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Areas of residential development in the southern Appalachian Mountains are characterized by low riparian zone nitrogen cycling and no increase in soil greenhouse gas emissions

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Abstract The critical role streamside riparian zones play in mitigating the movement of nitrogen (N) and other elements from terrestrial to aquatic ecosystems could be threatened by residential development in the southern Appalachian Mountains. Many studies have investigated the influence of agriculture on N loading to streams but less is known about the impacts of residential development. Here we consider the dynamics of changing riparian land use in the southern Appalachians that includes increased residential development at the expense of both forests and agriculture. We hypothesized that increased inputs of inorganic N from residential development will increase nitrogen cycling rates relative to forests, thereby preventing terrestrial N retention and increasing soil nitrate losses through leaching. In addition, we hypothesized that such development will increase emissions of N_2O, CO_2, and CH_4, all potent greenhouse gases. We found riparian soil potential N cycling rates as well as N_2O and CO_2 efflux to be much greater with agricultural land use compared to either forested or residential land use. Our data suggest that residential development of forested riparian ecosystems does not increase N cycling or removal and, thus, might allow for greater potential N leaching into streams. Both agricultural and residential land use exhibited CH_4 efflux while forested ecosystems were responsible for CH_4 uptake. Overall, regional greenhouse gas emissions are projected to decline as high N_2O and CO_2 emitting agricultural land is converted to residential use.

Keywords Land use change · Nitrogen · Riparian · Carbon dioxide · Methane · Nitrous oxide · Denitrification

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Introduction

Residential land use in the southern Appalachian Mountains has intensified over the last few decades and is expected to continue over subsequent decades (Gragson and Bolstad 2006; Kirk et al. 2012). Traditionally, human development in this region has consisted of small scale agriculture and low density residential development (Gragson and Bolstad 2006). However, current predictions expect 75% of the new development in the region to be of a suburban nature (Kirk et al. 2012), representing higher density residential areas. By 2030 it is expected that 67% of this development will be on previously forested land (Kirk et al. 2012).

Forested riparian zones (land adjacent to streams) retain nitrogen (N) moving toward the stream (Groffman et al. 2002) and therefore are critical for maintaining water quality. In the southern Appalachian Mountains (Webster et al. 2012) riparian zones are relatively narrow (Clinton et al. 2010) and sensitive to changes in land use (Turner et al. 2003). Indeed, agricultural and suburban land use has been shown to increase stream nitrate (NO_3^-) concentrations substantially compared to forested streams (Kaushal et al. 2011; Webster et al. 2012). In southern Appalachia, streams and rivers were found to be particularly sensitive to conversion of forests resulting in detrimental effects on the water purification services they provide (Rosemond et al. 2015). Under forested conditions, the main source of stream nitrate is microbial mineralization of terrestrial organic N. In contrast, waste water leaching is the dominant source of NO_3^- to streams in developed areas (Kaushal et al. 2011). Riparian zone degradation is one of the major causes of decreasing water quality in the US (Faustini et al. 2009).

Riparian ecosystems can retain up to 89% of the N produced from upland anthropogenic activities (Dosskey 2001; Vought et al. 1994) and up to 98% of forest upslope inputs (Fisher and Likens 1973; Pinay et al. 1989). This N retention results in the formation of hotspots for N and C accumulation which can lead to increased ecosystem productivity (Harms and Grimm 2008). Forested riparian zones in the southern Appalachian Mountains with high rates of N mineralization and nitrification have been shown to effectively mitigate nutrient influx associated with upslope disturbances (Knoepp and Clinton 2009). Additionally, redox conditions in the riparian zone are generally favorable for high rates of denitrification, the process responsible for converting inorganic nitrogen into gaseous forms (Davidson and Swank 1986).

Nitrogen loading from upslope positions results in increased rates of riparian N cycling (Groffman et al. 2002), which often coincides with greater emissions of nitrous oxide (N_2O) (Groffman et al. 1998; Hefting et al. 2003). Approximately 6% of global terrestrial N_2O emissions come from riparian zones (Bouwman et al. 2013; Groffman et al. 2000). Soils are capable of reducing, and thus consuming, N_2O but uptake <2% of emissions; as such decreasing atmospheric N_2O will likely not result from increased uptake but rather through emission reductions (Schlesinger 2013). In southern Appalachian Mountain riparian zones, pastures used for cattle grazing had emissions as high as 24.5 kg N_2O–N ha^{-1} yr^{-1} (Walker et al. 2002); restoration of a vegetative riparian zone through cattle removal and tree planting decreased emissions by 75% (Walker et al. 2009). Further, this restoration method shifted the source of N_2O from nitrification to denitrification (Walker et al. 2009) suggesting that a more complete reduction of NO_3^- by denitrification reduced N_2O emissions.

In addition to N_2O efflux, CO_2 and CH_4 efflux can be high in riparian zones; particularly as C cycling is coupled with N cycling. CO_2 emissions are well studied, with soil temperature and moisture being identified as the main controlling factors (Davidson et al. 2002). Processes of CH_4 and N_2O emissions, although also responsive to temperature and moisture, are complicated due to their sensitivity to oxygen concentrations and because net efflux rates are the result of both reduction and oxidation reactions (Tiedje et al. 1984). Soil moisture generally stimulates CH_4 emissions (Schlesinger and Bernhardt 2013), while CH_4 uptake rates have been found to be both stimulated and inhibited by soil moisture. Maximum CH_4 uptake rates often occur around 15% volumetric water content (Boeckx and Van Cleemput 1996). In general, soil aeration, regulated by texture and bulk density, controls long-term patterns of N_2O and CH_4 fluxes, while soil temperature, moisture and substrate availability (e.g. N supply and throughput) determine short-term responses (Werner et al. 2007).

The changes in land use in the southern Appalachians have the potential to alter regional soil nitrogen cycling and emission of greenhouse gases through effects on N cycling processes. For example, conversion of forest to grass dominated riparian systems (i.e. pasture or lawn) could result in increased rates of net soil CO_2 efflux because grasslands often have a greater CO_2 soil efflux than forests (Raich and Tufekciogul 2000). Rates of soil CH_4 uptake from the atmosphere often decreases when forest land is converted to agricultural use (Powlson et al. 1997). Additionally, while fertilizer additions in agricultural or residential land use generally increase rates of C sequestration (Tian et al. 2014) it also reduces soil CH_4 uptake potential (Steudler et al. 1989) resulting in net positive CH_4 emissions from agricultural pasture or residential lawns (Law et al. 2004).

The objective of this study was to assess rates of N cycling processes and greenhouse gas emissions in riparian areas under different land uses and elucidate relationships with edaphic drivers. We hypothesized that higher N cycling rates in riparian areas of agricultural and residential development would result in greater N_2O efflux due to increased rates of nitrification and denitrification relative to upland forested ecosystems. We further proposed that high rates of N cycling in agricultural and residential ecosystems would result in decreased CH_4 uptake and potentially greater CH_4 efflux, as well as greater CO_2 efflux compared to forested riparian areas. We examined these rates of greenhouse gas emissions in riparian zones to estimate the impact of land use change at a regional scale.

Materials and methods

Site description

The study was conducted in Macon County, North Carolina, in the Blue Ridge physiographic province in the southern Appalachian Mountains (Fenneman 1917). This region receives an average of 1700 mm of precipitation a year (Coweeta Long Term Ecological Research Database 1936–2013). The highest temperatures are between May and September (20 °C) and the lowest temperatures are between December and February (5 °C) (Laseter et al. 2012). The growing season starts in May and ends in September (Swift and Cunningham 1988). Historically, this region has been dominated by logging and agricultural activities with the majority of the region clear-cut in the early 1900s (Gragson and Bolstad 2006). Small scale agricultural activities occupied 22% of the landscape in the early 1900s and have steadily decreased to 4% as of 2010 (Bolstad and Vose 2005; Kirk et al. 2012). Both logging activities and agricultural land use have been significantly reduced since the 1960s (Gragson and Bolstad 2006). Currently, forested ecosystems represent about 86% of the riparian cover, however, residential land use (currently about 10%) is becoming more predominant and details of historic, current and projected residential land use have been extensively described in Kirk et al. (2012) and Gragson and Bolstad (2006).

We selected 8 riparian sites that included forest cover (N = 3), undisturbed since the 1920s; agricultural use (N = 3), comprised of managed pasture with and without grazing, and low density residential development (N = 2). All sites were adjacent to a first or second order headwater stream. At each site we established a 20 m wide and 80 m long riparian zone sampling area perpendicular to the stream. Two of the forested sites were on soils predominantly classified as a fine loamy, parasesquic, mesic Typic Hapludult (Evard-Cowee soil series; altitude: 818 and 815 m) while the third was mainly a fine-loamy, mixed, superactive, mesic Humic Hapludult (Saunook soil series; altitude 811 m). The agricultural sites included one Saunook soil series (altitude: 664 m; hay production only), a second with a mix of Evard-Cowee and Saunook soil series (53/47%, respectively, altitude: 661 m; limited cattle grazing with no access to the stream), and a third site classified as a mix of a coarse-loamy, mixed, superactive, mesic Oxyaquic Humudept (60%; Reddies fine sandy loam soil series) and Saunook soil series (27%; altitude: 761 m; cattle grazing with access to the stream). The residential sites were mainly classified as Saunook soil series; altitude: 661 m; tree dominated vegetation) and a mix of fine-loamy, isotic, mesic Typic Humudept (59%; Tuckasegee-Cullasaja soil series) and Evard-Cowee soil series (41%; altitude: 720 m; mix of lawn and tree vegetation). All soil series data were retrieved from the USDA Soil Survey (NRCS Soil Survey Staff 2014).

Field sampling

Measurements for greenhouse gas emissions were taken eight times between May 2012 and May 2013 (2012: May, July, September, November and December; 2013: February, March and May) at five locations in each site (CH_4 fluxes were only collected from November 2012 through May 2013). At each date, three locations were randomly selected within 3 m from the stream and two additional locations were placed up to 20 meters from the stream and at least 10 m apart. No differences were found based on sampling location along the hillslope and the sampling locations were, therefore, treated as replicates. In May, July, and November of 2012, and March and May of 2013, at each greenhouse gas measurement location, soil cores were collected for laboratory measurement of potential N cycling rates and soil abiotic characteristics, as described below. Soil bulk density was determined in April 2013 for all sites. Using precipitation data retrieved from the NOAA climate database for Macon County, NC (NOAA 1950–2013), we calculated cumulative 24 h and 48 h precipitation before sampling.

At every gas flux sampling date and location, we measured soil moisture and temperature at 5-cm depth in the mineral soil using a Hydrosense sensor (Campbell Scientific Inc., Logan, UT, USA) and soil thermometer, respectively. Soil samples (0–15 cm) were collected for nitrogen (N) cycling assays and edaphic characteristics using a 5-cm diameter stainless steel soil push tube from three randomly determined locations per site; soil samples were stored separately for analyses. We divided core samples into O-horizon (if present), 0–5, 5–10, and 10–15 cm mineral soil and stored samples in sealed plastic bags. Each soil sample was sieved to <2 mm and homogenized. Gravimetric soil moisture was determined by oven drying ~2 g of soil to constant weight at 105 °C. Assessments of available inorganic nitrogen (NO_3^- and NH_4^+) were determined using 2 M KCl extractions in March 2013 on freshly sieved soils for the top 10 cm (USEPA 1983a, b). Soil pH in water (2:1) was determined on air-dried soils as described in Robertson et al. (1999) in July 2012, November 2012, March and May 2013. Soil bulk density (g soil cm^{-3}) of the surface 0-15 cm was determined on air dried soils collected in April 2013 using a 4.3 cm diameter PVC pipe. These soils were also used for C and N contents using a Flash EA 1112 NC analyzer (Thermo Scientific).

Nitrogen cycling assays

We determined potential nitrification (pNTR) and potential denitrification (pDNF) on fresh soil samples using oxic and anoxic incubation techniques, respectively. pNTR was determined within 48 h of soil collection on field moist soils stored at 4 °C and pDNF was conducted on soils stored (4 °C) for less 7 days.

To assess pNTR we placed five grams of sieved soil (<2 mm) from each sample location near the stream (N = 8 plots (3 forest + 3 agriculture + 2 residential) × 10 plots per site = 80 samples) in separate 37 mL serum vials with 15 mL of media (0.33 g L^{-1} $(NH_4)_2SO_4$ and buffered with 0.14 g L^{-1} K_2HPO_4 and 0.027 g L^{-1} KH_2PO_4 in DI water). Each serum vial was wrapped and capped with aluminum foil to prevent evaporation and UV light inhibition of ammonia-oxidizing bacteria. After addition of the media, vials were gently shaken at 10 relative centrifugal force at 25 °C; 2 mL sub-samples were collected after 0.5, 2, ~7 (between 6 and 8 h) and 24 h of incubation using a cut-off pipette tip (to facilitate pipetting a slurry). Samples were centrifuged for 10 min at 11,000 rcf and the supernatant was immediately frozen at −20 °C until thawing for $NO_2^- + NO_3^-$ analysis using colorimetric methods (Bendschneider and Robinson 1952). pNTR rates were determined by linear regression analysis of changes in KCl solution NO_3^- concentration over time and are presented per soil dry weight. All regressions were significant with $r^2 \geq 0.8$. Based on the depth of the horizon sampling and its bulk density we determined total rate per gram of soil for each core.

Anoxic pDNF rates were determined using the acetylene block method (Groffman et al. 1999). Five grams of sieved soil (just 1 g for O-horizon samples due to limited sample) was added to 37 mL serum vials. Serum vials were purged with He for 1 min to displace oxygen from the vial, and then 5 mL of incubation media was added to the serum vials. Media consisted of dextrose (1 mM) and sodium nitrate (1 mM) in DI water purged for 30 min with He. Assays were initiated by replacing 4 mL of headspace with 99% pure acetylene (10% v/v). Samples were incubated at 20 °C while shaking (150 rpm) for 3 h. Gas subsamples were taken after 0.5 and 3 h, and stored in 3.5 mL vacutainers (Labco, Lampeter, UK) until analysis for N_2O on a GC-ECD with a 10-port Valco valve to prevent acetylene from saturating the detector. Rates of pDNF were determined via regression analysis of changes in headspace N_2O concentrations over time and calculated on a soil dry weight basis. All regressions were significant with $r^2 \geq 0.8$. Based on the depth of the horizon sampling and its bulk density we determined total rate per gram of soil for each core.

Greenhouse gas emissions

We measured net soil CO_2, CH_4 and N_2O fluxes between 09:00 and 16:00 h using static PVC flux chambers with an inner diameter of 15.1 cm and a height of 8 cm. The PVC collars were installed 1 h before flux determination to a soil depth of 10 cm. PVC lids were adapted with septa for gas sampling; 9 mL gas samples were taken using a ten cc plastic syringe at 1, 5, 10 and 30 min after placing the lid on the collar. Gas samples were analyzed for CO_2 using a LICOR-7000 (LICOR Inc., Lincoln, NE, USA) and for N_2O and CH_4 using a Shimadzu GC-ECD and GC-FID (Shimadzu Co., Kyoto, Japan), respectively. Fluxes were determined using linear regression analysis. Rates are presented as g C m^{-2} d^{-1} (CO_2), mg N m^{-2} d^{-1} (N_2O), and mg C m^{-2} d^{-1} (CH_4). We assumed flux measurements to be representative for the whole day as was found by Bremer et al. (1998). We used a trapezoidal integration approach to estimate a cumulative flux rate from July 2012–May 2013 (CO_2 and N_2O) and November 2012 through May 2013 (CH_4). Total riparian area (20 meters adjacent to a stream) was estimated using the buffer tool in ArcGIS 10.0 on the Coweeta LTER stream GIS data (Coweeta Long Term Ecological Research Database 1936–2013). We used our annual gas flux estimates to calculate changes in the contribution of the riparian area in CO_2 equivalents (CO_2-eq) (CH_4 = 86-CO_2-eq; N2O = 268-CO_2-eq (Myhre 2013)) fluxes over a 20 year timespan for Macon County, North Carolina based on projected land use changes from 2010-2030 (Kirk 2009). To provide an assessment of variance we have propagated the error of the annual fluxes.

Statistics

Greenhouse gas fluxes, potential N cycling rates and edaphic characteristics measured over time were tested for significant land use effects using a mixed model repeated measures approach restricted maximum likelihood (REML). Date and land use type were fixed effects, site was a random effect (Random: site, as well as interaction terms). We used Tukey post hoc mean separation test to identify significant differences among dates and land use type. If date and land use type interactions were significant, we tested land use type effect for each sample date using one-way ANOVA and Tukey post hoc mean separation analyses. Data were either log transformed or rank transformed (Conover and Iman 1981) if needed to acquire a normal distribution for parametric analyses. All errors depicted represent the standard error of the mean. The relationship between process drivers and gas flux rates were determined using Spearman correlation analysis on non-transformed data to determine predictors for greenhouse gas fluxes and N cycling rates. All descriptions of uncertainty are in the form of standard error (SE) of the mean calculated by taking an average of the respective site and determining the SE of the 2 (Residential) or 3 sites (Agriculture and Forested). All statistical analyses were conducted in JMP 11 (SAS Institute Inc., Cary, NC) and significant differences are indicative of $P < 0.05$ unless otherwise stated.

Results

Edaphic characteristics

Land use had a significant effect on soil temperature (Fig. 1; Table 1). Soil temperatures were greater in agricultural sites (15.4 ± 0.55 °C) compared to forested (12.4 ± 0.45 °C) and residential (13.5 ± 0.67 °C) sites on seven out of eight sample dates, with the greatest temperatures in July 2012 (24.0 ± 0.42 °C). Land use (Fig. 1; Table 1) showed no significant effect on soil moisture but sample dates differed significantly; land use and sample date interaction also tended to be significant ($p = 0.062$). Agricultural land use had greater soil moisture in five out of the eight sampling times (Fig. 1; Table 1).

Land use had a significant effect on soil pH, total N and extractable NH_4^+ and NO_3^- concentrations and bulk density of the surface 15 cm; land use and date interactions were not significant. Soil pH and total NH_4^+ and NO_3^- concentrations were greater in soils with agricultural land use compared to both residential and forested lands (Table 2); residential and forested sites were not significantly different. Soil pH was greater in agricultural land use compared to residential and forested land use for November 2012, March and May 2013 while both residential and agricultural soil pH where greater than forested in July 2012. Soil total N differed among sites and was greatest in agricultural sites, followed by residential and then forested land use types (Table 2). ($F_{2,6} = 11.5$, $p = 0.01$; Table 2).

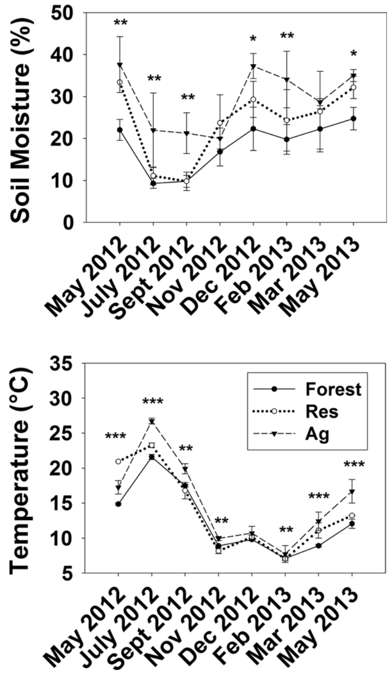

Fig. 1 Volumetric soil moisture and soil temperature in riparian forests of the southern Appalachian Mountains. The points indicate the mean and the *error bars* indicate the standard error of the mean (n = 2–3). *Asterisk* indicates Ag is significantly greater than Forest and Res (P < 0.05). *Forest* forested riparian zones, *Res* riparian zones in residential development, *Ag* riparian zones under agricultural development

Soil bulk density was greater in agricultural sites than forested and residential sites ($F_{2,5} = 12.2$, $P < 0.01$). Sample date had a significant effect on pH; pH was greater in May 2013 compared to July 2012. Land use effect on total C concentration was not significant (Table 2).

Nitrogen cycling

pNTR and pDNF rates were significantly affected by both land use and sample date and ranged from −0.2 to 3.4 μg N g_{soil}^{-1} d^{-1} and −0.2 to 122 μg N g_{soil}^{-1} d^{-1}, respectively (Fig. 2; Table S1). pNTR had a significant interaction between land use and sample date (Table 1; $F_{2,5} = 67.0$, $P < 0.001$). pNTR rates were greater in agricultural sites compared to forested and residential sites in May 2012 ($F_{6,14} = 5.1$, $P < 0.05$), November 2012 ($F_{7,16} = 13.9$, $P < 0.001$), March 2013 ($F_{7,16} = 7.4$, $P < 0.001$) and May 2013 ($F_{7,24} = 4.8$, $P < 0.001$); post hoc mean separation tests did not identify significant differences among sample dates. pDNF rates were greatest in agricultural sites; residential sites were greater than forests. July 2012 had the greatest pDNF rates while May 2013 had the lowest. O-horizon pNTR (Table S2) was responsible for 19 ± 11% (Forested) to 3 ± 2% (Res) of the overall site activity and 24 ± 4% (Forested) and 10 ± 21% (Res) of the pDNF activity (Table S2).

Greenhouse gas emissions and land use

The riparian soil CO_2 gas fluxes exhibited significant land use, sampling date and land use by sampling date interaction effects (Fig. 3a; Table 1). CO_2 flux was greater in Agricultural land use compared to

Table 1 Results for edaphic characteristics and greenhouse gas fluxes tested with linear mixed model statistics for land use and date

Variable	Land-use			Sampling date			Land-use × sampling date		
	df, df_{error}	F	P	df, df_{error}	F	P	df, df_{error}	F	P
Edaphic characteristics									
Soil temperature	2, 5	8.6	0.023	7, 271	580.0	<0.001	14, 271	9.7	<0.001
Soil moisture	2, 5	3.5	0.111	7, 260	26.1	<0.001	14, 260	1.7	0.062
pH	2, 5	15.7	0.007	3, 138	4.3	0.006	6, 138	1.1	0.37
Fluxes									
CO_2	2, 5	30.7	0.001	7, 258	20.9	>0.001	14, 258	2.0	0.017
CH_4	2, 5	3.4	0.12	4, 160	1.7	0.15	8, 160	1.3	0.23
N_2O	2, 8	3.6	0.080	7, 124	3.1	0.005	14, 123	0.53	0.91
Potential N-cycling									
Nitrification	2, 5	6.1	0.044	4, 106	1.5	0.21	8, 105	2.5	0.016
Denitrification	2, 5	67.0	<0.001	4, 169	18.5	<0.001	8, 169	0.8	0.58

Table 2 Soil properties (mean±SE) for bulk density (BD), pH, total carbon (C) and nitrogen (N), and extractable NH_4^+ and NO3$^-$ in the top 15 cm of mineral soil in the southern Appalachian Mountains

	BD (g/cm^3)	pH	C (mg/g)	N (mg/g)	NH_4^+ (mg N kg soil^{-1})	NO_3^- (mg N kg soil^{-1})
For	0.65 ± 0.06^b	5.0 ± 0.40^b	26.1 ± 1.3	1.1 ± 0.1^c	2.3 ± 0.6^b	0.05 ± 0.04^b
Res	0.69 ± 0.05^b	5.2 ± 0.51^b	27.2 ± 1.4	1.6 ± 0.1^b	3.0 ± 0.9^b	0.8 ± 0.6^b
Ag	1.08 ± 0.08^a	5.9 ± 0.42^a	24.6 ± 1.3	2.1 ± 0.1^a	9.3 ± 4.3^a	5.9 ± 2.3^a

Total C and N were determined using an Elementar Flash EA 1112 NC analyzer. NH_4^+ and NO_3^- concentrations are shown for March 2013. For = forest (N=3); Res = residential (N=2); Ag = agricultural (N=3); BD = bulk density. The letters indicate significant differences between land use types

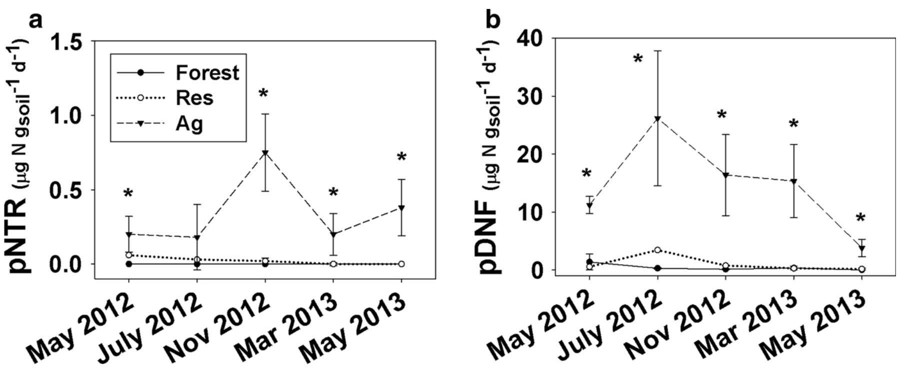

Fig. 2 Potential nitrification (**a**) and potential denitrification (**b**) rates for the different sampling dates (total including O-horizon and mineral soil 0–15) in the southern Appalachian Mountains. The *symbols* indicate the mean and the *error bars* indicate the standard error of the mean (n = 2–3). *Forest* forested riparian zones, *Res* riparian zones in residential development; *Ag* riparian zones under agricultural development. *Asterisk* indicates Ag is significantly greater than Forest and Res ($P < 0.05$)

residential land use in four of the eight sampling times, and agricultural land use was greater than forested systems in six out of the eight sampling times. Residential site CO_2 flux was greater than forested sites at only one sample date. Forest riparian sites showed a negative net CH_4 flux, (i.e. CH_4 consumption) at all sample times, while agricultural and residential sites varied between CH_4 production and CH_4 consumption. However, due to high variance, residential sites differed significantly from forested sites with a net CH_4 efflux in only one sample date (November 2012; $F_{7,30} = 2.3$, $P = 0.050$) and agricultural CH_4 flux rates did not differ from either forested or residential land use sites. Riparian N_2O fluxes varied greatly among sites, ranging from the least in forested sites (-12 ± 11 mg N m^{-2} y^{-1}) to the greatest in agriculture sites (428 ± 316 mg N m^{-2} y^{-1}), however, no significant land use effect was found. On the other hand, significant differences were observed between sampling dates where N_2O fluxes in May 2012 and July 2012 were greater than March 2013. The cumulative annual riparian CO_2 flux differed significantly with land use with a greater calculated annual flux in agricultural land compared to both residential and forested land use ($F_{2,5} = 22.1$, $P = 0.003$) (Table 3). Conversely, cumulative riparian CH_4 (Table 3; $F_{2,5} = 1.2$, $P = 0.39$) and riparian N_2O fluxes (Table 3; $F_{2,5} = 0.4$, $P = 0.71$) showed no significant land use effect. Currently, emissions of CO_2 account for greater than 97% of the total CO_2-eq of greenhouse gas emissions from riparian zones in this study; N_2O flux was relevant only in agricultural sites, contributing $\sim$3%, and CH4 flux was insignificant (<1%).

Land use in Macon County, North Carolina is predicted to shift, with agricultural use declining 0.4%, residential use increasing 2.6% and forest decreasing 2.2% between 2010 and 2030 (Fig. 4) (Kirk et al. 2012). These land use changes are used to estimate changes in annual riparian greenhouse gas

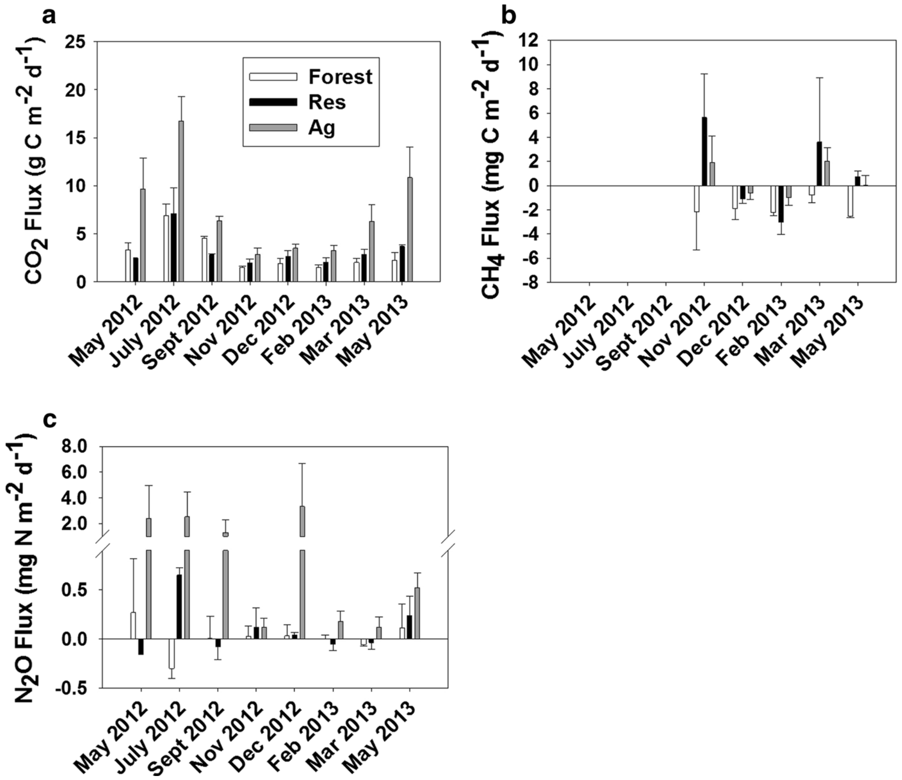

Fig. 3 CO_2 (**a**), CH_4 (**b**) and N_2O (**c**) fluxes. The *bars* indicate the mean and the *error bars* indicate the standard error of the mean. *Forest* forested riparian zones, *Res* riparian zones in residential development, *Ag* riparian zones under agricultural development (n = 2–3)

Table 3 Cumulative fluxes (mean ± SE) for CO_2, CH_4 and N_2O for the three land use types in the southern Appalachian Mountains

	CO_2 (kg C m^{-2})	CH_4 (mg C m^{-2})	N_2O (mg N m^{-2})
For	1.2 ± 0.1^{b}	-346 ± 101^{b}	-19 ± 9
Res	1.0 ± 0.0^{b}	247 ± 426^{a}	36 ± 8
Ag	2.0 ± 0.5^{a}	58 ± 97^{a}	385 ± 283

For = forest; Res = residential; Ag = pasture. Fluxes are July 2012-May 2013 (CO_2 and N_2O) and November 2012-May 2013 (CH_4). The letters indicate significant differences between land use types ($P < 0.05$)

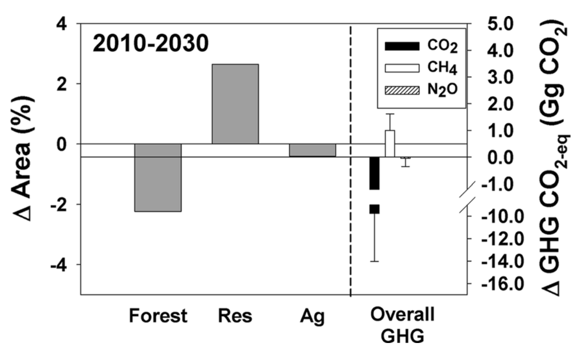

Fig. 4 Projected land use changes in the southern Appalachian Mountains from 2010–2030 based on Kirk (2009) and estimated regional riparian CO_2, CH_4 and N_2O fluxes for Macon County, NC. Greenhouse gas emissions (GHG) for all of Macon County's riparian zones are presented in CO_2-equivalent fluxes. The bars indicate the estimated change in area or GHG emission rate. *Forest* forested riparian zones, *Res* riparian zones in residential development, *Ag* riparian zones under agricultural development

emissions. Our estimates suggest that riparian soil CH_4 efflux will increase while both CO_2 and N_2O fluxes will decrease (Fig. 4). Overall changes in land use could result in an overall decrease in regional riparian CO_2-eq emissions by 0.7% during the 2010–2030 time period. Reductions in riparian CO_2 and N_2O emissions due to decreasing land area in agricultural use accounted for most of the reduction in greenhouse gas equivalents. On the other hand, county-wide riparian CH_4 emissions are predicted to increase due to increasing land area present in riparian residential land use, thus decreasing the CH_4 consuming forested ecosystems.

Drivers of fluxes and processes

Spearman correlation analyses (Table 4) found CO_2 fluxes to be positively correlated to soil temperature, pH and potential denitrification in all land use types. CO_2 flux was negatively correlated with 24 h cumulative precipitation in the forested sites only. CH_4 fluxes were positively correlated to soil temperature, soil moisture and potential denitrification. Analysis by land use type found a positive correlation between CH_4 efflux and soil moisture in residential land use. N_2O fluxes were positively correlated to soil temperature, pH, 48 h cumulative precipitation and potential nitrification and denitrification.

Correlation analysis between pNTR and pDNF and edaphic variables showed positive correlation with soil pH (pNTR, Pearson correlation coefficient (ρ) = 0.39; pDNF, $\rho = 0.58$; $P < 0.05$) (data not shown). Soil temperature at the time of sample collection was significantly correlated with pDNF rates ($\rho = 0.33$; $P < 0.01$) but had no relationship with pNTR. March 2013 NO_3^- concentrations showed a significant positive relationship with both pNTR ($\rho = 0.89$; $P < 0.01$) and pDNF ($\rho = 0.69$; $P < 0.01$) and NH_4^+ with pDNF ($\rho = 0.46$; $P < 0.05$).

Discussion

We estimated the consequences of residential development on previously agricultural or forested lands on riparian nitrogen transformations and greenhouse gas emissions in the southern Appalachian Mountains. This study suggests that the future will likely be characterized by lower nitrogen cycling rates, possibly less soil N retention and greater CH_4 emissions. Our data also indicate that due to a projected decrease in high greenhouse gas emitting agricultural lands, there would be no net effect of increased residential development on regional greenhouse gas forcing.

Land use effects on edaphic characteristics

The manner in which edaphic characteristics (soil bulk density, extractable NH_4^+ and NO_3^-, and total N) varied among different land use types in our study is similar to what has been found by others (Groffman et al. 1998; Walker et al. 2009). However, our finding of no land use effect on soil moisture dynamics contrasts with a study by Groffman et al. (2002) in an urban setting (Baltimore, MD USA) that showed significantly reduced soil moisture in sites with residential land use compared to forested sites; reductions were linked to decreased soil microbial

Table 4 Spearman rank correlations for greenhouse gas efflux rates and soil and environmental variables

Correlation variable	CO_2				CH_4				N_2O			
	All	For	Res	Ag	All	For	Res	Ag	All	For	Res	Ag
Temperature	**0.63****	**0.60****	**0.43****	**0.71****	**0.16***	0.08	0.13	0.02	**0.19***	0.01	0.12	**0.21***
Soil moisture	0.06	**−0.24***	−0.08	−0.06	**0.20****	0.00	**0.38**	−0.09	0.03	0.06	−0.17	**−0.20†**
pH	**0.33****	−0.08	0.24	**−0.24†**	0.16	0.14	−0.06	−0.06	**0.24****	0.10	0.11	−0.14
Precip 48 h	−0.04	−0.15	−0.06	−0.14	0.10	0.17	−0.14	0.04	**0.14***	0.02	0.10	0.09
Precip 24 h	**−0.14***	**−0.18†**	−0.20	**−0.18†**	0.06	0.15	−0.19	0.17	0.07	0.04	0.00	0.01
pNTR	0.18	−0.09	0.13	**−0.31***	0.18	0.11	−0.33	0.05	**0.22***	0.01	0.25	0.04
pDNF	**0.48****	**0.24†**	0.12	0.15	**0.28****	−0.03	0.18	0.15	**0.30****	−0.08	−0.14	**0.27***

The values indicate the correlation coefficient ρ (rho). Coefficients with $p < 0.1$ are shown in bold

For forested sites, *Res* residential sites, *Ag* agricultural sites, *pNTR* potential nitrification rates 0–15 cm mineral soil, *pDNF* potential denitrification rates 0–15 cm mineral soil

* $P < 0.05$

** $P < 0.01$

† $P < 0.1$

activity (Groffman et al. 2002). On the other hand, our soil temperature data are consistent with observations by Davidson et al. (1998) where land use effects on soil temperature were significant and temperatures in agricultural lands were greater compared to forested land; residential developments were in between.

Land use effects on nitrogen cycling

Studies by Groffman et al. (2000) and Hefting et al. (2003) in urban/residential riparian zones were characterized by large nitrogen inputs along with high nitrification and denitrification rates. In our study system residential land use resulted in greater total soil N concentration but extractable N (NH_4^+ and NO_3^-) along with pNTR and pDNF rates did not differ from forested systems. However, agricultural riparian systems had greater extractable and total N and exhibited pNTR and pNDF rates greater than both residential and forested sites; rates that were similar to those found in other studies (Groffman et al. 2000; Hefting et al. 2003). This suggests that while southern Appalachian residential riparian ecosystems may retain some of the additional N inputs, as evidenced by increased total N, N processing rates did not increase significantly. Observed increases in stream NO_3^- with increasing residential development (Webster et al. 2012) support this limited N retention hypothesis. A lack of riparian soil N retention combined with the demonstrated sensitivity of southern Appalachian in-stream processes to nutrient (N and P) additions (Rosemond et al. 2015) indicates stream ecosystem functions could be threatened by future residential development of forested ecosystems. The O-horizon, present only in the forested systems, was responsible for a large proportion of N cycling activity, demonstrating the important role organic horizons play in N processing and, thus, preventing N movement into streams under predominantly forested conditions.

Greenhouse gas emissions and land use change

Riparian forest CO_2 emissions in this study exceeded previous estimates for similar riparian forests in the region (Bolstad and Vose 2005). Similar rates (2.0–2.8 kg C m^{-2} y^{-1}), however, have been reported for forests generally in the region (Vose and Bolstad 2007). CO_2 flux rates for agricultural systems in our study were approximately three times greater than observed by Bolstad and Vose (2005). Although soil temperature was important in explaining CO_2 flux rates, an increase in soil moisture and high root density in pastures were also important likely drivers (Kellman et al. 2007). Our data puts forward the idea that the higher soil moistures and input of labile carbon from grasses in agricultural sites could contribute to higher CO_2 fluxes compared to forest sites. Previous studies have shown that CO_2 emissions were correlated with both temperature and soil moisture (Davidson et al. 2012). We hypothesized that the absence of a strong moisture effect in our study might be due to the relatively high rainfall of 2100 mm during our study period (July 2012–June 2013) compared to an average of 1700 mm for the ten prior years (Coweeta Long Term Ecological Research Database 1936–2013), which may have alleviated any soil moisture limitation. The negative correlation between total precipitation 24 h prior and CO_2 flux measurements is likely the result of reduced diffusion rates for both O_2 into and CO_2 out of the soil, reducing assessed respiration rates (Davidson et al. 2012). The reduction in CO_2 flux with decreasing soil pH in this study has been found in several previous studies and has been attributed to higher maintenance costs for microbes under more acidic conditions (Anderson and Domsch 1993) and potentially a shift to a fungal dominated community characterized by lower CO_2 production per unit microbial biomass (Blagodatskaya and Anderson 1998).

The forested riparian ecosystems in this study were distinguished from the other land uses in consistently consuming CH_4 (i.e. a net negative flux). In the southern Appalachian Mountains these riparian forests can be considered hotspots of CH_4 uptake (Le Mer and Roger 2001), which, when converted to either agricultural or residential development may become a CH_4 source. CH_4 consumption rates measured in the forested ecosystems in our study were on par with the high uptake rates found in tropical forests (190 – 700 mg C m^{-2} y^{-1}) (Verchot et al. 2000). We measured CH_4 production rates in both the residential and agriculture ecosystems of $\sim$3 mg C m^{-2} y^{-1}, rates similar to those measured in loam grassland soils (Boeckx et al. 1997). Within each land use type, CH_4 flux was best explained by a positive correlation with soil temperature (across all sites) and soil moisture (residential only); a finding that is consistent with other studies (Verchot et al. 2000, Werner et al. 2007). Soil CH_4 consumption may also partly respond to forest density. In the urban forests of Baltimore CH_4 consumption was 30% less compared to rural or suburban forests (Goldman et al. 1995). Here we find a similar response in that the riparian zones of the residential areas are partly forested but consume less CH_4 than the undeveloped riparian forests.

We found biologically relevant N_2O fluxes only in the agricultural ecosystems ($\sim$500 mg N m^{-2} y^{-1}). Fluxes measured in our study were comparable to emissions measured by others in riparian zones exposed to nutrient inputs (Groffman et al. 1998; Hefting et al. 2003) and within other agricultural ecosystems (Matson et al. 1998). High rates of 2000 mg N m^{-2} y^{-1} measured in high nitrate loaded forested riparian buffers adjacent to agricultural land in the Netherlands (Hefting et al. 2003) were not equaled here. Similar to other studies, N_2O production was positively correlated with soil temperature (Smith et al. 1998). N_2O was also positively correlated with pH, although this result may potentially be an artifact of higher soil pH in the agricultural sites as a negative relationship between pH and N_2O fluxes is expected based on greater N_2O:N_2 ratios of gaseous production under acidic conditions (Van den Heuvel et al. 2011). On the other hand, a higher pH generally also corresponds to a greater total denitrification rate that may enhance N_2O production. Higher precipitation over the previous 48 h was weakly but significantly associated with higher N_2O emissions and could indicate a lag effect in the microbial response to increases in soil moisture (Sexstone et al. 1985). Over all sites and in the sites with agricultural land use, potential denitrification proved the best predictor for N_2O emissions and, therefore, denitrification is the most likely pathway for N_2O production in the studied ecosystems.

Scaling-up to Macon County

Our emissions results coupled with projections of regional land use change (Kirk et al. 2012) estimate that overall CO_2 and N_2O emissions will decrease by 2030 due to a reduction in the total riparian area with agricultural land use. However, the replacement of forests with residential development may effectively shift riparian zones from a net CH_4 sink into a net source. The combined effect of the CO_2 and N_2O decrease and the CH_4 increase, however, is a net reduction in the CO_2-eq of greenhouse gas emissions. Additionally, the deforestation due to increasing residential development, will result in the removal of a large C pool in the form of aboveground biomass (Bolstad and Vose 2005) and reduce future CO_2 sequestration (Soussana et al. 2004). Similarly, the effect of forest removal on greenhouse gas emission depends on post-harvest usage (e.g. furniture, bioenergy, etc.) but these components are beyond the scope of the present study. Although the error of cumulative CO_2-equivalent emissions were about half of the mean change in emissions our data suggest that, solely based on riparian zone soil greenhouse gas emissions in this study, the projected reduction of agricultural land cover is predicted to reduce overall regional gas emissions.

Conclusions

Agricultural land use supports the largest fluxes of greenhouse gases in southern Appalachian Mountain riparian zones. Projected changes in land use suggest that conversion of agricultural land to residential development will result in decreased greenhouse gas emissions. On the other hand, increases in residential development at the expense of forested land, results in a moderate increase in emissions by transforming soils from a net CH_4 sink into a CH_4 source. Hence, overall, projected patterns of land use change would result in no net alteration of total riparian CO_2-eq greenhouse gas emissions. Our results also found that riparian zone N cycling and removal was largely driven by denitrification. However, conversion of forested riparian zones to residential development with increased N inputs due to fertilization and septic system installation resulted in no increase in the N removal capacity resulting in potentially negative effects on water quality.

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