher in the mesquite soil (17.7 g C kg⁻¹) than in the sacaton soil (13.4 g C kg⁻¹) and 3.4-fold higher than the open soils (5.21 g C kg⁻¹). Differences in total N in the top 20 cm followed similar patterns, with N content of the mesquite soil (4.8 g N kg⁻¹) 3.4-fold higher than the sacaton soil (1.4 g N kg⁻¹) and nearly 10 fold higher than the open soil (0.5 g N kg⁻¹). Soil NO₃⁻ contents were more extreme, with NO₃⁻ content of the mesquite soil (71.8 mg kg⁻¹) nearly 10 times higher than the sacaton (7.2 mg kg⁻¹) and nearly 50 times higher than open soils (1.5 mg kg⁻¹).

Environmental Variables

Throughout the study, soil surface Ts were significantly (p < 0.001) lower under the shaded mesquite canopy, averaging 23.4°C over 15 mo compared with 26.9°C in the open sites and 28.5°C in the sacaton sites (Fig. 1). Daily air Ts during the 2003 monsoon season revealed the same pattern, averaging 25.5°C for the mesquite sites and 1.9°C warmer outside the mesquite community (average of 27.4°C for the open and sacaton sites, Fig. 2b and 2d). Belowground soil Ts during the 2003 monsoon season were also significantly lower (p < 0.001) in the mesquite sites (23.4°C at 15 cm and 22.7°C}
at 30 cm) compared with the open and sacaton sites (28.2°C at 15 cm and 28.2°C at 30 cm), but significant differences ($\rho = 0.480$) were not found between the open and sacaton sites (Fig. 2b and 2d).

Soils were extremely dry (SM potentials $< -1500$ kPa to 10 cm) when monitoring began in early July 2002. In the first 6 mo of 2002, the SPRNCA received only 15.5 mm of precipitation, and monitoring was preceded by more than 100 d with no rainfall. During the 2002 monsoon period of July 16 through September 9, 238.0 mm of precipitation (81.2% of annual total) was recorded and 0- to 10-cm SM potentials averaged $-351.0$ (mesquite), $-548.0$ (open), and $-638.7$ kPa (sacaton). The 2003 winter and spring precipitation totals were higher than 2002, as 40.0 mm of rain fell from January 1 to July 11. Monsoon precipitation in 2003 totaled only 95.2 mm (62.8% of annual total), resulting in SM potentials at the 0- to 10-cm depth averaging $-944.6$ (mesquite), $-1048.3$ (open), and $-1283.4$ kPa (sacaton) over the monsoon season (Fig. 2).

No differences in total precipitation were measured during the 2003 monsoon between the open and sacaton sites on opposite sides of the mesquite community, but during the same time the total rainfall in the mesquite sites was lower by an average of 36%. Despite the reduced rainfall input, SM potentials (0–10 cm) averaged over the 15-mo monitoring period were significantly ($\rho = 0.015$) higher in the mesquite sites, averaging $-732.9$ kPa, compared with $-866.4$ (open) and $-1114.6$ kPa (sacaton).

### Carbon Dioxide

Measured soil CO$_2$ emissions were minimal from all sites (average: $32.1 \pm 14.6$ mg CO$_2$ m$^{-2}$ h$^{-1}$) during the premonsoon of early July 2002. Subsequent monsoon rainfall (> 50 mm over 7 d) stimulated plant and microbrial respiration, and CO$_2$ production averaged 383.4 ± 51.8 mg CO$_2$ m$^{-2}$ h$^{-1}$ across all sites on July 26. Over the 15-mo monitoring period, CO$_2$ efflux closely followed rainfall patterns, with the lowest fluxes measured following periods of limited precipitation during the warm season (Fig. 3). During the 2002 monsoon, no significant differences ($\rho = 0.125$) in CO$_2$ production were found between sites, as efflux averaged 242.0 ± 64.3 (mesquite), 240.6 ± 51.8 (open), and 224.9 ± 62.9 mg CO$_2$ m$^{-2}$ h$^{-1}$ (sacaton). In the fall (2002) and winter (2003), average CO$_2$ production fell to 34.1 ± 13.4 mg CO$_2$ m$^{-2}$ h$^{-1}$ in the mesquite sites, efflux statistically equal ($\rho = 0.205$) to the sacaton sites (28.1 ± 4.4 mg CO$_2$ m$^{-2}$ h$^{-1}$) but significantly ($\rho = 0.020$) greater than the open sites (22.2 ± 4.7 mg CO$_2$ m$^{-2}$ h$^{-1}$). During the 2003 monsoon, the mesquite sites showed the highest average CO$_2$ flux (180.6 ± 80.6 mg CO$_2$ m$^{-2}$ h$^{-1}$), significantly greater than production in the open (124.1 ± 63.8 mg CO$_2$ m$^{-2}$ h$^{-1}$, $\rho = 0.003$) and sacaton (153.4 ± 70.0 mg CO$_2$ m$^{-2}$ h$^{-1}$, $\rho = 0.023$) sites.

The CO$_2$ sensors installed in 2003 for hourly measurement of ambient CO$_2$ concentrations (0 to 15 cm above the soil surface) showed variable response to precipitation in the open and sacaton sites, with peaks as high as 2000 µg CO$_2$ L$^{-1}$ and averaging 587 ± 327 µg CO$_2$ L$^{-1}$ throughout the monsoon season (Fig. 2c). However, a less variable response of soil mineralization to precipitation was found under the mesquite canopy, where ambient CO$_2$ concentrations averaged 442 ± 152 µg CO$_2$ L$^{-1}$ during the same time period (Fig. 2a).

The isotopic signature of respired CO$_2$ reflected the variations in the vegetation and soils (Table 1). Throughout the monsoon, fall, and winter of 2002–2003, CO$_2$ respired from the C$_3$ mesquite site was significantly ($\rho < 0.001$) more depleted in $^{13}$C than CO$_2$ arising from the open (C$_4$ and C$_5$ mix) and sacaton (C$_4$) sites (Fig. 4). The differences in isotopic composition were smallest in the 2002 premonsoon when mesquite $^{13}$CO$_2$ averaged $-21.5\%e$ while the open/sacaton $^{13}$CO$_2$ averaged $-18.8\%e$. As the monsoon progressed, the differences between the mesquite and open/sacaton sites increased, and by early September of 2002, $^{13}$CO$_2$ values averaged $24.3\%e$ in the mesquite and $-16.7\%e$ in the open/sacaton sites. Thereafter, the CO$_2$ isotopic signature from the mesquite sites averaged $-20.3\%e$ during the drier fall periods and $-22.6\%e$ when soils were moist, while the $^{13}$CO$_2$ average in the open and sacaton sites ranged from $-16.7\%e$ (dry soils) to $-18.3\%e$ (following nonmonsoon precipitation).

Following the first year of monitoring at the SPRNCA, stepwise linear regression models were developed to predict CO$_2$ production using the T, SM, and rainfall data obtained on each gas sampling date. The models showed that rainfall and near-surface soil T accounted for a significant portion of variability in CO$_2$ efflux in the mesquite ($r^2 = 0.7080; \rho = 0.008$), open ($r^2 = 0.5411, \rho = 0.009$), and sacaton ($r^2 = 0.7080, \rho = 0.001$) sites from July 2002 through April 2003. During the monsoon (2003) period, SM alone was the strongest predictor of CO$_2$ production in the mesquite ($r^2 = 0.6783, \rho = 0.004$) and sacaton areas ($r^2 = 0.5918, \rho = 0.009$). Although soil T was the strongest predictor of CO$_2$ efflux in the open areas ($r^2 = 0.2692$), T alone did not explain a significant portion of variability in net respiration ($\rho = 0.087$). The installation of data loggers to collect daily averages in 2003 improved the ability of regression models to predict CO$_2$ flux in the open and mesquite sites (Table 2).

### Nitrous Oxide

Nitrous oxide production in SPRNCA soils strongly reflected vegetation and precipitation patterns (Fig. 3b), as N$_2$O emissions averaged 21.1 ± 13.4 (mesquite), 2.1 ± 4.4 (open), and 3.9 ± 5.2 µg N$_2$O m$^{-2}$ h$^{-1}$ (sacaton) during the 2002 monsoon. Nitrous oxide production remained highest in the mesquite sites during the fall and winter of 2002–2003, when total N$_2$O emissions ranged from 16.5 (sacaton) and 31.0 (open) to 53.5 mg N$_2$O m$^{-2}$ (mesquite).

Decreased precipitation during the 2003 monsoon corresponded to $> 60\%$ reductions in average N$_2$O efflux from the mesquite sites compared with the monsoon 2002, to 8.5 ± 5.2 µg N$_2$O m$^{-2}$ h$^{-1}$, but this decrease was not significant ($\rho = 0.123$) due to the large spatial variability in N$_2$O production. Decreased monsoon precipitation in 2003 had the opposite effect in the open sites, where N$_2$O
production increased significantly ($p = 0.050$) in response to decreases in SM, to $5.9 \pm 4.9 \mu g \text{N}_2\text{O} \text{m}^{-2} \text{h}^{-1}$. A similar, nonsignificant ($p = 0.879$) trend was seen in the sacaton sites, where $\text{N}_2\text{O}$ efflux was $4.0 \pm 3.5 \mu g \text{N}_2\text{O} \text{m}^{-2} \text{h}^{-1}$ during the 2003 monsoon.

Stepwise linear regression models were developed to predict $\text{N}_2\text{O}$ production during the monsoon of 2002 using the T, SM, and rainfall data. The best model, using data collected in the mesquite sites, accounted for 23.2% of the variability in $\text{N}_2\text{O}$ efflux, but was not significant ($p = 0.165$) in its ability to predict $\text{N}_2\text{O}$ production. The expanded data collection in 2003 increased the ability of regression models to predict $\text{N}_2\text{O}$ production (Table 2), as SM, above-soil CO$_2$ concentration, and soil T at 30 cm significantly predicted $\text{N}_2\text{O}$ production in all sites from June through September 2003 (Table 2).

**Methane**

Premonsoon flux measurements in July 2002 following ~100 rain-free days revealed CH$_4$ consumption rates close to zero (Fig. 3c). Monsoon precipitation induced the development of a sizeable CH$_4$ sink that continued through the winter 2002 and spring 2003, averaging $25.7 \pm 6.8$ (mesquite), $32.6 \pm 8.8$ (open), and $20.1 \pm 6.8 \mu g \text{CH}_4 \text{m}^{-2} \text{h}^{-1}$ (sacaton) from July 2002 through April 2003 (Fig. 3c). The total 2002 monsoon CH$_4$ consumption was highest in the open sites, totaling 61.1 mg CH$_4$ m$^{-2}$.
whereas the seasonal totals for the sacaton and mesquite sites were 29.6 and 45.6 mg CH$_4$ m$^{-2}$, respectively, while the total nonmonsoon season CH$_4$ consumption ranged from 118.8 mg (sacaton) to 159.0 mg (mesquite) to 160.4 mg CH$_4$ m$^{-2}$ (open).

Lack of rain in May and June 2003 reduced the soil CH$_4$ sink strength by 25 to 55% at all sites, but CH$_4$ consumption was restored with the onset of monsoon rainfall in July 2003 and thereafter averaged 26.4 ± 6.8 and 30.1 ± 10.8 µg CH$_4$ m$^{-2}$ h$^{-1}$ in the mesquite and open sites through the end of the monsoon season. During the same time period, CH$_4$ fluxes in the sacaton sites indicated a shift from a soil sink to a source, as early July measurements showed substantial CH$_4$ production (> 85 µg CH$_4$ m$^{-2}$ h$^{-1}$). Monsoon precipitation input decreased the net CH$_4$ efflux but the CH$_4$ production in the sacaton continued through July (55.9 ± 22.5 µg CH$_4$ m$^{-2}$ h$^{-1}$) and August (6.9 ± 2.7 µg CH$_4$ m$^{-2}$ h$^{-1}$).

Laboratory incubations of open area soils collected in July 2002 showed that under near-optimum environmental conditions (234 kPa, 20°C), large potential CH$_4$ consumption rates were measured to a depth of 45 cm. Maximum potential oxidation rates were found at a 10- to 15-cm soil depth (Fig. 5).

During the monsoon of 2002, the best regression model (sacaton) showed that SM accounted for only 28.8% of the variability in CH$_4$ consumption ($r^2 = 0.140$). Models also showed that near-surface (0–10 cm) SM accounted for only 4.9 (mesquite) to 31.4% (open) of the variability in CH$_4$ consumption from July 2002 through May 2003. The expanded data collection during the second monsoon season increased the ability of regression models to predict CH$_4$ flux (Table 2). Soil moisture had the strongest influence on CH$_4$ flux in the sacaton site, while SM and dew point accounted for CH$_4$ flux variability in the open site. In the mesquite site, air T, dew point T, and SM interacted to significantly predict CH$_4$ consumption from June through September 2003.

**Greenhouse Gas Emissions under Different Seasonal Rainfall Patterns**

This 15-mo study period encompassed two monsoon seasons with widely different rainfall patterns. Monitoring revealed net GHG emissions for the 2002 monsoon of 310.1 (mesquite), 298.0 (open), and 308.7 g m$^{-2}$ (sacaton). During the post monsoon season (October 2002 through July 2003), average daily GHG emissions were

![Fig. 4. Isotopic composition of carbon dioxide respired from soil surface in three SPRNCA vegetation sites on measurement dates during monsoon and post-monsoon (July through December) 2002. Symbols are averaged values of two carbon dioxide collections per site on each sampling date, plus or minus standard deviation.](image)
lower for all three sites, but the length of the post- monsoon period vs. the monsoon period (> 300 d vs. 57 d) increased the overall GHG emissions to 450.0 (mesquite), 330.5 (open), and 345.8 g m⁻² (sacaton) for the non-monsoon seasons. The 60% decrease in monsoon rainfall in 2003 compared with 2002 decreased GHG emissions to 219.1 (mesquite), 150.0 g m⁻² (open), and 186.5 g m⁻² (sacaton). The CH₄ emissions in 2003 did not significantly affect the overall GWP of the sacaton sites, as total GHG emissions without the added CH₄ production totaled 185.5 g m⁻² (Amundson et al., 1989; Conant et al., 2004). During the monsoon of 2003, CO₂ sensors recorded extreme responses to precipitation in the open and sacaton sites, but not in the mesquite sites (Fig. 2a, 2c). The spikes in ambient CO₂ concentration were likely due to environmental factors present in the open and sacaton sampling sites. These sites were in exposed areas and subject to more wind movement, which would lower the soil atmospheric pressure and increase out-gassing of porespace CO₂ during periods of turbulent monsoon activity. The exposed nature of the open and sacaton sites may also have led to increased soil disturbance and mixing of the surface layers during precipitation. The 35% decrease in rainfall reaching the mesquite soil surface, and the thick layer of organic matter under the mesquite canopy, would both reduce precipitation impacts on CO₂ evolution.

The variations in isotopic composition between the mesquite, open, and sacaton soils may reflect historic shifts in the SPRNCA vegetation. The average biomass δ¹³C values of C₄ plants (−13%) are distinct from C₃ plants (−26%) (Smith and Epstein, 1971). The deepest soils of all three vegetation sites bear a strong isotopic signature of C₄ plants, suggesting that the SPRNCA was dominated by grasslands until recent geologic time. Indeed, mesquite encroachment into grasslands, thought to result from overgrazing, fire suppression, and climate change, has been well documented in the southwest USA (Archer, 1995; Martin et al., 2003). Only the upper soils (0–5 cm) of the SPRNCA bear a strong isotopic signature of the current dominant vegetation.

Through the summer and fall of 2002, weekly precipitation (total rainfall in 7 d preceding the measurement date) was significantly (ρ < 0.005) correlated with δ¹³C of the respired CO₂ of the mesquite (r = −0.87), responded significantly to soil T (Table 2), in agreement with studies performed in a variety of ecosystems (Rey et al., 2002; Conant et al., 2004). Rey et al. (2002) investigated controls on CO₂ efflux at a Mediterranean site and found that soil respiration was controlled by T when soils were moist (volumetric > 20%) but during dry periods, respiration was limited by SM. Taken together, these results indicate that higher soil respiration rates in response to T increases may be constrained by low SM in semiarid soils.

During the wet monsoon of 2002, SM exerted the strongest control on CO₂ efflux in the higher C content soils (mesquite and sacaton), while soil T was the strongest controller of CO₂ efflux from the low C content (open) site. In the presence of adequate SM, both C pool size and C/N have been shown to be strong controllers of net soil respiration in semiarid soils (Conant et al., 2000), and the strong response to moisture input measured in the higher C/N soils (mesquite and sacaton) indicates that respiration in these sites is not limited by C availability. Shading and higher organic C content of mesquite and sacaton soils may have slowed moisture loss following precipitation input, but lack of shading and low C availability would have increased evaporative drying in the open area in response to increased Ts, reducing the net CO₂ flux. Thus, the T control on CO₂ efflux from the open sites may also reflect SM influences.

DISCUSSION

It was long thought that seasonal severe droughts created unfavorable conditions for microbial activity in semiarid life zones. Yet, recent studies have shown that arid and semiarid soils can be significant contributors to atmospheric N₂O (Peterjohn and Schlesinger, 1991; Martin et al., 2003) and CO₂ (Amundson et al., 1989; Conant et al., 2004), and can act as a terrestrial sink for atmospheric CH₄ following precipitation (Striegel et al., 1992; Wang et al., 2003). By quantifying the SM controls on trace gas flux in semiarid riparian soils over several seasons, this work will aid in the development of models estimating the potential contributions of these ecosystems to future global change.

Moisture Controls on Carbon Dioxide Flux

Data encompassing 15 mo of monitoring showed significant correlations of CO₂ efflux and SM in all three vegetation systems during all seasons, as might be expected from results of previous work showing strong SM influences on soil respiration in semiarid systems (Amundson et al., 1989; Conant et al., 2004). During the monsoon of 2003, respiration rates in the SPRNCA also
open \((r = -0.75)\), and sacaton \((r = -0.83)\) sites. Mixing models showed that nearly 98% of the CO₂ respired from the mesquite soils during the 2002 monsoon was C₃-C. Following the monsoon, the CO₂ isotopic values decreased to 63% C₃-C during the dry periods and to 80% C₃-C after precipitation events. Carbon dioxide respired from the open and sacaton soils averaged 52.3 ± 0.6% C₃-C during the monsoon. Thereafter, CO₂ respired from the open and sacaton sites was enriched (62.3 ± 3.9%) in C₃-C during dry periods and depleted (52.9 ± 5.7%) in C₃-C following precipitation events. These differences in isotopic composition of CO₂ produced in the mesquite soils versus the open and sacaton sites are striking, but simply reflect that the respired CO₂ bore isotopic signatures closely resembling that of the mineralizing plant litter (Ludlow et al., 1976). After July, a distinct pattern emerged whereby the isotopic signature of respired CO₂ became more enriched in C₃-C during dry periods and less C₃-enriched following rainfall. The C₃-enriched CO₂ more closely reflects the isotopic signature of deeper soils, suggesting that microbial activity increases downward where moisture availability may be higher during dry periods. Upon soil rewetting, surface heterotrophic activity increases and the isotopic signature of the CO₂ respired more closely resembles that of the surface organic C. This scenario is quite plausible, given the very sandy texture (75–83% sand, 0–10 cm) of the SPRNCA surface soils. These coarse-textured upper soils allow diffusion of atmospheric gases from the surface, preventing the development of O₂ limitations on deep soil microbial respiration.

**Moisture Controls on Nitrous Oxide Flux**

The distribution of nutrients in the SPRNCA vegetation systems is spatially heterogeneous, with excess C and N located under the established mesquite. Mesquite, like many savanna plant species, biologically fix N and have been found to contain leaf N three times higher than non-N-fixing plants (Shearer and Kohl, 1989). Tiedemann and Klemmedson (1973) found that N availability was up to 15 times higher in soils underneath mesquite trees than in nearby grassy spaces. The N₂O fluxes measured in the SPRNCA ecosystem reflect these vegetation differences (15-mo averages: 11.5 [mesquite], 3.7 [open], and 3.2 μg N₂O m⁻² h⁻¹ [sacaton]) and were within the range reported in other arid life zones. Martin et al. (2003) reported peak fluxes of 6.8 ± 1.7 μg N₂O m⁻² h⁻¹ under mesquite canopies in North Texas rangelands, while Peterjohn and Schlesinger (1991) found denitrification N losses of 12.9 μg N₂O m⁻² h⁻¹ in a Chihuahuan Desert system and Johansson et al. (1988) reported fluxes averaging 4.0 μg N₂O m⁻² h⁻¹ from a tropical savanna during the dry season.

Model predictions of significant correlations between both SM and CO₂ concentrations and N₂O efflux such as those found in the mesquite and open sites may be expected, as C and N mineralization rates generally increase following the rewetting of a dry soil (Cui and Caldwell, 1997; Franzluebbers et al., 2000). Rapid changes in soil water potential associated with rewetting cause microbes to undergo osmotic shock, inducing cell lysis and/or a release of intracellular solutes (Halverson et al., 2000) and yielding pulses of C and N as the remaining microbes mineralize the labile cell contents (Kieft et al., 1987).

The wide variation in soil and seasonal weather conditions at the SPRNCA suggest that several microbial processes may be responsible for N₂O production in the three vegetation systems. The high organic C availability in the mesquite soils, in combination with extended periods of SM levels greater than field capacity, could potentially induce the activity of denitrifiers (Peterjohn and Schlesinger, 1991). However, SM levels higher than 80% field capacity were measured only three times during the summer of 2002 (following rainfalls of 30 mm or greater), and were never measured during the summer of 2003, suggesting that the SM conditions necessary for denitrifier activity were only transient in SPRNCA soils. In systems where SM potentials do not favor denitrification, autotrophic nitrifying microbes have been shown to account for a large portion of N₂O efflux (Parton et al., 1988; Davidson et al., 1993), but McLain and Martens (2005b) found that mineralization of added ammonium and nitrite to SPRNCA soils was extremely slow, suggesting that autotrophic nitrification is not a dominant process in this system. Aerobic heterotrophic denitrification by soil fungi has been shown to dominate N₂O production in grasslands (Laughlin and Stevens, 2002), and McLain and Martens (2005b) reported that applications of cycloheximide, an inhibitor of fungal activity, suppressed N₂O production while additions of streptomycin, a bacterial inhibitor, stimulated N₂O emissions in laboratory incubations of SPRNCA soils. Taken together, these data suggest that the activity of soil fungi may account for much of the N₂O production in this system. Cooke and Rayner (1984) report that fungal populations are not restricted to soil water films as are bacterial populations and thus, soil fungi are able to maintain growth and activity even under dry conditions. The ability to tolerate conditions of low soil moisture may introduce an obvious advantage for fungal populations in semiarid soils, and may account in part for the increased N₂O production in open area soils during the drier monsoon of 2003. In the low C open soils, heterotrophic fungi may have had to compete with heterotrophic bacteria for C substrates in 2002. Reduced competition for C in the drier 2003 monsoon may have increased fungal activity and net N₂O efflux.

**Moisture Controls on Methane Flux**

Increases in CH₄ consumption after precipitation have been reported in other arid systems. In Mojave Desert soils, CH₄ consumption following a 15-mm rainfall increased by 250%, from 17.1 to 42.9 μg CH₄ m⁻² h⁻¹ (Striegl et al., 1992). The SPRNCA CH₄ flux increased from 3.3 ± 4.7 μg CH₄ m⁻² h⁻¹ in early July of 2002 (after more than 100 d without precipitation) to 26.7 ± 11.4 μg CH₄ m⁻² h⁻¹ in mid-July. A similar increase was measured in 2003, when CH₄ uptake increased from 16.6 ± 11.4 μg CH₄ m⁻² h⁻¹ premonsoon to 29.9 ± 11.4 μg CH₄ m⁻² h⁻¹ following moisture input.
Although the response of methanotroph activity to precipitation agrees with published findings, the sizeable CH$_4$ consumption by SPRNCA soils nearly year-round was surprising, as studies have indicated that the rapid drying common to surface soils of semiarid ecosystems may inhibit CH$_4$ oxidation (Schnell and King, 1996). Schnell and King (1996) found methanotrophic activity to be substantially inhibited at water potentials below $-500$ kPa and yet, SPRNCA soils showed near-maximum in situ CH$_4$ consumption rates through the winter and spring of 2003, when SM potentials in the top 20 cm of soils layer averaged $-800$ kPa. Porespace CH$_4$ concentration data from a semiarid rangeland (McLain and Martens, 2004) indicate that extended drying common to Southwestern soils promotes a shift in CH$_4$ oxidation activity to deep soil layers where moisture is retained, allowing methanotrophs to remain active during periods of extended surface soil dryness, and laboratory incubations showed that under optimum SM and T conditions, SPRNCA CH$_4$ consumption occurred to 45 cm, confirming the presence of methanotroph activity through the soil column. Such a vertical shift in maximum CH$_4$-oxidizing activity with moisture input may be unique to semiarid and arid ecosystems. In many temperate zone soils, methanotrophic bacteria are confined to near-surface layers as diffusive transport of CH$_4$ and O$_2$ from the atmosphere limits their activity (Born et al., 1990). However, as evidenced by the CO$_2$ isotopic signature, the high sand content of SPRNCA soils reduces limitations on soil gas transport, allowing substrates critical to CH$_4$ oxidation activity to diffuse to methanotroph populations at deeper depths.

The high porosity of the SPRNCA soils makes the monsoon 2003 CH$_4$ production in the sacaton sites all the more anomalous. Methane production is a strictly anaerobic process and yet, significant CH$_4$ efflux from the sacaton was measured through 2 mo of the monsoon season. One plausible explanation is that this large, localized belowground CH$_4$ source results from termite activity. Termites, which contain methanogenic bacteria in their hindgut, produce 20–150 Tg of CH$_4$ per year on a global scale (Bachelet and Neue, 1993; Madigan et al., 1997). Subterranean termites can consume over 50% of arid land net primary production, and thus they are the prominent invertebrate cycling C and other nutrients in desert grasslands (Silva et al., 1985). Peters and Conrad (1995) tested well-aerated soils adjacent to termite colonies in South Africa and reported as many as 17 600 methanogens g$^{-2}$ soil.

**Global Change and Trace Gas Fluxes in Semiarid Soils**

At present, it is unclear how global change will alter precipitation and water availability in semiarid areas of the southwestern USA. Some scenarios suggest increased winter precipitation and decreased summer precipitation (Magaña et al., 1997), similar to the rainfall patterns observed in the current study in the winter and monsoon of 2003. The 60% decrease in monsoon rainfall in 2003 compared with 2002 decreased net soil CO$_2$ efflux by 40% and decreased N$_2$O production by more than 30% across all vegetation sites. Methane consumption fell by nearly 65% in 2003 compared with 2002, a decrease attributable solely to CH$_4$ production in the sacaton plots, while soil CH$_4$ consumption in the mesquite and open plots was statistically equal in 2002 and 2003.

By adding the monsoon net soil GHG production to the non-monsoon production, it is estimated that the SPRNCA produced 681.0 $\pm$ 70.0 g m$^{-2}$ of net GHG in 2002 and 560.6 $\pm$ 97.4 g m$^{-2}$ in 2003. Taken together, these data indicate that a rainfall shift from one dominated by summer rainfall to increased winter precipitation may decrease the net GWP of the SPRNCA soils by as much as 18%. Of course, definitive conclusions on the net (soil plus vegetation) GWP represented by the SPRNCA in current and future climates cannot be made without taking into account the vegetation, which may represent a significant CO$_2$ sink. However, because arid and semiarid soils represent more than 30% of the terrestrial surface of the earth and are increasing in area, projected rainfall shifts may represent a negative feedback on global warming.

**CONCLUSIONS**

Although semiarid riparian ecosystems can be affected by severe drought and are often characterized by extremely sandy soils, this study confirmed that riparian soils of southeastern Arizona contribute to atmospheric burdens of N$_2$O and CO$_2$. In addition, soils of the SPRNCA act as a considerable year-round terrestrial sink for atmospheric CH$_4$, although localized areas represent a seasonal source of CH$_4$, possibly related to termite activity. We found that the soil C and N mineralization and trace gas fluxes closely reflect vegetation patterns and are highly responsive to moisture input. Predicted shifts in precipitation patterns to increased winter rains may decrease the net GWP of the trace gases produced and consumed by these soils. This work suggests that semiarid soils cannot be discounted in studies estimating the impact of terrestrial ecosystems on current and future global warming.

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