

Biochar Incorporation into Pasture Soil Suppresses in situ Nitrous Oxide Emissions from Ruminant Urine Patches

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Nitrous oxide (N_2O) emissions from grazing animal excreta are estimated to be responsible for 1.5 Tg of the total 6.7 Tg of anthropogenic N_2O emissions. This study was conducted to determine the in situ effect of incorporating biochar, into soil, on N_2O emissions from bovine urine patches and associated pasture uptake of N. The effects of biochar rate (0–30 t ha^{-1}), following soil incorporation, were investigated on ruminant urine-derived N_2O fluxes, N uptake by pasture, and pasture yield. During an 86-d spring-summer period, where irrigation and rainfall occurred, the N_2O fluxes from ^{15}N labeled ruminant urine patches were reduced by >50%, after incorporating 30 t ha^{-1} of biochar. Taking into account the N_2O emissions from the control plots, 30 t ha^{-1} of biochar reduced the N_2O emission factor from urine by 70%. The atom% ^{15}N enrichment of the N_2O emitted was lower in the 30 t ha^{-1} biochar treatment, indicating less urine-N contributed to the N_2O flux. Soil NO_3^- -N concentrations were lower with increasing biochar rate during the first 30 d following urine deposition. No differences occurred, due to biochar addition, with respect to dry matter yields, herbage N content, or recovery of ^{15}N applied in herbage. Incorporating biochar into the soil can significantly diminish ruminant urine-derived N_2O emissions. Further work is required to determine the persistence of the observed effect and to fully understand the mechanism(s) of the observed reduction in N_2O fluxes.

ANTHROPOGENIC EMISSIONS of nitrous oxide (N_2O) are of environmental interest since N_2O is a greenhouse gas (Forster et al., 2007) and because tropospheric N_2O emissions are currently the primary source of stratospheric nitrogen oxides. These are involved in catalytic destruction of ozone (Ravishankara et al., 2009). Globally, total anthropogenic emissions of N_2O are estimated at 6.7 Tg $N yr^{-1}$ (Denman et al., 2007), with an estimated 1.5 Tg of this total due to the excreta of grazing animals (Oenema et al., 2005).

Intensively managed, grazed pastures receive N inputs as a result of fertilizer application and excreta deposition. A single ruminant urine deposition results in N rates of up to 1000 kg N ha^{-1} in the urine patch, creating “hot spots,” where soil N concentrations exceed the pasture plants’ immediate demands (Haynes and Williams, 1993). Subsequent transformation of this urinary-N, which is predominantly urea-N, initially leads to the creation of a significant ammonium (NH_4^+) pool in the soil. Nitrification of this NH_4^+ pool creates nitrate (NO_3^-). Transformation of these inorganic-N pools results in N_2O being produced via nitrification, nitrifier-denitrification, or denitrification (Wrage et al., 2001).

Biochar has been defined by Lehmann and Joseph (2009) as a C-rich product that is manufactured by thermal decomposition of organic material under a limited oxygen supply at relatively low temperatures (<700°C). Pyrolysis of biomass during bioenergy production results in biochar being produced as a waste product. It has been suggested that the incorporation of biochar into soils could offset anthropogenic carbon dioxide emissions by sequestering the embodied C (Lehmann and Joseph, 2009). However, the exact half-life of biochar materials incorporated into soils is still unresolved (Lehmann, 2007). Besides potentially sequestering C, biochar may also provide agronomic benefits (Sohi et al., 2010) and alter the N transformation rates within the soil (Clough and Condrón, 2010; and references therein). Examples of N fluxes and transformations affected by biochar addition include inorganic-N leaching (Singh et al., 2010), ammonia volatilization (Steiner et al., 2010), N fixation (Rondon et al., 2007), and N_2O emissions (Spokas et al., 2009; van Zwieten et al., 2010).

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Abbreviations: CEC, cation exchange capacity; VOC, volatile organic carbon; WFPS, water-filled pore space.

Several laboratory-based studies have documented the suppression of N₂O emissions as a result of biochar addition to soils. Cayuela et al. (2010) demonstrated that biochar, produced from green waste and poultry manure, reduced soil N₂O emissions relative to a control soil when incubated for 60 d at 20°C and 80% water-filled pore space (WFPS). Rondon et al. (2005) demonstrated reductions in N₂O emissions of 50 and 80%, following the incorporation of biochar into the soil under soybean and grass systems, respectively. Yanai et al. (2007) concluded that varying the soil moisture status caused biochar to either stimulate or suppress N₂O emissions due to its effect on soil aeration, since the denitrification mechanism for N₂O production is aeration dependent. An experiment by Singh et al. (2010) used repacked soil columns, into which were mixed poultry and wood waste biochars. After several wetting–drying cycles, the N₂O emissions were reduced by up to 72%. Using an unweathered biochar in a laboratory experiment, Clough et al. (2010) found the effect of biochar incorporation (20 t ha⁻¹) initially stimulated N₂O emissions in the presence of ruminant urine, although the cumulative N₂O flux over time was not significantly different from a urine-only treatment. Thus, biochar incorporation into soil can affect N₂O fluxes, but detailed field data are lacking. There have, to our knowledge, been no reports of in situ work performed in pastures under urine treatments.

The objective of this study was to assess the impact of adding biochar to a pasture soil with respect to pasture yield and N uptake, soil inorganic-N concentrations, and the potential for biochar to mitigate N₂O fluxes from ruminant urine patches.

Materials and Methods

Pasture Establishment

A runout perennial ryegrass (*Lolium perenne* L.) pasture situated at Lincoln University (43°38'58" S, 172°27'53" E), on a Templeton silt loam soil (Hewitt, 1998), was renovated in May (autumn) 2009 (Table 1). The pasture was cultivated to a depth of 0.30 m, using a rotocultivator. Unweathered biochar, manufactured from Monterey pine (*Pinus radiata*) (Table 2), was then incorporated to a depth of 0.10 m at rates of either 0, 15, or 30 t ha⁻¹, according to experimental treatment (see below). This was achieved by spreading the biochar material onto the plots and then making a shallow pass with the rotocultivator. The trial area was then rolled with a Cambridge roller to pro-

duce a fine seedbed tilth before sowing with a forage perennial ryegrass (cultivar Samson) at a rate of 12.5 kg ha⁻¹ in rows 0.14 m apart. After ryegrass emergence, urea fertilizer was applied twice—83 kg ha⁻¹ on 9 Sept. 2009, and 50 kg ha⁻¹ on 28 Oct. 2009. To suppress broadleaf weed growth, a selective herbicide (Jaguar, Bayer CropScience, Research Triangle Park, NC) was applied (1.5 L ha⁻¹) on 21 Oct. 2009. A fungicide to prevent stem rust (Proline, Bayer CropScience) was applied (0.2 L ha⁻¹) on 19 Nov. 2009.

Treatments and Experimental Design

On 13 Nov. 2009, headspace chamber bases (diam. 0.39 m, stainless steel), which protruded 0.10 m into the soil, were installed. These contained an annular water trough. During gas sampling events, insulated, stainless steel headspace covers with 0.10-m-high walls created an 11.6-L headspace when they were placed on the bases. The headspace cover sat on the annular water-filled trough, creating a gas-tight seal. Located immediately adjacent to each gas sampling chamber was a soil sampling plot (0.37 m × 0.43 m) (Fig. 1).

Four biochar-urine treatments, replicated five times, were set up on the field trial area. Two of these treatments, consisting of nil biochar plus nil urine (control) and nil biochar plus urine (0U), were positioned on the 0 t ha⁻¹ biochar plots (Fig. 1). The biochar at 15 t ha⁻¹ plus urine (15U) and biochar at 30 t ha⁻¹ plus urine (30U) treatments were sited on the 15 and 30 t ha⁻¹ plots, respectively (Fig. 1). Before urine application, pasture was cut to a height of 0.05 m to simulate grazing. Then, urine was collected from dairy cows at the Lincoln University dairy farm (43°39'2" S, 172°27'13" E) that had been grazing perennial ryegrass/white clover (*Trifolium repens* L.) pasture. The urine contained 5 g N L⁻¹ when collected. This urine was split into two portions. One portion was enriched with ¹⁵N-labeled urea to 4.963 atom% ¹⁵N, with a final urinary-N concentration of 10 g N L⁻¹, before applying it only to pasture within the gas sampling chambers at a rate of 930 kg N ha⁻¹. The second portion had urea, at natural abundance, added so that the concentration of urinary-N also equaled 10 g N L⁻¹. This was added to the soil sampling plots, adjacent to the gas sampling chambers, at the same N rate. Urine was applied on 26 Nov. 2009.

Field Sampling, Analyses and Micrometeorological Measurements

Soil bulk densities (Mg m⁻³) of the main plots were determined 5 mo after pasture renovation on 15 Oct. 2009. These were determined by taking a soil core (0.073 m diam. × 0.075 m deep) and drying the soil at 105°C for 48 h to determine gravimetric moisture content (θ_v) of the sample and calculating the bulk density. Soil surface pH measurements were taken on 33 occasions following urine-treatment application, from 2 d before urine application until 86 d after urine application, using a flat-surface pH electrode (Broadley-James, Irvine, CA), calibrated with appropriate buffer solutions. Gas samples were taken for N₂O flux determinations on the same days as the soil surface pH measurements. On each gas-sampling occasion at 0, 15, and 30 min, after positioning the headspace cover, headspace N₂O samples (10 mL) were taken manually using glass syringes fitted with three-way taps and compressed into 6-mL Exetainer tubes

Table 1. General soil properties at the experimental site.†

Soil property	
pH	5.5
Olsen phosphorus (mg kg ⁻¹)	28.4
Potassium (cmol _c kg ⁻¹)	0.84
Calcium (cmol _c kg ⁻¹)	3.6
Magnesium (cmol _c kg ⁻¹)	0.90
Sodium (cmol _c kg ⁻¹)	0.12
Cation exchange capacity (cmol _c kg ⁻¹)	14
Total base saturation (%)	39
Available nitrogen (kg ha ⁻¹)	45
Anaerobically mineralizable nitrogen (μg g ⁻¹)	31

† Soil tests were performed commercially by Hill Laboratories, Hamilton, NZ. Soil sample depth was 0 to 0.075 m. Thirty soil cores were taken from the site, bulked, and submitted for analysis, $n = 1$.

Table 2. Biochar physical and chemical properties.

Analysis	Result	Method
Cation exchange capacity (cmol _c kg ⁻¹)	8.0	1 g biochar:50 mL silver thiourea (Blakemore et al. 1987)
Anion exchange capacity (cmol _c kg ⁻¹)	4.0	Compulsive exchange method (Sparks, 1996)
pH _(H₂O)	7.8	1 g biochar:10 mL water (Blakemore et al. 1987)
pH _(CaCl₂)	7.4	1 g biochar:10 mL 0.01 M CaCl ₂ (Blakemore et al. 1987)
Electrical conductivity (dS m ⁻¹)	0.5	1 g biochar:10 mL water (Blakemore et al. 1987)
Particle density (Mg m ⁻³)	1.1	Using a conventional pycnometer (density bottle) and displacement with kerosene (Rasul et al., 1999)
Bulk density (Mg m ⁻³)	0.4	Mercury displacement (Pastor-Villegas et al., 2006)
Surface acidity (moles H ⁺ kg ⁻¹)	1.4	Boehm titration (Boehm, 1994)
Specific surface area (mg g ⁻¹)	127.4	Iodine absorption method (ASTM, 2009)
N content (mg g ⁻¹)	0.65	Total C and N were analyzed using a LECO CNS-2000 Elemental analyzer (LECO, Australia)
C content (mg g ⁻¹)	772	As for N content
C:N ratio	1187	–
Volatile organics found	Ethanol	As described by Clough et al. (2010)
Biochar particle size fractions	45 to 15 mm (24.1%), 15 to 7 mm (33.8%), 7 to 5.6 mm (1.13%), 5.6 to 4 mm (10.6%), 4 to 2 mm (15.2%), 2 to 1mm (4.7%), ≤ 1mm (10.6%)	

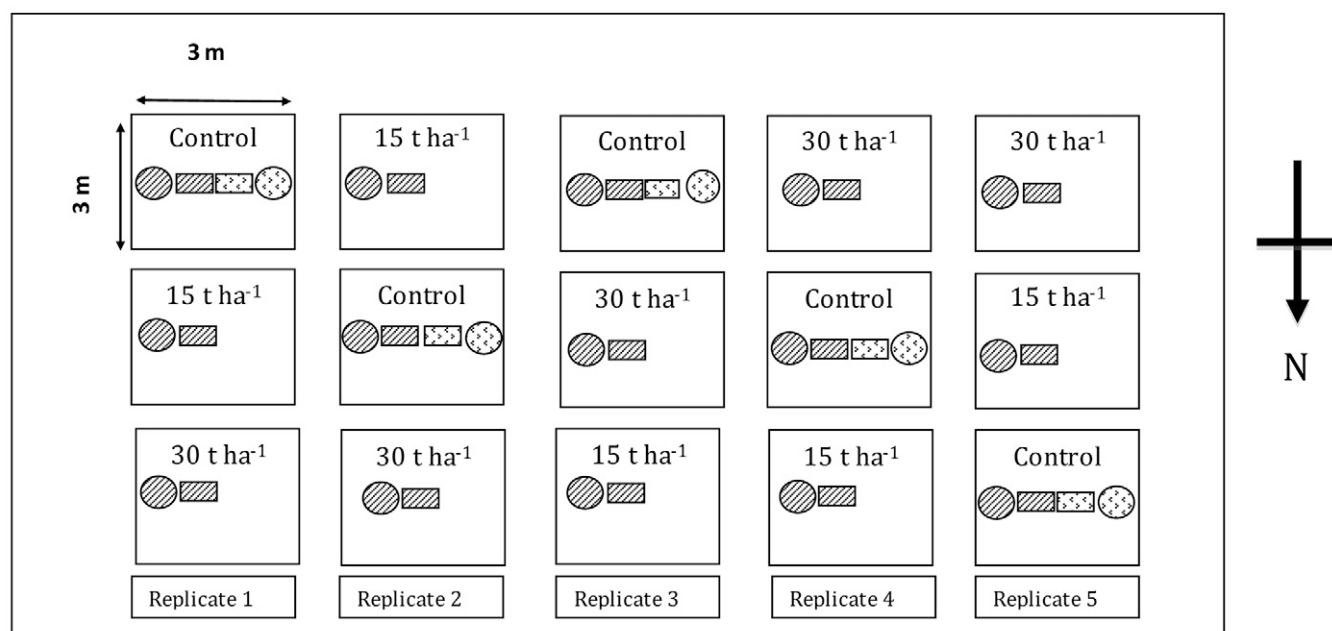
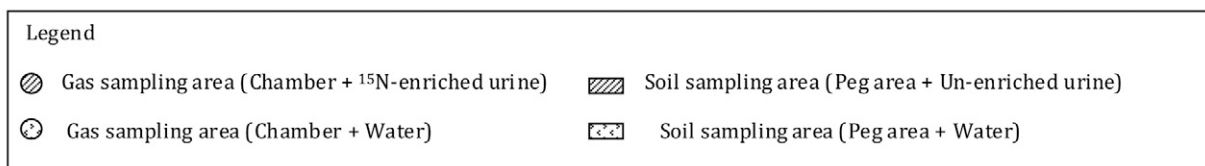


Fig. 1. Field trial layout showing the position of the gas chambers and soil sampling plots within the biochar treated plots (0, 15, or 30 t ha⁻¹).

(Labco Ltd., High Wycombe, UK). Immediately before analysis, these gas samples were brought to ambient pressure using a double-ended needle and analyzed on a gas chromatograph (8610, SRI Instruments, Torrance, CA) linked to an autosampler (Gilson 222XL, Middleton, WI), as described by Clough et al. (2010). A further 15-mL-headspace gas sample was taken and placed into 12-mL Exetainer tubes and equilibrated to atmospheric pressure, before analysis for N₂O-¹⁵N enrichment

using automated continuous-flow isotope-ratio mass spectrometry, as described by Stevens et al. (1993).

Soil cores (0.025 m diam. × 0.075 m depth) were taken on 17 occasions over the course of the study to monitor θ_s and inorganic-N concentrations. On each occasion, two soil cores were taken from each soil sampling plot, bagged and mixed, and then immediately transported to the laboratory where a subsample of soil was dried at 105°C for 24 h to determine

θ_g . Another 10-g subsample of moist soil was shaken with 100 mL of 2M KCl for 1 h and then filtered (Whatman No. 42), with the extracts analyzed, using flow injection analysis (Blakemore et al., 1987) for ammonium N ($\text{NH}_4^+\text{-N}$) and nitrate N ($\text{NO}_3^-\text{-N}$).

Pasture dry matter yields were determined on the gas chamber areas (on Days 21, 43, and 58) by hand harvesting the herbage at a height of 0.05 m. This herbage was dried at 65°C for 48 h, finely ground to <200 μm , and analyzed for its total N content and atom% ^{15}N enrichment using Dumas combustion and isotope ratio continuous-flow mass spectrometer (Sercon, UK).

Meteorological data (air temperature and rainfall) and the soil temperature at 0.10 m soil depth were obtained from the nearby meteorological station.

Statistical analyses were performed using Minitab version 15.1 (Minitab, 2006). Tests for normality showed the N_2O flux data were skewed and so these were log transformed ($\ln[\text{flux}+1]$) before statistical analyses, with N_2O fluxes compared on individual sampling days and for cumulative fluxes over the sampling period. Analysis of variance was used to determine if treatment means were equal. Where significant differences were detected, two-sample t tests were used to further identify differences between specific treatment means.

Results

Soil Analyses and Meteorological Measurements

Soil moisture (θ_g) did not differ significantly due to biochar or urine treatments for any given sampling day, averaging 18.8, 19.3, 17.9, and 16.7% for the control, 0U, 15U, and 30U treatments, respectively, with maximum and minimum mean values of 26.7 and 6.5%, respectively, corresponding to WFPS values of 67 and 16% (Fig. 2). As the summer season progressed, θ_g declined over time, due to evapotranspiration exceeding sporadic and infrequent rainfall, but θ_g increased following irrigation or substantial rainfall events. The average daily soil temperature (0.10 m depth) ranged from 13.2 to 25.6°C, following trends in the average daily air temperature, which ranged from 8.7 to 23.6°C (Fig. 2).

Surface soil pH became elevated following urine application and remained higher ($P < 0.01$) in plus-urine treatments, when compared with the control, until Day 86 (Fig. 3).

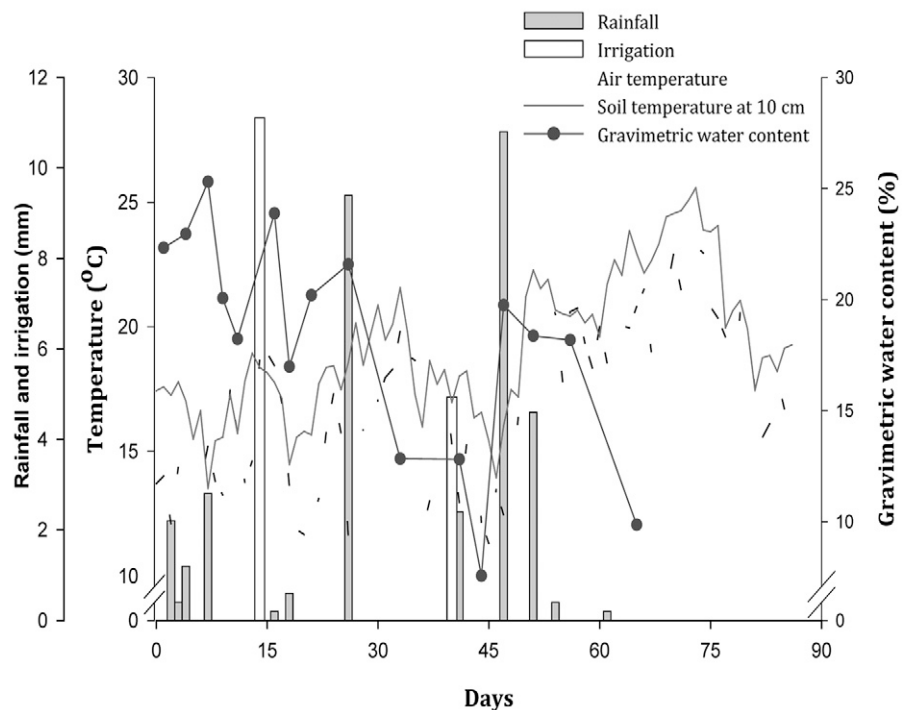


Fig. 2. Rainfall, soil and air temperatures over the 86-d experimental period at the meteorological station site 3 km from the trial site. Gravimetric water content values were determined from in situ sampling at the field site.

When comparing only the biochar-urine treatments, there was a trend for the soil surface pH to be higher with increasing biochar rate when sampled between Days 7 to 47, but statistically significant differences ($P \leq 0.05$) only occurred on Day 16 and between Days 38 to 47, when the 30U treatment had a surface soil pH higher than in the 0U treatment (Fig. 3). Soil bulk densities did not change significantly, despite the addition of biochar, with 0U, 15U, and 30U treatments having bulk densities (\pm standard deviation) of

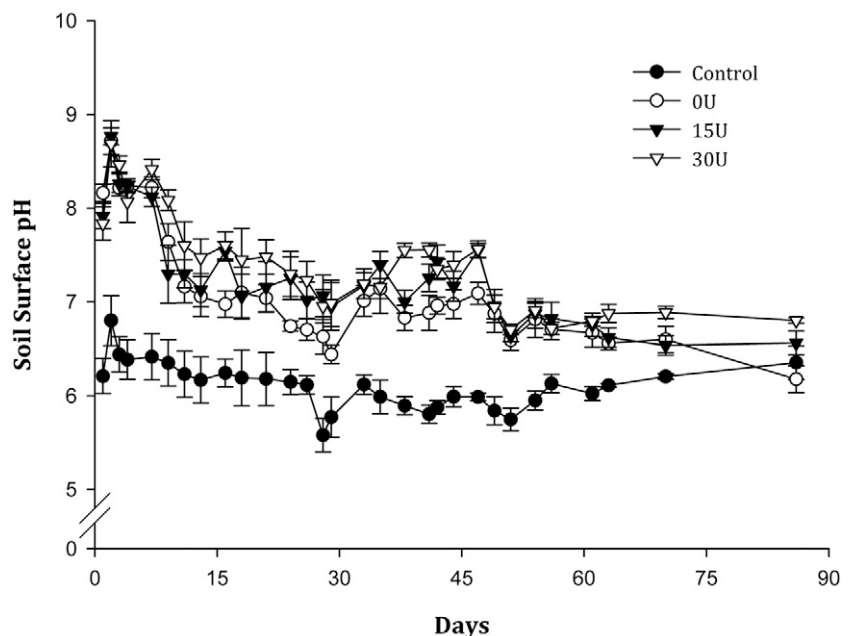


Fig. 3. Soil surface pH over time, following urine application (error bars \pm one standard error of the mean, $n = 5$).

1.29 (0.12), 1.29 (0.12), and 1.29 (0.10) Mg m⁻³, respectively.

The inorganic-N concentrations increased significantly ($P < 0.01$) with urine addition and NH₄⁺-N reached maximum mean concentrations of 180 to 234 µg g⁻¹ dry soil between Days 4 to 7 (Fig. 4). There was a trend for soil NH₄⁺-N concentrations to be higher with increasing rates of biochar-urine after Day 21, but this was not statistically significant ($P \geq 0.09$; Fig. 4). By Day 65, soil NH₄⁺-N concentrations were still elevated in the 30U treatment when compared with the 0U treatment ($P < 0.05$; Fig. 4). Mean soil NO₃⁻-N concentrations were significantly higher ($P < 0.05$) under biochar-urine treatments than in the control, from Day 9 onward, peaking at 72 µg g⁻¹ dry soil in the 0U treatment on Day 26. Between Days 11 to 44, there was a trend for soil NO₃⁻-N concentrations to be lower with increasing biochar rate and this was statistically significant on Days 11, 18, and 26 (Fig. 4).

Herbage Yields and Nitrogen Contents

No statistical differences in dry matter yield, due to treatment, occurred on Day 21, although the trend was for higher dry matter yield when urine was present (Table 3). By Day 43, dry matter yields were higher ($P < 0.01$) under biochar-urine treatments than in the control; but by Day 58, only the 15U treatment had a higher ($P < 0.05$) dry matter yield than in the control (Table 3). When comparing just the biochar-urine treated plots, increasing the biochar rate had no significant effect on dry matter yields (Table 3). There was insufficient growth for harvesting of dry matter at Day 86 when the final N₂O flux measurements were made.

At Day 21, only the herbage in the 0U and 15U treatments had a N level higher than in the control ($P < 0.05$); but by Days 43 and 58, all biochar-urine-treated herbage had higher ($P < 0.01$) N levels than in the control (Table 3). Comparing only the biochar-urine treatments, there were no significant differences in dry matter N percent as biochar rate was increased, at any time, although the trend was for lower N contents with increasing biochar rate on Days 21 and 43 (Table 3).

Nitrogen uptake by the herbage, a function of N percent and dry matter yield, was higher ($P \leq 0.05$), on all occasions, when urine was present, ranging from 1.3 to 9.0 g m⁻² (Table 3). The addition of biochar to the soil had no effect on N uptake in the presence of urine (Table 3).

The atom% ¹⁵N enrichment of the herbage in the control was at natural abundance, whereas in the biochar-urine treatments the atom% ¹⁵N enrichment was significantly higher ($P < 0.01$), ranging from 3.556 to 3.991 (Table 3). Recovery of applied ¹⁵N in the herbage did not vary due to the addition of biochar at any time with total ¹⁵N recovery in the herbage after 58 d, ranging from 14.3 to 17.5% (Table 3).

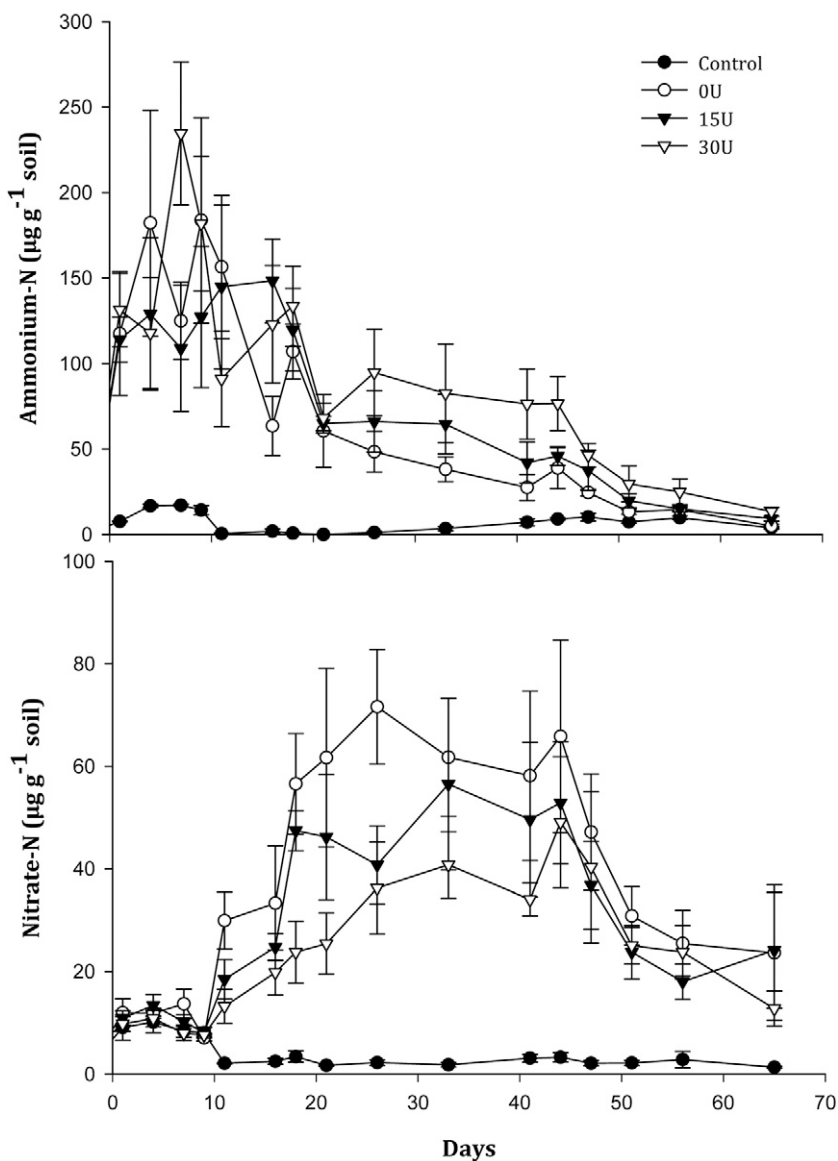


Fig. 4. Soil ammonium N and nitrate N concentrations over time, following urine application (error bars \pm one standard error of the mean, $n = 5$).

Nitrous Oxide Fluxes

Fluxes of N₂O were significantly higher ($P \leq 0.05$) than in the control when urine was present, in all or some of the biochar-urine treatments, from Days 1 to 35, and Days 44, 47, and 54 (Fig. 5a). Between Day 4 to approximately Day 35, when comparing only the biochar-urine treatments, there was a trend for N₂O fluxes to decrease with increasing rates of biochar, with N₂O fluxes from the 30U treatment being statistically lower ($P \leq 0.05$) than from the 0U treatment during this period on Days 4, 7, 13, 24, and 26 (Fig. 5a). The cumulative N₂O fluxes were higher under urine deposition when compared with the control. When the biochar-urine treatments were compared against each other, the N₂O fluxes from the 30U treatment were lower ($P < 0.05$) than in either the 0U or 15U treatments (Fig. 5b). When the mean cumulative N₂O-N fluxes were expressed as a percent of urine-N applied, the 0U, 15U, and 30U treatments had respective emissions of 0.15, 0.16, and 0.07%, with statistically lower emissions from the 30U treatment ($P < 0.05$). When expressed as an emission factor

Table 3. Biochar-urine treatment effects on dry matter yields, herbage N content, N uptake, ¹⁵N enrichment, and percent ¹⁵N recovery.

Variable	Day	Treatment†				ANOVA result	
		Control	0U	15U	30U	All treatments‡	Biochar-urine treatments only§
Dry matter yield (g m ⁻²)	21	153 ± 67	199 ± 40	199 ± 31	242 ± 41	ns¶	ns
	43	103 ± 15	224 ± 53	185 ± 57	182 ± 46	#	
	58	44 ± 15	91 ± 19	104 ± 31	82 ± 34	#	ns
Herbage N content (%)	21	2.7 ± 0.3	4.5 ± 0.3	4.5 ± 0.2	3.3 ± 1.8	#	ns
	43	2.5 ± 0.2	4.1 ± 0.3	3.9 ± 0.4	3.7 ± 0.2	*	ns
	58	2.9 ± 0.2	4.3 ± 0.3	3.9 ± 0.3	4.1 ± 0.4	*	ns
N uptake (g m ⁻²)	21	4.0 ± 1.7	8.87 ± 1.60	8.89 ± 1.07	8.28 ± 4.77	#	ns
	43	2.5 ± 0.3	9.03 ± 1.73	7.27 ± 2.84	6.70 ± 1.73	*	ns
	58	1.3 ± 0.5	3.88 ± 0.81	3.97 ± 1.01	3.30 ± 1.99	*	ns
Atom% ¹⁵ N	21	0.41 ± 0.02	3.62 ± 0.16	3.72 ± 0.11	3.55 ± 0.23	*	ns
	43	0.38 ± 0.01	3.94 ± 0.06	3.99 ± 0.10	3.89 ± 0.09	*	ns
	58	0.38 ± 0.01	3.72 ± 0.14	3.77 ± 0.12	3.69 ± 0.10	*	ns
¹⁵ N recovery (%)	21	–	6.85 ± 1.24	7.05 ± 0.99	6.11 ± 3.53	–	ns
	43	–	7.63 ± 1.49	6.26 ± 2.54	5.60 ± 1.53	–	ns
	58	–	3.09 ± 0.75	3.20 ± 0.82	2.60 ± 0.94	–	ns

* *P* < 0.05.† Treatments: Control (nil urine and nil biochar); 0U (urine and nil biochar); 15U (urine and biochar at 15 t ha⁻¹); 30U (urine and biochar at 15 t ha⁻¹).

‡ ANOVA comparing all treatments.

§ ANOVA comparing only the urine treatments (0U, 15U, and 30U). Error beside mean values equals ± standard error of the mean.

¶ ns, not significant.

P < 0.10.

(N₂O-N from the biochar-urine treatment in question, minus the N₂O-N from the control, divided by the urine-N applied), the 0U, 15U, and 30U treatments had mean emission factors of 0.12, 0.13, and 0.04%, respectively.

As anticipated, the ¹⁵N enrichment of the N₂O from the urine-¹⁵N treated plots remained higher than in the control treatment throughout the entire period of the study (Fig. 6). When comparing the biochar-urine treatments, there was a trend for the atom% ¹⁵N enrichment of the N₂O to be lower with increasing rates of biochar from Day 11 to 33, and this was statistically significant (*P* ≤ 0.05) on Days 16 and 28 (Fig. 6). The mean percent recovery of ¹⁵N applied, as N₂O-N, equated to 0.86 (0.43), 0.88 (0.84), and 0.23% (0.10) (standard deviation in brackets), with no statistical difference between these values (*P* = 0.15).

Discussion

Increases in soil surface pH, and the duration of the pH increase, were typical of what is expected following ruminant urine deposition onto pasture (Jarvis and Pain, 1990). This increase occurs due to urea hydrolysis, whereas the subsequent decline in pH is a result of H⁺ ions being released during ammonia (NH₃) volatilization (Sherlock and Goh, 1984) and nitrification (Wrage et al., 2001).

Elevation of soil NH₄⁺-N concentrations resulted from the hydrolysis of urine-derived urea. The small increase in soil NH₄⁺-N concentrations in the control treatment (water only) was possibly due to mineralization of organic matter. Soil NH₄⁺ is in chemical equilibrium with aqueous NH₃ in the soil and significant volatilization of NH₃ may occur when the soil pH is elevated (>7.0), as occurs under urine patches. Loss of NH₃ was not measured in the current experiment and we can only speculate the NH₃ loss amount. For urine patches in grazed

pastures, NH₃ loss is commonly thought to be 10 to 20% of urine-N deposited (Sherlock et al., 2008). The remaining soil NH₄⁺ pool can be taken up by pasture plants, become immobilized by soil microbes, or be oxidized further to NO₃⁻-N. The latter process explains the observed increase in soil NO₃⁻-N concentrations under the biochar-urine treatments.

In this current study, biochar addition clearly influenced soil inorganic-N dynamics, with lower NO₃⁻-N concentrations at the highest rate of biochar (30U), when compared with the 0U treatment, and trends for higher NH₄⁺-N under the 30U treatment. It is well recognized that biochar materials are able to promote adsorption of NH₃ (Clough and Condon, 2010; and references therein). Thus, biochar in the soil under a urine patch potentially creates a sink for the NH₃. We propose that one possible mechanism for the reduced NO₃⁻ concentrations and lower N₂O emissions observed under the 30U treatment was the uptake and adsorption of NH₃ by the biochar. Adsorption of urinary-derived NH₃ by the biochar would have increased with increasing biochar rate. This would serve to reduce the soil NH₄⁺-N pool available to nitrifiers and the NO₃⁻-N pool subsequently formed. If such adsorbed NH₃ is extractable with 2M KCl, it would explain the observed trend for higher NH₄⁺-N concentrations at the highest biochar rate (30U).

A further factor demonstrating that biochar altered the soil inorganic-N pool was the reduced ¹⁵N enrichment of the N₂O flux in the 30U treatment, indicating that the source of the inorganic-N that the N₂O was derived from came from an inorganic-N pool with a lower proportion of urine-N than in the 0U treatment.

Thus, we propose that under the highest rate of biochar, NH₃ formation and its subsequent adsorption onto and/or into the biochar reduced the inorganic-N pool available for

nitrifiers and thus NO_3^- -N concentrations were reduced. Then, since the NO_3^- -N pool had a lower concentration, the ^{14}N dilution arising from soil mineralization was relatively greater, thus lowering the ^{15}N enrichment of the N_2O source pool(s). Consistent with this is the lower N_2O flux from the 30U treatment, as a percent of urine-N applied, and as a cumulative N_2O flux. Soil N_2 fluxes were not measured in this study and the relatively alkaline nature of biochar, when compared with soil, may possibly have favored further reduction of N_2O to N_2 . This could explain a lower N_2O flux but not the differences in ^{15}N enrichment observed.

An alternative theory to explain lower soil NO_3^- -N concentrations in the presence of biochar was drawn by Singh et al. (2010), following the incorporation of either poultry- or woodchip-derived biochar to soil columns and a 5-mo incubation with three wetting-drying cycle differences in NH_4^+ -N and NO_3^- -N leaching being observed. Singh et al. (2010) concluded that these differences could have been due to increases in the sorptive properties of the biochars. Other studies have demonstrated increases in soil cation exchange capacity (CEC) over longer periods (600–8700 yr) due to the oxidation of biochar surfaces or the adsorption of organic matter to the biochar particles (Liang et al., 2006). It seems unlikely that after only 14 mo such mechanism would have occurred, but these cannot be ruled out and future studies need to examine short-term changes in CEC.

Chemicals that inhibit nitrification lead to a prolonged occurrence of NH_4^+ -N in the soil and lower NO_3^- -N concentrations—a trend observed in the 30U treatment in the current study. It has been previously noted that biochar contains volatile organic compounds (VOCs) that are known nitrification inhibitors. For example, Clough et al. (2010) found α -pinene in an unweathered biochar. In the current study, ethanol was the only VOC detected in the biochar before its incorporation into the soil, which was several months before urine deposition. Thus, it is assumed that the effect of ethanol, if any, would have been negligible by the time urine was applied. Other nonvolatile microbially inhibiting compounds may have existed in the biochar. Spokas et al. (2010) hypothesized that ethylene, a known microbial inhibitor, was microbially produced from biochars and that ethylene may be the cause of the observed changes in microbial dynamics and

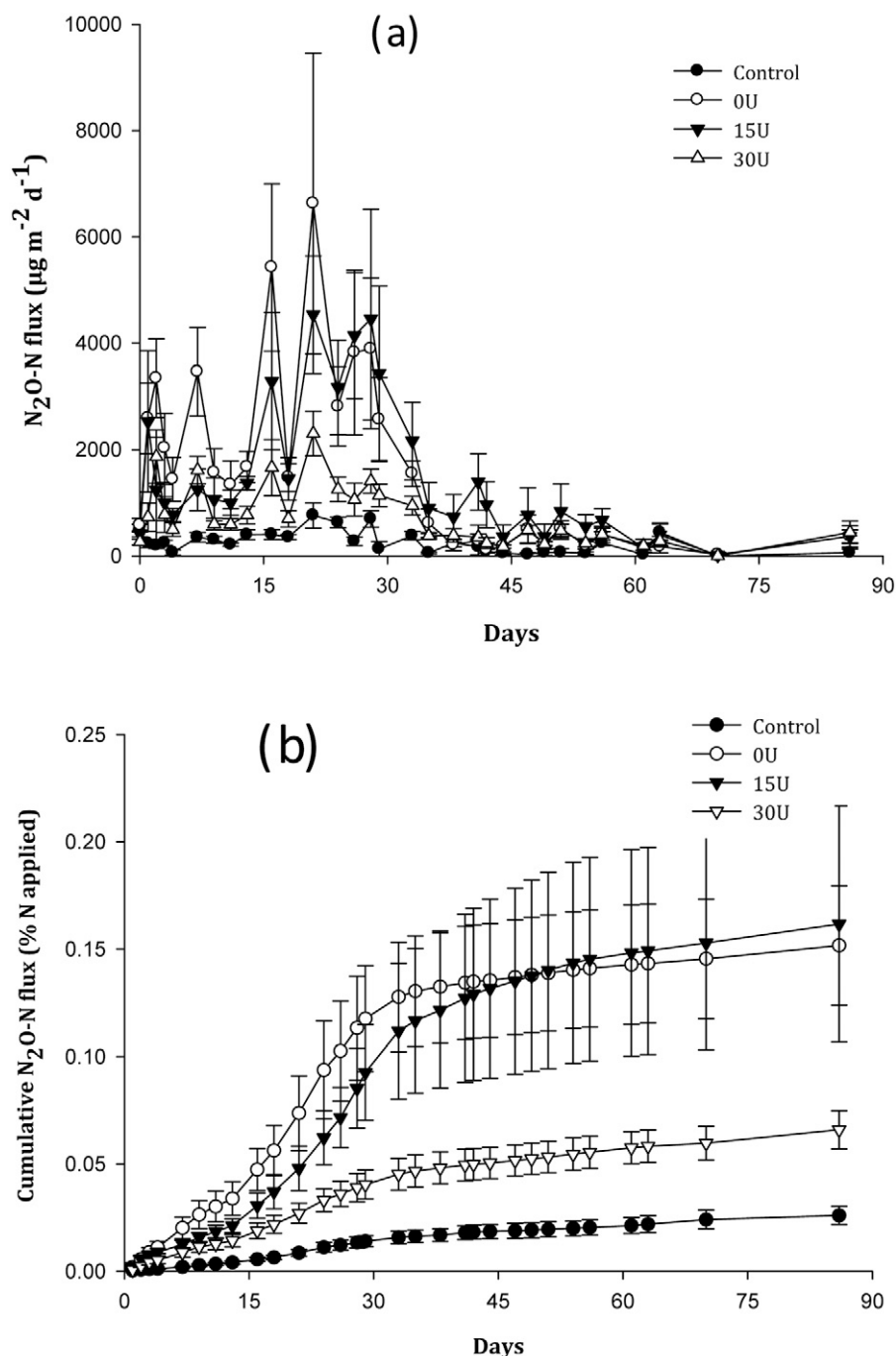


Fig. 5. (a) Geometric mean nitrous oxide emissions from different treatments following urine application (error bars \pm one geometric standard error of the mean, $n = 5$); (b) Nontransformed cumulative loss of N_2O from urine-treated soils, showing the amount of N emitted as N_2O -N as a percent of the total N applied to the plots. Nil urine is also plotted to show control emissions. (Error bars \pm one standard error of the mean, $n = 5$).

N_2O suppression. This interesting theory needs testing with respect to longevity of ethylene production in the soil. The biochar in the current study had been in the soil for approximately 7 mo (May–November) before urine treatment.

The addition of fire-derived charcoal to forest soils has been shown to enhance native soil organic matter mineralization (Wardle et al., 2008a), albeit in forest soils, highlighting the current lack in our understanding of how biochar might affect native soil C pools (Wardle et al., 2008b). At the high rate of biochar used here, the dilution of the ^{15}N pool, supplying

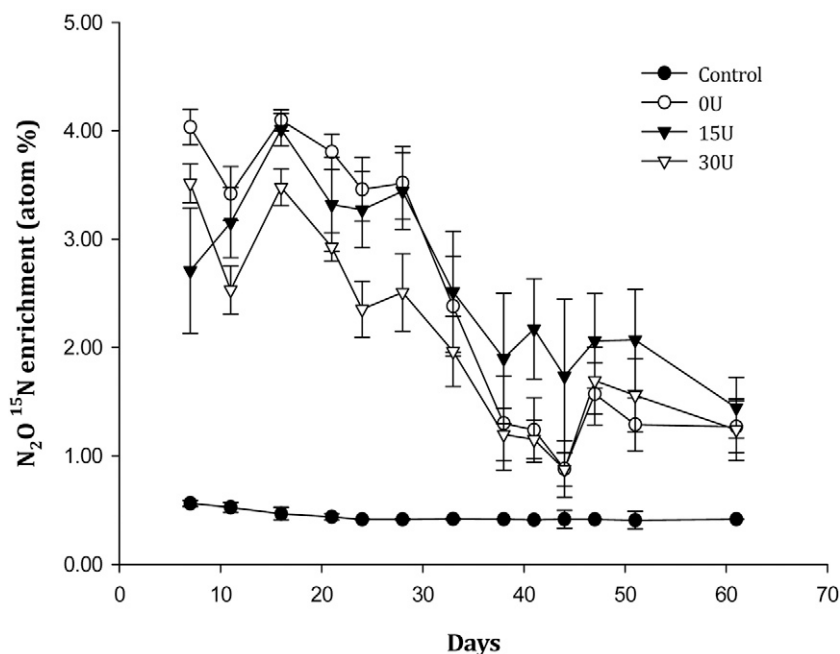


Fig. 6. Nitrous oxide ¹⁵N atom% enrichment determined for treatments (error bars \pm one standard error of the mean, $n = 5$).

the N₂O flux, could potentially have occurred as a result of enhanced mineralization of soil organic matter. But had this been the case, we might have expected to observe an increase in the size of the inorganic-N pool under the 30U treatment and this was not observed.

The soil microbial-¹⁵N pool was not measured in the current study and this should be included in future studies to further elucidate the mechanisms of biochar perturbation of the N cycle.

Soil moisture conditions were consistent with summer soil conditions, and given that denitrification is expected to dominate at WFPS values >60%, the soil moisture conditions (WFPS range of 16–67%) predominantly favored nitrification mechanisms as N₂O-forming pathways. However, denitrification and nitrifier-denitrification may still operate at anaerobic microsites under aerobic soil conditions (Müller et al., 2004; Russow et al., 2009). During Days 15 to 35, when the N₂O-¹⁵N enrichment was generally less in the 30U treatment, there was also considerable rainfall or irrigation, and the highest N₂O fluxes occurred. Denitrification of NO₃⁻-N as an N₂O production mechanism is definitely plausible under these conditions. As a percent of the urine-N applied, the cumulative N₂O fluxes were low when compared with the New Zealand specific N₂O emission factor for urine-N, which is currently set at 1.0% of urine-N excreted (Kelliher et al., 2005) and with other studies as noted below. This was most likely a function of the drier summer soil conditions, despite the irrigation, and this study needs to be repeated under winter conditions to see if similar reductions in cumulative N₂O emissions occur under the 30U treatment.

The fact that dry matter yields were not detrimentally affected by biochar addition indicates that there are no apparent negative effects of biochar incorporation under the conditions of this trial. The lower percent N of the dry matter harvested from the 30U treatment on Day 21 is consistent with what was seen in the inorganic-N pool at this time, with less inorganic-N

equaling less N uptake at this time. Had this been under a grazing regime, this would have produced a positive feedback since lower dry matter N would have resulted in lower dietary N intake and subsequent urine-N excretion. Lower rates of urine-N excretion would reduce subsequent derived N₂O emissions.

Surprisingly, the addition of biochar did not translate into statistically different soil bulk densities. At the highest rate of biochar (30 t ha⁻¹), the area of the soil-sampling core, used to determine bulk density, would have received 12.6 g of biochar, which at its measured bulk density of 0.4 Mg m⁻³ equates to 3.13 × 10⁻⁵ m³ of biochar. Assuming all this was equally distributed within the target depth of 0.10 m, the soil bulk density core, with a depth of 0.075 m, could have contained 2.35 × 10⁻⁵ m³ of biochar. A theoretical bulk density under such ideal mixing, and using the nil biochar soil as a reference, would equal 1.23 Mg m⁻³, which is within one standard deviation of the bulk density determined at 30 t ha⁻¹. Thus, further replication of the bulk density sampling, or changes in the method, are required if changes in bulk

density at biochar rates up to 30 t ha⁻¹ are to be determined. It should be noted, however, that even a change in soil bulk density from 1.30 to 1.23 Mg m⁻³ is sufficient to potentially affect soil processes.

Under the field conditions experienced here, the addition of biochar at 30 t ha⁻¹ reduced cumulative N₂O emissions by approximately 50% relative to the urine-only treatment (Fig. 5b). Due to the relatively dry season, the N₂O emissions, expressed as a percent of N applied, were relatively low (0.2% of N applied). To provide some context, Clough et al. (2009) found N₂O emissions ranged from 1.3 to 1.7% of urine-N applied over 78 d following almost identical rates of urine-N application, under similar soil and pasture conditions, after applying urine in midfall, whereas Van Groenigen et al. (2005) reported a 1.4% loss as being typical. Nevertheless, once N₂O fluxes from the controls are considered, the 30 t ha⁻¹ treatment yielded a N₂O emission factor of just 0.04% compared with 0.12% from the urine-only treatment. Thus, 30 t ha⁻¹ of biochar reduced the N₂O emission factor from urine by around 70%. The lower soil NO₃⁻ concentrations under the 30 t ha⁻¹ biochar treatment suggest that had NO₃⁻ leaching occurred, there would have been lower NO₃⁻ losses at this rate of biochar used. These results are strongly encouraging from an environmental viewpoint and warrant further intensive work under winter conditions when leaching and N₂O emissions are higher. In summary, this study has demonstrated that biochar can reduce N₂O emissions from ruminant urine patches in situ. Thus, if other studies confirm the relatively long residence time expected of biochar in the soil, then the “win-win” situation of both sequestering C while reducing N₂O emissions may prove achievable. However, further study is still required to determine seasonal effects and the effects of repeated deposition onto soil-biochar matrices, which vary with biochar size, rate, and soil type.

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