Science of the Total Environment 543 (2016) 601–608

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

The effect of lignite on nitrogen mobility in a low-fertility soil amended with biosolids and urea

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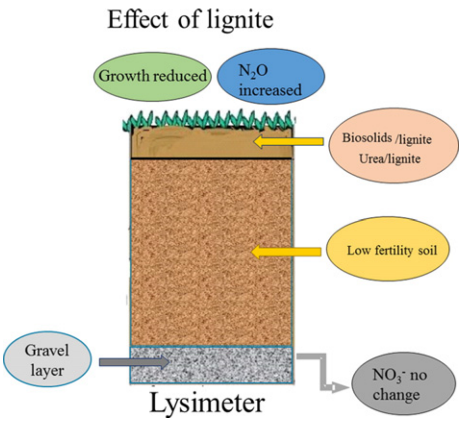
HIGHLIGHTS

- Lignite reduces the beneficial effects of urea and biosolids on plant growth.
- Lignite has minimal effect on nitrate leaching and plant metal uptake.
- Lignite exacerbates nitrous oxide emissions from soil.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 July 2015
Received in revised form 16 November 2015
Accepted 16 November 2015
Available online 23 November 2015

Editor: D. Barcelo

Keywords:
Black urea
Coal
Fertilizer
Lysimeter
Sewage sludge

ABSTRACT

Lignite has been proposed as a soil amendment that reduces nitrate (NO_3^-) leaching from soil. Our objective was to determine the effect of lignite on nitrogen (N) fluxes from soil amended with biosolids or urea. The effect of lignite on plant yield and elemental composition was also determined. Batch sorption and column leaching experiments were followed by a lysimeter trial where a low fertility soil was amended with biosolids (400 kg N/ha equivalent) and urea (200 kg N/ha equivalent). Treatments were replicated three times, with and without lignite addition (20 t/ha equivalent). Lignite did not reduce NO_3^- leaching from soils amended with either biosolids or urea. While lignite decreased NO_3^- leaching from an unamended soil, the magnitude of this effect was not significant in an agricultural context. Furthermore, lignite increased cumulative N_2O production from soils receiving urea by 90%. Lignite lessened the beneficial growth effects of adding biosolids or urea to soil. Further work could investigate whether coating urea granules with lignite may produce meaningful environmental benefits.

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http://dx.doi.org/10.1016/j.scitotenv.2015.11.075
0048-9697/

1. Introduction

Countries with sewage treatment plants produce approximately 27 kg (dry mass) of biosolids (sewage sludge) per person per year (Hue, 2014). Biosolids can be used to rebuild low-fertility or degraded soils (Rigby and Smith, 2013; Robinson et al., 2011), but may have detrimental effects through contributing to nitrate (NO_3^-) leaching (Correa et al., 2006b) and due to accumulation of heavy metals in both soils and plants (Civeira and Lavado, 2008). Most nitrogen (N) in biosolids is present as organic N, which only oxidizes slowly, but there are often high concentrations of ammonium (NH_4^+) and NO_3^- (Correa et al., 2006a). This can result in a large flush of NO_3^- leaching if sufficient rainfall occurs shortly after application. High concentrations of NO_3^- in soil can also result in large emissions of N_2O (Di and Cameron, 2002), a greenhouse gas that has a global warming potential 298 times that of CO_2 (Ravishankara et al., 2009).

Knowles et al. (2011) reported that NO_3^- leaching from biosolids applied to soil could be mitigated by mixing the biosolids with biochar, produced by pyrolyzing wood-waste. However, biochar is not available in sufficient quantities for large-scale commercial operations and thus it is currently expensive (US\$200–US\$500) per ton (Kulyk, 2012). Lignite, a low grade coal (Kabe et al., 2004) may be an alternative option for reducing NO_3^- leaching from biosolids. Lignite is globally abundant with ca. 195×10^9 t of proven and recoverable lignite resources, (WEC, 2010) including 333×10^6 t located in New Zealand. Lignite has a similar structure to many biochars (Kwiatkowska et al., 2008). Typically, biochar comprises 54.9% carbon (C), 2.14% hydrogen (H), 4.97% N and 20.04% oxygen (O) (Ozcimen and Karaosmanoglu, 2004), whereas lignite has 65% C, 5% H, 1.2% N and 27.8% O (Janos et al., 2011). Lignite has a greater number of organic functional groups than biochar, with a resultant higher Cation Exchange Capacity (CEC) 20–70 $cmol_c$/kg (Wong et al., 1996), compared to 20–35 $cmol_c$/kg for a typical biochar (Gundale and DeLuca, 2007). The higher CEC of lignite may provide greater retention of NH_4^+ and thus the lower the potentially for NO_3^- leaching loss.

There is a paucity of scientific research examining the effects of unmodified lignite on NO_3^- leaching. Commercially, however, lignite has been combined with urea $CO(NH_2)_2$ and sold as "black urea"(Ferguson, 2002). In South Africa, van Vuuren and Claassens (2009), have reported that in pot trials and field trials the yield of maize (*Zea mays* L.) increased by 20–46% when "black urea" was applied and compared with standard urea. They also showed that 10–20% and 30–50% less "black urea" was required than normal urea was required when applied as topdressing on an alkaline and acidic soil respectively. ARTH (2009) reported that the fertilizer requirements of field grown maize were reduced by 15–35% when "black urea" and "black DAP (lignite coated di-ammonium phosphate fertilizer) were applied, compared to the uncoated fertilizers. There is little scientific validation of these claims. In contrast, there are many studies demonstrating heavy metal sorption by lignite (Domańska and Smolinska, 2012; Doskocil and Pekar, 2012; Jezierski et al., 2000). Qi et al. (2011) showed that lignite mixed with dewatered biosolids sludge could reduce heavy metal leaching. Simmler et al. (2013) also demonstrated that lignite could reduce plant cadmium (Cd) uptake from biosolids-amended soils. Lignite may also offset potentially toxic effects of high copper (Cu) and zinc (Zn) concentrations (Lafferty and Hobday, 1990) that are typically found in biosolids and which can accumulate in a soil. We aimed to evaluate the combined effect of lignite amendments on both N and trace metal mobility in a soil..

We hypothesised that incorporating lignite into soils amended with biosolids would (i) reduce N leaching as a result of increased CEC and (ii) reduce the plant uptake of heavy metals. These hypotheses were tested using batch studies, column-leaching studies and a lysimeter experiment.

2. Materials and methods

2.1. Soil

Lismore Stony Silt Loam (NZ classification: Pallic Orthic Brown Soil) was collected (0–30 cm depth) from the Ashley Dene sheep farm at Lincoln University (43°39′05.82″S 172°19′41.47″E), New Zealand. The low-fertility Lismore soil (Table 1) was formed from gravelly glacial outwash gravels and has a variable depth of silty loess deposited at the surface. The soil was air-dried to a gravimetric moisture content (θ_g) of 11.9% and sieved to <2 mm. Table 1 gives the chemical properties of the soil.

2.2. Biosolids

Biosolids were obtained from the Kaikōura Regional treatment works (42°21′47.78″S 173°41′20.32″E), New Zealand. Some 160 kg of stockpiled and weathered biosolids were collected and homogenized using a concrete mixer and passed initially through a 20 mm sieve. A 2 kg sub-sample was then passed through a 2 mm nylon sieve. Biosolids θ_g equalled 53%. Table 1 gives the properties of the biosolids.

2.3. Lignite

Three types of powdered lignites were provided by Solid Energy New Zealand Ltd. The New Vale lignite (NV), a low calorific value lignite, was sourced from an open cast mine in Southland, New Zealand, (46°08′23.80″S 168°45′11.62″E), the Charleston lignite, was sourced from Charleston open cast mine near Charleston, West Coast, New Zealand (41°54′51.77″S 171°25′58.62″E), and the Millerton lignite, was sourced from the Millerton section of the Stockton open cast mine on the West Coast, New Zealand (41°39′47.67″S 171°51′52.17″E). The lignites were sorted on a crusher with an air swept classifier, which separated the lignite particles based on size (Simmler et al., 2013). Table 1 shows the chemical properties of the respective lignites.

The pH of the soil, biosolids and lignites was determined in water using a sample: water ratio (w/w) of 1:2.5 following the method of Blakemore et al. (1987), using a Mettler Toledo, GmbH, Switzerland. Carbon (C) and N concentrations were determined using an Elementar Vario MAX CN analyser (Elementar GmbH Germany). The CEC was measured with the silverthiourea method described by Blakemore et al. (1987). Extractable NH_4^+ and NO_3^- concentrations in the soil and biosolids were determined with a 2 M KCl extract following the method of Blakemore et al. (1987) and Clough et al. (2001).

Water soluble C (WSC) was determined using cold (20 °C) and hot (80 °C) water extracts (Ghani et al., 2003). To measure WSC, 3 g of oven dried material and 30 mL of cold distilled water were placed in polypropylene centrifuge tubes on an end-over-end shaker for 30 min and then centrifuged for 20 min at 2253 *g*. The extracts were then decanted off and filtered through 0.45 μm cellulose nitrate membrane filters. The sample remaining in the centrifuge tube had a further 30 mL of distilled water added before it was then placed in a hot water bath at 80 °C for 16 h, where after it was centrifuged and filtered as before. Total carbon (TC), inorganic carbon (IC) and total organic carbon (TOC) concentrations of the WSC samples were measured using a TOC-5000A analyser (Shimadzu Oceania Pty Ltd., NSW, Australia).

Element concentrations were measured in acid digests by the ICP-OES (Varian 720-ES, Melbourne, Australia). Samples (0.5 g dry weight) of soil, lignites, biosolids or pasture (harvested from the lysimeters) were digested in 5 mL HNO_3/1 mL H_2O_2 (Merck hydrogen peroxide 30%) at 175 °C for 20 min. The digest was diluted with deionized water (Milli Q, Barnstead, EASYpure RF, 18.2 MΩ-cm) to a volume of 25 mL and filtered through a Whatman 52 filter paper (Simmler et al., 2013). A Wageningen reference soil (ISE 989) and plant (IPE 100) material were analysed for quality assurance (van Dijk and Houba, 1998).

Table 1
Physicochemical properties of the materials used in the experiments. Values represent the mean ($n = 3$) except pH (median). Values in brackets are the standard error of the mean. Values with the same letter are not significantly different at the 5% level (ANOVA with Fisher's test).

	Lismore stony silt loam	Biosolids	Lignites		
			New Vale	Charleston	Millerton
pH (H_2O)	6.3	4.5	4.5	4.1	3.4
Moisture %	11.8 (0.02)^d	48.7 (0.008)^a	38 (0.36)^c	47.9 (0.38)^b	1.2 (0.002)^e
NH_4^+(mg/kg)	7.9 (2.9)^b	130 (7.3)^a	n/a	n/a	n/a
NO_3^-(mg/kg)	181 (10.8)^b	1352 (2.5)^a	n/a	n/a	n/a
CEC ($cmol_c$/kg)	12.6 (0.2)^d	16.7 (0.7)^b	43.6 (0.8)^a	14.7 (0.2)^c	2.1 (0.3)^e
Base saturation (%)	45.5 (1.5)^c	106.9 (2.3)^b	115.3 (0.5)^b	125.2 (2.5)^a	15.3 (4)^c
Bulk density (g/cm^3)	1.1	0.7	0.6	0.8	0.7
Total C (g/kg)	48.3 (3.7)^e	296 (4.9)^d	862 (3.6)^a	558 (13.7)^b	515 (6)^c
Total N (g/kg)	3.8 (0.08)^d	30.7 (0.6)^a	12.4 (0.08)^b	8.7 (0.4)^c	9.2 (0.2)^c
C/N	12.9 (0.1)^d	9.7 (0.2)^e	69.8 (0.3)^a	64.5 (1.8)^b	56.3 (0.4)^c
Water soluble carbon-cold (WSC) (mg/kg)	382 (2)^b	n/a	901(30)^a	203 (8)^c	3.4 (3)^d
Water soluble carbon-hot (WSC) (mg/kg)	728 (17)^b	n/a	3028 (63)^a	1026 (4)^b	77 (4)^c
P (mg/kg)	991.2 (21)^b	3463 (248)^a	57.6 (0.2)^d	478.3 (50)^c	4.2 (0.3)^d
S (mg/kg)	486.7 (5)^c	6736 (450.2)^b	6539 (35)^b	6180 (589)^b	13,799 (455)^a
Ca (mg/kg)	5393 (216)^c	9455 (534)^b	17,502 (119)^a	1850 (190)^d	51.9 (1.1)^e
Mg (mg/kg)	1638 (68)^c	2994 (55)^a	2815 (11)^b	779.4 (85)^d	13.4 (0.8)^e
K (mg/kg)	2330 (102)^b	3014 (173)^a	219 (2)^c	295 (21)^c	30.8 (1.6)^d
Na (mg/kg)	160 (9.1)^b	299 (12)^a	176 (1.1)^b	94 (3.7)^c	69 (1.5)^d
Al (mg/kg)	23,371 (865)^a	17,351 (500)^b	2488 (44.7)^c	3629 (48.9)^c	134 (1.3)^d
B (mg/kg)	7.0 (0.2)^{cd}	nd	36.3 (0.1)^b	211.2 (24)^a	23.4 (0.6)^{bc}
Cu (mg/kg)	7.3 (0.1)^b	637.3 (39)^a	2 (0)^b	3.85 (0.4)^b	1.9 (0.0)^b
Cd (mg/kg)	0.17 (0.001)^b	2.3 (0.1)^a	0.06 (0.007)^c	0.1 (0.0)^{bc}	0.04 (0.0)^c
Fe (mg/kg)	18,186 (450)^a	8352 (221)^c	12,918 (145)^b	3490 (198)^d	1704 (184)^e
Mn (mg/kg)	355 (1)^a	189 (2.2)^c	280 (3)^b	30.3 (2)^d	1.45 (0.1)^e
Zn (mg/kg)	81 (3)^b	1047 (69)^a	9 (1)^c	20 (2.2)^c	35.5 (1.2)^{bc}

nd — not detected; n/a — not analysed.

2.4. Batch sorption experiments

Batch sorption experiments were carried out with the three lignites using an ambient (matrix) solution of 0.01 M $CaCl_2$ solution containing 100 mg/L NH_4^+ [pH 5.1 as $(NH_4)_2SO_4$)] or NO_3^- (pH 7.0 as KNO_3) following the method of Wang et al. (2010). Samples (20 g of dry matter) were weighed into 250 mL centrifuge tubes, replicated thrice. Controls were prepared with no sample addition. Then 200 mL of either the $(NH_4)_2SO_4$ or KNO_3 solution was added and the samples were placed on an end-over-end shaker for 6 h. Previous experiments had indicated that this was the minimum time required to reach an approximate equilibrium between the solution and the material (data not shown). Based on the sorption experiments, the NV lignite was selected for further experimentation because it had the highest CEC (Table 1) and showed the greatest capacity to sorb NH_4^+.

The effect of pH on sorption was determined for the NV lignite. Batch sorption experiments used NV lignite (10 g) and the $CaCl_2$–$(NH_4)_2SO_4$ solution at a ratio of 1:10. The pH values of these mixtures were adjusted by adding 50 μL, 100 μL, 125 μL, 150 μL, 175 μL, 200 μL and 250 μL of 10 M KOH to give pHs of 4.4, 4.9, 5.2, 5.5, 6.0, 6.3, and 6.7, respectively. After agitation, the samples were centrifuged at 1862 *g* for 10 min and filtered (Whatmann 52), then analysed for residual NH_4^+ concentrations using flow injection analysis (FIA; Alpkem FS 3000 twin channel analyser, Texas, USA).

2.5. Column leaching experiments

Leaching columns (4 cm height × 4 cm diameter), with an internal volume of 50.3 mL, were filled with mixtures of biosolids (sieved to <2 mm), NV lignite (<1 mm) and quartz sand (<1 mm) and maintained at 20 °C. The total dry weight of the materials added was 30 g. The biosolids ratio (by weight) was 5 parts in each treatment, lignite was added at 0, 1, 2, 3, 4, 5 g and the total weight brought to 30 g by adding appropriate weights of quartz sand. Each column was irrigated daily with 5 mL of deionized water. Column bulk densities ranged between 1.1 g/cm^3 and 1.5 g/cm^3. The eluent was collected weekly and analysed

Fig. 1. *Left*—Installation of lysimeters; *Right*: Gas chambers just before the gas collection.

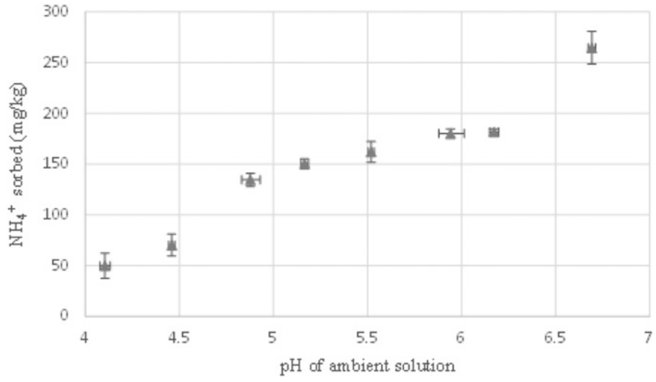

Fig. 2. NH_4^+ sorbed (mg/kg) by the NV lignite from a 100 mg/L NH_4^+ solution at various solution pH values. Material: solution ratio 1:10. Bars represent the standard error of the mean (n = 3).

for both NO_3^- and NH_4^+ concentrations using FIA. Columns were leached under laboratory conditions (20 °C) for at least three months, or until the NH_4^+ and NO_3^- concentrations in the eluent had stabilized at levels ≤ 5% of the concentrations recorded in the initial flush.

Data were analysed using Minitab® 16 (Minitab Inc., State College, Pennsylvania, USA). Data sets were analysed using ANOVA with Fisher's Least-Significant-Difference post-hoc test to compare means. The level of significance was 0.05.

2.6. Lysimeter field experiment

2.6.1. Lysimeter setup

Eighteen undisturbed soil monolith lysimeters 0.5 m in diameter, and 0.7 m deep, containing Lismore stony soil, were taken from the Ashley Dene sheep farm Canterbury, New Zealand (43°39′05.82″S 172°19′ 41.47″E). The lysimeters were installed at the Lincoln University Field Service Centre (Fig. 1). The design of lysimeter castings and method of sampling is described in detail by Cameron et al. (1992).

There were six treatments, each replicated three times. Biosolids, NV lignite and urea were applied separately at rates of 400 kg N/ha, 20 t/ha and 200 kg N/ha respectively. A further three treatments consisted of either biosolids + lignite, urea + lignite and a control with no addition applied.

The application of each treatment occurred on the 16th of May 2012. To stimulate biosolids amendment to soil, the top 10 cm of soil in each lysimeter was removed and mixed with the applicable treatment in a concrete mixer for one minute. The control lysimeters were treated in an identical manner. Following treatment applications 0.5 g of tetraploid perennial ryegrass (*Lolium perenne* L. var. Bronsyn) was broadcast by hand over each lysimeter. Ten litre containers were installed at the base of the lysimeters for leachate collection.

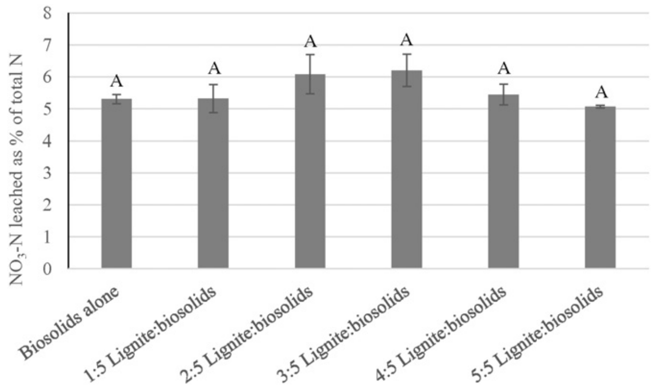

Fig. 3. NO_3^-–N leached, as a percentage of N applied, from columns with NV lignite mixed with biosolids. Number ratios indicate the mass of lignite (g): mass of biosolids (g). Bars represent the standard error of the mean (n = 3). Bars with the same letter are not significantly different at the 5% level (ANOVA with Fisher's test).

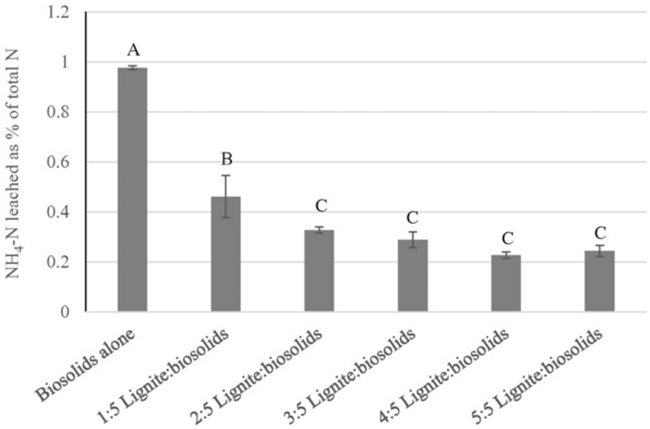

Fig. 4. NH_4^+–N leached, as a percentage of N applied, from columns with NV lignite mixed with biosolids. Number ratios indicate the mass of lignite (g): mass of biosolids (g). Bars represent the standard error of the mean (n = 3). Bars with the same letter are not significantly different at the 5% level (ANOVA with Fisher's test).

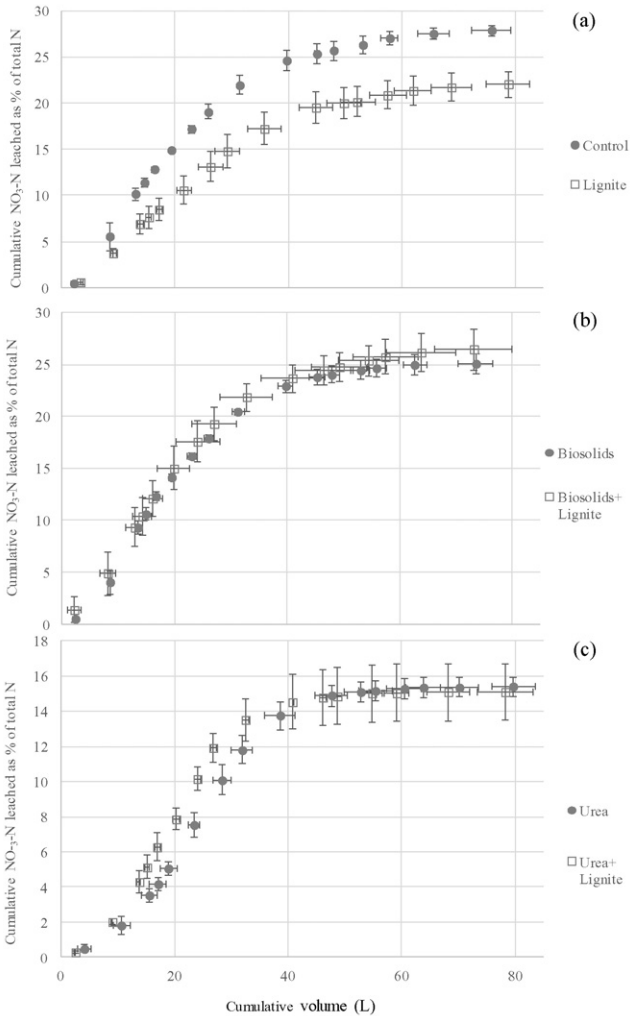

Fig. 5. Cumulative NO_3^-–N leached as percentage of total N applied in each lysimeters. (a) comparison of lignite treatment with control lysimeters, (b) biosolids treatment with biosolids + lignite treatment lysimeters, (c) urea treatment with urea + lignite treatment lysimeters.

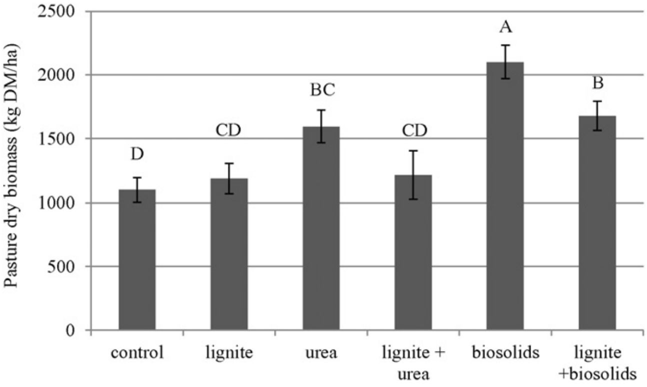

Fig. 6. Total biomass (DM) of pasture harvested from each lysimeter, calculated per hectare. Bars represent the standard error of the mean (n = 3). Bars with the same letter are not significantly different at the 5% level (ANOVA with Fisher's test).

2.7. Sample collection

2.7.1. Leachate

Lysimeter drainage was collected bi-weekly or more frequently following heavy rain. The volume of drainage was measured and a 70 mL subsample taken and stored immediately in a freezer for subsequent analysis of both NO_3^- and NH_4^+ using FIA.

2.7.2. Herbage

Herbage was harvested on three occasions (28th of Sep 2012, 16th of Jan 2013 and 15th of Mar 2013) when pasture reached typical pre-grazing levels of dry mater (DM). Hand shears were used to clip the pasture to a height of 2 cm.

2.8. Climate and irrigation

Simulated rainfall was applied (if required) to all lysimeters to supplement a shortage of natural rainfall with the aim of meeting the 75th percentile of rainfall based on a 25 years rainfall record.

2.9. Gas sampling—collection and analysis

2.9.1. Soil moisture and temperature

The average soil water content in the lysimeter (0–15 cm depth) was measured using a Hydrosense moisture probe (15 cm) (Campbell Scientific, Utah, USA). Soil temperature was recorded using a 107-L temperature sensor (Campbell Scientific, Utah, USA) to measure the soil temperature at 7.5 cm depth. A data logger (CR23X, Campbell Scientific, Utah, USA) was used to collect soil moisture and temperature information every ten minutes during the N_2O measurement periods, while hourly and daily averages were also recorded throughout the experiment. Both moisture and temperature probes were installed prior to N_2O gas sample collection.

2.9.2. Nitrous oxide gas collection

A standard closed chamber method (Fig. 1) similar to that described by Hutchinson and Mosier (1981) was used to determine N_2O emissions from the lysimeters. Sampling was carried out over a four week period starting 7th May 2013, in which samples were collected every day for seven days and every second or third day for the remaining weeks. An initial gas sample was taken prior to treatment application. Gas samples were collected between 12.30 pm and 2.30 pm. The gas chamber was constructed from a metal cylinder, insulated on the outside with 2.5 mm thick polystyrene foam to avoid heating of the chamber head space during sampling. An annular ring mounted on the monolith lysimeters formed a U-shaped water trough around the lysimeter to which the chamber was fitted during sampling to create an air-tight seal. A rubber septum in the chamber surface facilitated gas sampling. At each sampling time, the chamber was placed on top of the lysimeter for a total of 60 min, and three samples (25 mL), were collected. Samples were collected in 6 mL Exetainer® vials which had been pre-evacuated (−1 atm) according to de Klein et al. (2001). The air temperature was recorded prior to sampling followed by measurements of the chamber air temperature at 20, 40 and 60 min.

Nitrous oxide concentrations were determined at New Zealand's National Centre for Nitrous Oxide Measurement (NZ-NCNM) at Lincoln University, New Zealand using a gas chromatograph (GC) (SRI 8610 gas chromatograph; SRI Instruments, CA, USA) fitted with a ^{63}Ni electron capture detector (ECD), and linked to an autosampler (Gilson 222 XL; Gilson Inc., WI, USA). PeakSimple software (SRI Instruments, CA, USA) was used to control and monitor the ECD. The N_2O fluxes were (g N_2O–N ha/d) was calculated using the change in headspace N_2O concentration (μL/L) over time and the protocols and equations of Hutchinson and Mosier (1981). A full description of the GC and its operation can be found elsewhere (Kelliher et al., 2012).

3. Results and discussion

Batch sorption experiments revealed there was negligible NH_4^+ sorption by the Lismore soil and the Charleston and Millerton lignites. In contrast, there was significant NH_4^+ sorption by the NV lignite. Fig. 2 shows the NH_4^+ sorption by the NV lignite at solution pHs between 4.1 and 6.7. Ammonium sorption by the NV lignite increased with increasing pH. This is consistent with there being a pH dependent variable charge on the NV lignite.

Table 2
Chemical properties of the pasture grown on the lysimeters. Values represent the mean (n = 3). Values in brackets are the standard error of the mean. Values with the same letter are not significantly different at the 5% level (ANOVA with Fisher's test).

	Soil treatments					
	Control	Lignite	Biosolids	Biosolids + lignite	Urea	Urea + lignite
Total C (g/kg)	439 (2.5)^{ab}	441 (2.3)^{ab}	442 (2.1)^{a}	443 (0.8)^{a}	441 (1.3)^{ab}	434 (3.7)^{b}
Total N (g/kg)	25.3 (0.8)^{a}	24.2 (0.6)^{a}	25.3 (1.6)^{a}	25 (2.1)^{a}	24 (1.6)^{a}	23.8 (0.3)^{a}
P (mg/kg)	4511 (145)^{ab}	4585 (93) ^{ab}	4084 (124)^{b}	4121 (121)^{b}	4421 (237.3) ^{ab}	4738 (265)^{a}
S (mg/kg)	2292 (119)^{a}	2714 (74)^{a}	2469 (228)^{a}	2408 (226)^{a}	2729 (270.5)^{a}	2826(78)^{a}
Ca (mg/kg)	7898 (569)^{a}	6888 (150)^{b}	7920 (309)^{a}	7502 (331)^{ab}	7917 (147)^{a}	8270 (220)^{a}
Mg (mg/kg)	914 (18.8)^{bc}	983 (40.9)^{ab}	840 (53.8)^{c}	918 (20)^{b}	921 (82.4)^{bc}	1073 (26.3)^{a}
K (mg/kg)	24,170 (967)^{ab}	23,888 (389)^{ab}	21,055 (982)^{c}	21,158 (319)^{c}	21,609 (780)^{bc}	25,274 (1244)^{a}
Na (mg/kg)	1461 (40)^{a}	1464 (114)^{a}	1887 (274)^{a}	1925 (352)^{a}	1819 (176)^{a}	1304(75)^{a}
Al (mg/kg)	429 (107) ^{ab}	422 (45) ^{ab}	279 (35) ^{b}	400 (54.7) ^{ab}	357 (26.7) ^{ab}	519 (89.8) ^{a}
Cu (mg/kg)	4.4 (0.3)^{b}	4.5 (0.3)^{b}	6.2 (0.4)^{a}	5.3 (0.4)^{ab}	5.2 (0.4)^{ab}	5.1 (0.2)^{b}
Cd (mg/kg)	0.07 (0.05)^{a}	0.01 (0.0)^{a}	0.02 (0.01)^{a}	0.02 (0.0)^{a}	0.02 (0.0)^{a}	0.02 (0.0)^{a}
Fe (mg/kg)	327 (68)^{ab}	324 (35)^{ab}	231 (28)^{b}	306 (35.9)^{ab}	295 (12)^{ab}	392 (70)^{a}
Mn (mg/kg)	20.7 (2)^{c}	33.9 (5.6)^{c}	23.4 (3.6)^{c}	24.1 (1.3)^{c}	76 (11.2)^{b}	102 (12.3)^{a}
Zn (mg/kg)	15.4 (0.7)^{b}	14.8 (0.2)^{b}	21.9 (2)^{a}	20.0 (1)^{a}	15.1 (0.5)^{b}	16.3 (1)^{b}

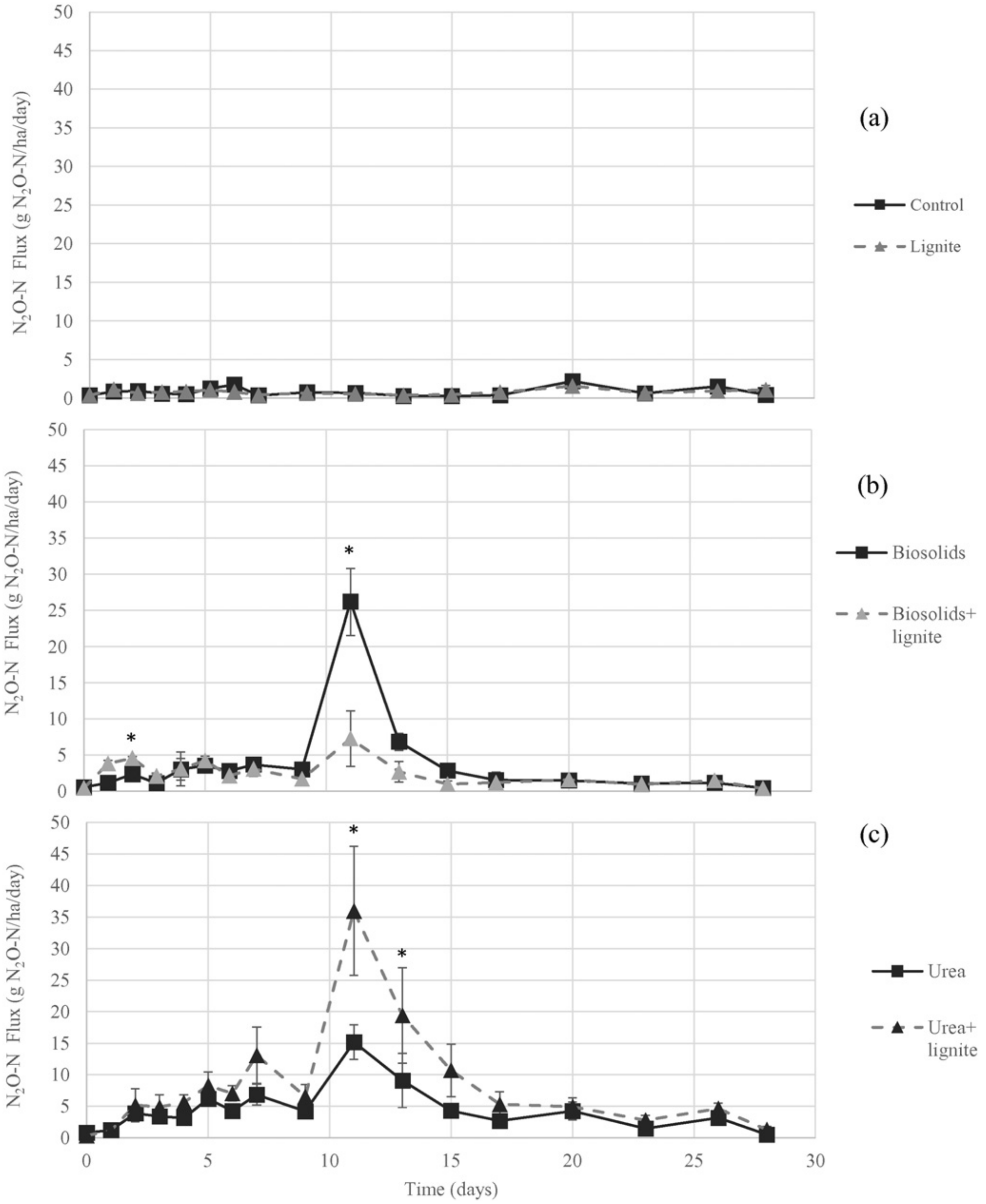

Fig. 7. Daily N_2O fluxes (g N_2O–N ha/day) over time showing (a) flux between control and lignite treatments (b) biosolids and biosolids + lignite and (c) urea and urea + lignite treatments over a 28 day period. Error bars are standard error of the mean (n = 3). Asterisks denote significant differences ($p < 0.05$).

Nitrate sorption on the lignite did not occur during the batch sorption and this is consistent with the negative surface charge on the NV lignite (Simmler et al., 2013). Lignite materials have been adopted to adsorb NO_3^- by modifying the surface using chemical ($ZnCl_2$) and thermal activation (Khan et al., 2011). Given that most mineral-N in aged biosolids is in the form of NO_3^- (Bernal et al., 1998; Smith et al., 1998), it is unlikely that lignite would prevent the initial flush of N leaching from biosolids-amended soil. The results of the column leaching study agree with this supposition, with the addition of increasing rates of NV lignite making no difference to the amount of NO_3^- leached (Fig. 3) and where the amount of NO_3^-–N lost was ca 5-fold greater than the highest NH_4^+ loss.

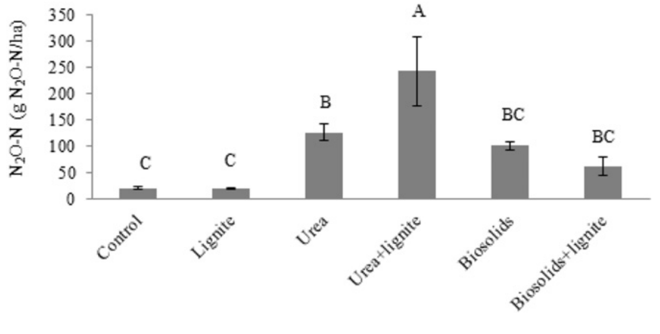

Fig. 8. Average cumulative N_2O loss (g N_2O–N/ha/day) over 28 days. Error bars are standard error of the mean (n = 3). Values with the same letter are not significantly different at the 5% level (ANOVA with Fisher's test).

In contrast, younger biosolids, which have a significant NH_4^+ component of their mineral N, may leach less N if amended with lignite to retain NH_4^+ Increasing the amount of NV lignite added to the biosolids significantly reduced the mass of NH_4^+–N that leached from the columns (Fig. 4). However, above a NV lignite:biosolids ratio of 2:5, there was no further decrease in NH_4^+–N leaching.

The total cation exchange sites in the columns equated to 2.0×10^{-3} mol of negatively charged sites and this was significantly higher than the total potential NH_4^+–N available (assuming complete mineralisation of both NV lignite and biosolids) of 1.1×10^{-5} mol.

However, NH_4^+–N compete with other cations Al^{3+}, Ca^{2+}, K^+ and Na^+ for these sites. The positive charge from these ions in our columns was >0.006 mol, in excess of the total moles of negative charged surface.

A second mechanism for NH_4^+–N leaching reducing with as increasing NV lignite rate could be the microbial immobilization of NH_4^+, due to increasing availability of water WSC as lignite rates increase (Ghani et al., 2003).

Between April and November, the lysimeters received 1105 mm of rainfall + irrigation, equating to 221 L per lysimeter. The monthly average air temperature in April was 12 °C, decreased to 5.5–6.5 °C in June–July, before increasing in spring to 10–11 °C in October–November. The total N leached as NH_4^+–N from the lysimeters varied between 6.7–10 mg which is equivalent to 0.33 and 0.50 kg/ha (data not shown) and was insignificant compared to the NO_3^-–N leached (524–3207 mg, equivalent to 26 kg/ha–160 kg/ha).

The high CEC of the NV lignite (Table 1) indicates that adding the NV lignite to the Lismore soil will increase the total CEC. This increase in CEC may be offset by the acidic pH of the NV (Table 1) compared to the Lismore soil (6.3). The contrasting effects of increased CEC and reduced pH caused by lignite addition have been highlighted by Pehlivan and Arslan (2006) and Simmler et al. (2013).

Sorption of NH_4^+ by the lignite may result in prolonged retention of N in the plant root-zone allowing greater plant uptake, and reducing N-leaching. Richards et al. (1986) showed that lignite significantly increased the growth of tomato and two ornamental plants which they attributed to the high CEC of the lignite (ca. 60 $cmol_c$/kg).

Fig. 5 shows the NO_3^-–N leached as a percentage of the total N (soil N and amendments) in the top 10 cm of soil, i.e. the soil into which the treatments were mixed. The lignite-only treatment leached less NO_3^-–N compared to the control ($p < 0.05$). However, in the biosolids and urea treatments, the addition of lignite had no significant effect on the amount of N leached. The lack of any effect of lignite on N-leaching from the biosolids can be explained if most of the mineral N in the biosolids was present as NO_3^-, which the batch sorption and column leaching experiments demonstrated was not sorbed by the lignite. However, the lack of any effect of lignite on NO_3^-–N leaching from the urea treatment was unexpected, since urea hydrolyses to form NH_4^+ and it was expected that this would be partially retained by the lignite. Since the addition of lignite increased CEC by 5.56% potentially alter the retention of all urea-N as NH_4^+ on the increased CEC.

Our lysimeter experiment was conducted from autumn to spring, which is when most leaching from pasture occurs (Di and Cameron, 2007) and when pasture growth is low relative to the summer months. Our lysimeters produced between 1000 and 2500 kg DM/ha. *L. perenne* L. is reported to produce 14,200–23,400 kg DM/ha/yr. (Glassey et al., 2010) with most of this growth occurring in the warmer months. The pasture in our experiments removed the equivalent of 25–62.5 kg N/ha, less than the amount of N added (200–400 kg N/ha equivalent). Therefore, it is unlikely the pasture would have been unable to remove any additional NH_4^+ that was detained in the root-zone by the lignite.

In our study, the lignite was incorporated into the top 10 cm of soil in order to try and modify urea-N cycling. In contrast, previous studies have used “black urea”, which is a mixture of urea and lignite. Thus, our results do not necessarily indicate that adding lignite to urea as “black urea” would be ineffective in reducing NO_3^-–N leaching. However, our results do indicate that the addition of lignite to soil is unlikely to reduce N leaching from surface-applied urea.

The growth of pasture increased following the addition of urea, biosolids and biosolids + lignite ($p < 0.05$). Adding lignite to the biosolids, however, reduced the pasture yield (Fig. 6) compared to biosolids alone, whereas adding lignite + urea did not significantly reduce yield compared to urea alone. In the control soil, the addition of lignite had no effect on pasture yield. The treatments had only a minor effect on the elemental composition of the pasture (Table 2) with the addition of biosolids significantly increasing the pasture Zn concentration, while lignite addition did not reduce heavy metal concentrations in any treatment.

There were no detectable N_2O emissions (<2.5 g N_2O–N/ha) from the control or lignite treatments over the 28 d period (Fig. 7a). The addition of biosolids alone did not significantly increase N_2O emissions over the entire experimental period (Fig. 8). Fig. 7b shows that during the experimental period, the biosolids + lignite treatment emitted significantly more N_2O than the biosolids alone treatment on day 3 and visa-versa on day 10. The addition of urea increased daily and cumulative N_2O emissions (Fig. 8) and this increase was exacerbated by lignite (Figs. 7c, 8). This may have been a consequence of the increased availability of lignite derived WSC enhancing denitrification, since WSC has been shown to correspond to denitrification rates (Burford and Bremner, 1975) or lignite addition may have altered (Table 1), soil physical properties which may have resulted in higher (Schmidt et al., 1999) N_2O emissions.

4. Conclusions

The addition of lignite to soil did not significantly offset the increase in NO_3^- leaching caused by adding biosolids or urea. There was a small reduction in NO_3^- leaching from unamended soil, which corresponded to the increase in cation exchange sites in the lysimeter by 3.33 mol. This reduction is unlikely to be significant in an agricultural context. Lignite exacerbated N_2O emissions from soils receiving urea. Furthermore, lignite lessened the beneficial growth effects of adding biosolids or urea to soil. Future work should investigate whether coating urea granules with lignite results in lower reactive N losses from pastures.

Acknowledgements

We gratefully acknowledge the Centre for Integrated Biowaste Research (CIBR) for funding this research.

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