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RESEARCH ARTICLE

Increasing thermal drying temperature of biosolids reduced nitrogen mineralisation and soil N_2O emissions

Sean D. C. Case[1] · **Beatriz Gómez-Muñoz**[1] · **Jakob Magid**[1] · **Lars Stoumann Jensen**[1]

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Abstract Previous studies found that thermally dried biosolids contained more mineralisable organic nitrogen (N) than the raw or anaerobically digested (AD) biosolids they were derived from. However, the effect of thermal drying temperature on biosolid N availability is not well understood. This will be of importance for the value of the biosolids when used to fertilise crops. We sourced AD biosolids from a Danish waste water treatment plant (WWTP) and dried it in the laboratory at 70, 130, 190 or 250 °C to >95 % dry matter content. Also, we sourced biosolids from the WWTP dried using its in-house thermal drying process (input temperature 95 °C, thermal fluid circuit temperature 200 °C, 95 % dry matter content). The drying process reduced the ammonium content of the biosolids and reduced it further at higher drying temperatures. These findings were attributed to ammonia volatilisation. The percentage of mineralisable organic N fraction (min-N) in the biosolids, and nitrous oxide (N_2O) and carbon dioxide (CO_2) production were analysed 120 days after addition to soil. When incubated at soil field capacity (pF 2), none of the dried biosolids had a greater min-N than the AD biosolids (46.4 %). Min-N was lowest in biosolids dried at higher temperatures (e.g. 19.3 % at 250 °C vs 35.4 % at 70 °C). Considering only the dried biosolids, min-N was greater in WWTP-dried biosolids (50.5 %) than all of the laboratory-dried biosolids with the exception of the 70 °C-dried biosolids. Biosolid carbon mineralisation (CO_2 release) and N_2O production was also the lowest in treatments of the highest drying temperature, suggesting that this material was more recalcitrant. Overall, thermal drying temperature had a significant influence on N availability from the AD biosolids, but drying did not improve the N availability of these biosolids in any case.

Keywords Sewage sludge · Mineralisation · Anaerobic digestion · Waste water treatment · Agriculture · Soil

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✉ Sean D. C. Case
case@plen.ku.dk

[1] Department of Plant and Environmental Sciences, University of Copenhagen, Thorvaldsensvej 40, 1871 Frederiksberg, Denmark

Introduction

Sewage effluent from urban sources is often treated at waste water treatment plants (WWTPs) (Arthurson 2008). Treated sewage sludge can be suitable for use as agricultural fertiliser as it contains significant amounts of plant-available nutrients such as nitrogen (N) and phosphorous. Treated sludge application is a common agricultural practice in many countries worldwide; it can be applied to fields directly or after treatment by one of a number of processes, such as dewatering, anaerobic digestion (AD), composting, alkaline stabilisation, pelleting or thermal drying (Lu et al. 2012). Waste water treatment sludge treated by one of these methods is often termed biosolids (Clarke and Smith 2011).

Thermal drying is a standard WWTP-biosolid processing method and is used in a number of facilities globally (Fytili and Zabaniotou 2008; Bennamoun et al. 2013). Biosolids can be dried at a wide range of temperatures (inlet temperatures in WWTPs range from 65 to 480 °C), but in practice they are mostly dried at temperatures below 200 °C (Chen et al. 2002; Silva-Leal et al. 2013; Bennamoun et al. 2013). Drying greatly reduces water content, therefore reducing transport costs, and

ensures a stable product free from pathogenic microbes. However, this comes at the cost of significant energy input (Stasta et al. 2006).

Drying processes vary greatly and result in biosolids with a wide range of physical and chemical properties (Bennamoun et al. 2013). The effect of drying temperature on biosolid N availability is not well understood. During the drying process, biosolids can lose up to 80 % of its ammonium (NH_4^+) content as ammonia (NH_3) via volatilisation (Smith and Durham 2002). Despite the loss of N, several studies have observed that the predominantly organic N remaining in thermally dried biosolids were more available to soil than the organic N in fresh biosolids (Smith and Durham 2002; Rigby et al. 2009; Silva-Leal et al. 2013). However, this finding may depend on biosolid drying temperature; Matsuoka et al. (2006) found that N mineralisation was lower in biosolids dried at higher drying temperatures (180 vs 120 °C); a finding that they suggested could be due to the increased stability of organic N in biosolids dried at higher temperatures.

Greenhouse gas (GHG) emissions from agriculture, such as carbon dioxide (CO_2) and nitrous oxide (N_2O), are significant contributors to global climate change (IPCC 2013). Soil N_2O emissions vary greatly with soil water content and with fertiliser-N addition (Dobbie and Smith 2003; Rees et al. 2013). Biosolids may increase soil N_2O emissions following amendment (López-Valdez et al. 2011); however, the effects of thermally dried biosolids on soil N_2O emissions have only been investigated in one recent study (Yoshida et al. 2015).

An incubation study was conducted to quantify the effect of thermal drying of AD biosolids and the influence of thermal drying temperature on subsequent soil N availability and N_2O emissions. In order to address the aforementioned research gaps, three hypotheses were tested:

- Biosolid NH_4^+ concentrations decrease with thermal drying, and decrease further at higher drying temperatures.
- Thermal drying increases the mineralisable organic N fraction (min-N) of biosolids and N_2O production following soil amendment.
- Increasing biosolid drying temperature decreases biosolids min-N and N_2O production following soil amendment.

Materials and methods

Soil and biosolid treatments

Soil was collected in Aug. 2013 from one of the permanent treatments in the CRUCIAL long-term field trial in Taastrup, Denmark (Poulsen et al. 2013). The treatment had received NPK fertiliser annually since 2003, containing at least 94 kg inorganic N ha^{-1} $year^{-1}$ and 9 kg P ha^{-1} $year^{-1}$. Each year, the plots were planted with a grain crop (one of wheat, oats, barley, ryegrass, or rapeseed). The sandy loam soil (a Luvisol according to FAO-UNESCO revised 1990 legend classification, Adhikari et al. (2014)) was collected using hand tools (to a depth of 20 cm), sieved to 4 mm, and stored at 4 °C in the dark for 2 weeks.

Anaerobically digested (AD) and thermally dried WWTP biosolids (FD) were sourced from Randers municipality WWTP, Denmark. The biosolids were produced from raw sewage sludge and were then anaerobically digested for 32 days at 37 °C to produce biogas, and then dewatered to approximately 20 % dry matter content using a belt press. The biosolids were then moved into a belt drier system, which had a feed temperature of 95 °C and a thermal fluid circuit temperature of 200 °C (see Bennamoun et al. (2013) for a description of this type of system), and were dried to a target dry matter content of 90–95 %.

Further, thermally dried treatments were created from AD biosolids by heating in a laboratory oven at 70, 130, 190, or 250 °C until the water content was less than 5 % (hereafter named LD70, LD130, LD190, and LD250, respectively). Pretests demonstrated that the biosolids took less time to dry as drying temperature increased, approximately 18, 6, 2.5, and 1.5 h at 70, 130, 190, and 250 °C, respectively. All biosolids were coarsely ground and passed through a 4-mm sieve.

Soil and biosolid physical and chemical properties

Soil pH at the start and end of the incubation was analysed using a PHM210 pH metre (Radiometer analytical, UK) in a 1:5 ratio soil to DI water (*w*:*w*), 1 h after mixing. For total carbon (C) and N contents, soil and biosolids were dried at 105 °C for a minimum of 24 h and ground finely to <0.5 mm. Samples were analysed using the Dumas combustion method on an elemental analyser connected to a continuous flow isotope mass spectrometer (Sercon ANCA-GSL, 20–20, Crewe, UK). Since the vast majority of the inorganic N is removed from the biosolids during the combustion process, total N from this analysis was used as the organic N content of biosolid samples in subsequent mineralisation calculations. Soil water contents at pF 2 and 1 (−100 and −10 kPa matric potential, respectively) were determined using the sandbox method (The American Society of Agronomy 1965). The soil had an NH_4^+ content of 0.35 ± 0.31 mg NH_4^+-N kg^{-1}, a NO_3^- content of 5.44 ± 0.04 mg NO_3^--N kg^{-1}, a total C content of 14.43 ± 0.26 g C kg^{-1}, a total N content of 1.45 ± 0.03 g N kg^{-1}, and a pH of 7.4 ± 0.1 (in H_2O).

Sampled soils were stored at 4 °C until inorganic N extraction, which was conducted within 24 h. For determination of inorganic N content in soil and biosolids, samples were mixed with 1 M KCl (1:4 ratio *w*:*w* for soil, 1:40 for biosolids), turned with an overhead shaker for 1 h, and then filtered

through Whatman no. 44 filter paper (GE Healthcare, UK). Extracts were stored at 4 °C for a maximum of 24 h or frozen at −20 °C before analysis. The extracts were analysed for NH_4^+ and NO_2^-/NO_3^- contents using a FIAstar 5000 flow injection analyser (Foss Analytical, Denmark).

Incubation preparation

Samples of 45-g soil (dry weight) were packed to a bulk density of 1.3 g cm^{-3} (close to natural field conditions), wetted to pF 2, and pre-incubated for 14 days in the dark at 15 °C. On day 0 of the incubation, the biosolids were mixed into the soil at a rate of 2 % (dry weight), and the mixture was repacked to 1.3 g cm^{-3}. There were seven treatments in total: soil only control (C), soil + dewatered AD biosolids (S-AD), soil + WWTP-dried biosolids (S-FD), and soil + laboratory-dried AD biosolids dried at 70, 130, 190, or 250 °C (S-LD70, S-LD130, S-LD190, and S-LD250, respectively). Half of the replicates were adjusted to a moisture content equivalent to pF 2 (field capacity) and the other half to pF 1 (near saturation); these moisture levels corresponded to 60 and 96 % water-filled pore space, respectively (at the bulk density applied). There were three replicates for each treatment.

Following biosolid addition, the samples were incubated at 15 °C in the dark for 160 days. Plastic caps were placed loosely on top of the jars to limit moisture losses by evaporation while allowing air to enter. Water contents were maintained gravimetrically and monitored at least every 7 days. Soils were sampled destructively on days 0, 3, 7, 14, 42, 80, 120, and 160 for NH_4^+ and nitrate (NO_3^-) contents. Soil N_2O and CO_2 emissions were analysed on days 0, 1, 2, 3, 5, 7, 10, 16, 24, 48, 80, 120, and 160 (see below).

Inorganic N availability

The equation to calculate the mineralisable organic N fraction (min-N) in the biosolids was taken from Smith and Durham (2002) (Eq. 1).

$$Min\text{–}N(\%) = \frac{(N_s - N_a - N_c)}{N_{org}} * 100 \quad (1)$$

Where N_s is the mineral-N concentration in biosolid-amended soil at the end of the incubation period, N_a is the amount of NH_4^+-N supplied to the soil in the biosolids, N_c is the mineral-N concentration of the control soil, and N_{org} is the amount of organic N added to the soil by the biosolids. All units are mg N kg^{-1}.

N_2O and CO_2 emissions

Soil N_2O and CO_2 emissions were analysed using the static chamber method (Livingston and Hutchinson 1995). Soil samples were placed in air-tight 500-ml glass jars (John Kilner & Co., Liverpool, UK) fitted with a butyl rubber septum in the lid and closed. Gas samples were taken at 0 and 120 min following enclosure using a 10-ml syringe, then injected into 3 ml vials (Labco, UK). The linearity of the gas concentration increase was pre-tested using mixed soil and biosolid samples over 2 h. A gas chromatograph (GC) was used to analyse concentrations of N_2O and CO_2 (Bruker 450-SC, Germany). The GC was fitted with a thermal conductivity detector (TCD; for CO_2) operating at 350 °C, and an electron capture detector (ECD; for N_2O) operating at 200 °C. On the ECD channel, the gas was injected into a Hayesep N pre-column (length 0.5 m), and subsequently the Hayesep D column (length 2 m). On the TCD channel, CO_2 was injected into a Hayesep N pre-column (length 0.5 m), and the fraction of oxygen, dinitrogen (N_2), carbon monoxide, CH_4, and CO_2 was passed into the Porapak QS column (length 2 m). The oven temperature was 50 °C, and the carrier gas was argon with 5 % CH_4. Results were calibrated against certified gas standards (Air Products, Waltham on Thames, UK).

The percentages of total N (organic + inorganic N) emitted as N_2O-N (N_2O%) and total C emitted as CO_2-C (CO_2%) were calculated. This was done by (1) multiplying the mean hourly gas flux at two consecutive time points by the hours in between them and (2) dividing this result by total soil N or C content (organic + inorganic N, total C content) in soil as appropriate. Only N_2O emissions were analysed during the course of the study, denitrification losses in the form of N_2 were not taken into account, and so a full account of N losses from biosolid-amended soil during the incubation was not possible.

Statistical analysis

All statistical analyses were performed using R version 3.2.1 (The R Project 2015). For all parameters, treatments at pF 2, and then at pF 1, were compared using a one-way ANOVA. Tukey's honest significant difference test was used to find differences between treatments at the same moisture content. The ANOVA tables with results can be found in the supplementary information (Tables S1 and S2).

Results and discussion

Physical and chemical properties of biosolids

The AD biosolids (AD) had the highest NH_4^+ content, with the dried biosolids having only between 71 % (LD70) and 12 % of this total (LD190, Table 1, $p < 0.05$). This loss of NH_4^+ was expected, as a significant fraction of NH_4^+ volatilises to NH_3 during the thermal drying process (Smith and Durham 2002).

Table 1 Physical and chemical properties of the biosolids

	AD	FD	LD70	LD130	LD190	LD250
Ammonium content (mg NH_4^+-N kg^{-1})	8,982 (365) a	3,425 (37) d	6,375 (106) b	4,643 (29) c	1,089 (31) e	1,146 (65) e
Nitrate content (mg NO_3^--N kg^{-1})	72.87 (5.42) a	0.00 (0.57) b	0.54 (0.02) b	0.68 (0.03) b	0.15 (0.02) b	4.51 (0.20) b
Total combustible C content (g C kg^{-1})	284.0 (2.4) b	293.3 (1.4) a	300.4 (4.0) a	300.5 (4.3) a	297.8 (2.4) a	290.2 (1.5) b
Total combustible N content (g N kg^{-1})	45.0 (0.5) -	46.0 (0.3) -	45.1 (0.3) -	45.8 (0.6) -	44.8 (0.5) -	45.8 (0.5) -
Mineral-N fraction (% of total N)	16.8 %	6.9 %	12.4 %	9.2 %	2.4 %	2.4 %
$C:N_{tot}$ ratio	5.36 (0.03) -	5.94 (0.01) -	5.84 (0.11) -	5.96 (0.17) -	6.48 (0.02) -	6.19 (0.06) -
pH	8.4 (0.1) a	7.3 (0.1) b	6.9 (0.1) c	6.6 (0.1) d	5.8 (0.1) e	6.5 (0.1) d
Dry matter content (%)	18.7 (0.6)	95.0 (0.0)	95.0 (0.1)	97.4 (1.5)	99.5 (1.2)	99.9 (0.7)

Values indicate mean (standard error in brackets). Letters indicate a significant difference ($p < 0.05$) between treatments: AD = dewatered AD biosolids, FD = WWTP-dried biosolids, and LD70, LD130, LD190, and LD250 = laboratory-dried AD biosolids dried at 70, 130, 190, or 250 °C, respectively

Ammonium concentrations decreased with drying temperature up to 190 °C, but did not decrease further at the highest drying temperature (LD250, Table 1). This finding confirmed our first hypothesis and was consistent with another study in which inorganic N contents were found to be lower in biosolids dried at a higher temperatures (180 compared to 120 °C) (Matsuoka et al. 2006). Biosolid NO_3^--N contents were low in the AD treatment (72.9 ± 5.4 mg NO_3^--N kg^{-1}) and almost zero in the dried biosolids (Table 1). Organic N contents of the biosolids were not significantly different (Table 1, $p > 0.05$), which was expected as drying has only previously been observed to affect overall organic N content of biosolids by a small amount (Matsuoka et al. 2006). Therefore, total N (inorganic and organic N contents added together) contents were greatest in the AD treatment, 11 % greater than mean for all dried treatments ($p < 0.01$, Table 1).

The AD and LD250 treatments had the lowest total C contents; however, they were only lower by 5 and 3 % C, respectively, than the mean for the other dried treatments (the mean was 298 g C kg^{-1}, Table 1). It was possible that as significant amounts of C- and non-C-containing constituents were lost during the drying process (e.g. NH_4^+-N, volatile organic compounds such as volatile fatty acids), the proportion of C in the dried products was increased in the materials. It could be expected that at the highest drying temperatures the C in the biosolids were lost as CO_2 due to thermochemical decomposition (~5 % mass loss at 250 °C), which could explain the decrease at the highest drying temperatures (Sanchez et al. 2009).

Biosolid pH was significantly higher in AD (8.4 ± 0.1) than in all the dried biosolids (between 5.8 and 7.3 for LD190 and FD, Table 1). Biosolid pH decreased with increasing drying temperature until 190 °C (LD190, 5.8 ± 0.1), possibly driven by the volatilisation of NH_3, a process that releases the protons from NH_4^+. However, at 250 °C, it increased again to 6.5 ± 0.1 (LD250, Table 1), perhaps due to volatilisation of volatile fatty acids (Sommer et al. 2013).

Nitrogen mineralisation

Inorganic N concentrations were monitored for 160 days following biosolid addition to soil (Fig. 1a–d). With biosolids of any drying temperature, day 0 soil NH_4^+ concentrations were consistently lower than soils mixed with undried biosolids, with the exception of S-LD130 (205 ± 21 mg NH_4^+-N kg^{-1}, Fig. 1a). Soil NH_4^+ concentrations were lower later in the incubation; soil NH_4^+ concentrations from day 80 onwards remained below 10 mg NH_4^+-N kg^{-1} at pF 2 and below 38 mg NH_4^+-N kg^{-1} at pF 1 (Fig. 1a, b).

Soil NO_3^- contents were lower than 30 mg NO_3^--N kg^{-1} on day 0 and increased over the course of the incubation in all biosolid-amended treatments to a maximum 120 days after biosolid addition (Fig. 1c, d, $p < 0.001$). On this day, the greatest soil NO_3^- concentrations in soils at pF 2 were in S-AD, followed by S-FD. In soils amended with laboratory-dried biosolids, NO_3^- concentrations increased less with increasing drying temperature, e.g. from 427 to 206 mg NO_3^--N kg^{-1} for S-LD70 and S-LD250, respectively (Fig. 1c, $p < 0.001$). At pF 1, only the S-AD and S-FD treatments developed significant amounts of NO_3^- by day 120 (Fig. 1d). All other treatments had a soil NO_3^- content of less than 23 mg NO_3^--N kg^{-1} throughout the incubation.

Inorganic N contents were at a maximum on day 120, and so the mineralisable organic N fractions (min-N) on this day were considered to be the most realistic estimate of biosolid N availability to plants. On this day, at pF 2, min-N for S-AD and S-FD was not significantly different ($p > 0.05$, 46.4 ± 2.9 % and 50.5 ± 1.4 %, respectively, Fig. 2a). The min-N for S-AD and S-FD were high but were within the ranges of values for mineralisation found elsewhere in the literature (Table 2, Rigby et al. 2016). S-LD130, 190, and 250 had a significantly lower min-N than S-AD ($p < 0.05$, Fig. 2a), and biosolid min-N decreased consistently with increasing drying temperature (from 35.4 ± 0.4 % for S-LD70 to 19.3 ± 1.2 % for S-LD250, Fig 2a).

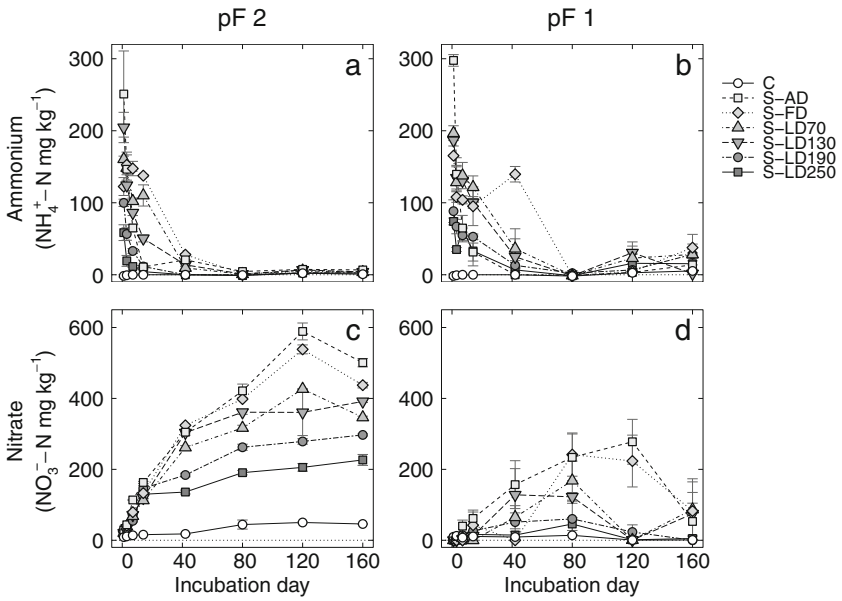

Fig. 1 The effect of biosolids on **a**, **b** soil NH_4^+ concentrations and **c**, **d** soil NO_3^- concentrations during the incubation in soil at pF 2 (**a**, **c**) and pF 1 (**b**, **d**). *Points* indicate mean, *error bars* denote standard error. The *treatment letters* signify the following: C = soil only, S-AD = soil + dewatered AD biosolids, S-FD = soil + WWTP-dried biosolids, and S-LD70, S-LD130, S-LD190, and S-LD250 = soil + laboratory-dried AD biosolids dried at 70, 130, 190, or 250 °C, respectively. The *horizontal dotted line* indicates 0

None of the thermally dried biosolids had a significantly higher min-N than AD biosolids. Therefore, our second hypothesis was not confirmed. We could not fully explain why thermally dried biosolid amendment had the same or less min-N than AD biosolids from our data alone. Thermal drying reduced the inorganic N content of AD biosolids, and as a result, increased the CN ratio of the biosolids slightly from 5.36 to 5.84–6.48 (Table 1). However, an increase in CN ratio is not directly indicative of increased recalcitrance and certainly not within such a narrow range as this. Instead, we suggest that an alteration in the biochemical and physical configuration of the organic components (which are mostly proteins and amides in biosolids) may have occurred during drying (see discussion below under carbon mineralisation) that also affected N mineralisation properties.

Min-N decreased in biosolids with increasing drying temperature, a finding that supported our third hypothesis (Fig. 2). A similar finding was observed by Matsuoka et al. (2006), who found that min-N was lower in 180 °C dried biosolids compared to 120 °C (Table 2). The authors speculated that at higher drying temperatures, lower min-N may be related to the lower decomposability of organic matter.

Min-N was lower in biosolids dried in the laboratory at 130 °C than for WWTP-dried biosolids. This suggested that other features of the drying process other than drying temperature was affecting min-N, discussed at the end of this section.

Min-N was also analysed in soils maintained at pF 1 (near saturation). The min-N of biosolid-amended treatments maintained at pF 1 was lower than at pF 2 (Fig. 2b). S-AD min-N was 10.8 ± 7.2 %, which was significantly different from S-

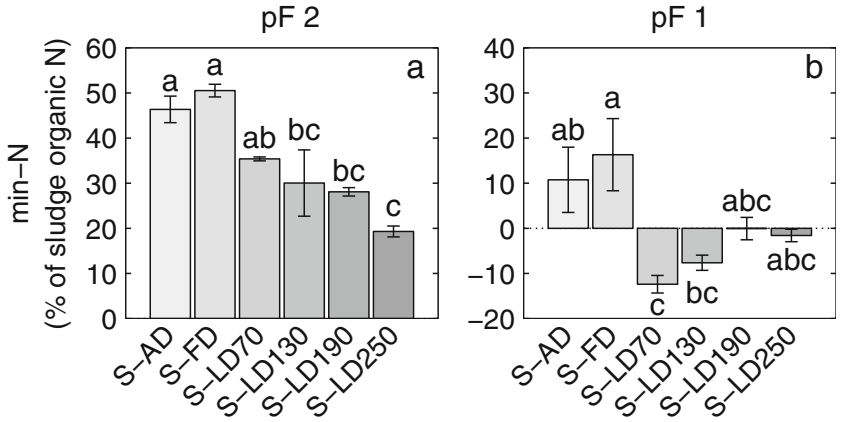

Fig. 2 The min-N of organic biosolid N, 120 days after addition to the soil at pF 2 (**a**), or pF 1 (**b**). *Letters* indicate groupings of treatments that are not significantly different from each other ($p > 0.05$). *Error bars* denote standard error. The *treatment letters* signify the following: S-AD = soil + dewatered AD biosolids, S-FD = soil + WWTP-dried biosolids, and S-LD70, S-LD130, S-LD190, and S-LD250 = soil + laboratory-dried AD biosolids dried at 70, 130, 190, or 250 °C, respectively. A *horizontal dotted line* indicates 0

Table 2 A summary of the effect of thermal drying on biosolid N contents and availability from the literature

Ref.	N availability parameter	Experimental conditions	Soil preparation	Biosolids type	Biosolids drying temp. (°C)	Biosolids tot. N content, % change (g N kg^{-1})	Biosolids NH_4^+-N content, % change (g N kg^{-1})	N availability, % change (%)	Additional information
Laboratory incubations									
1	Min-N (% of organic N)	25 °C, 56 days. Loamy sand or calcareous clay arable UK soil.	Soil and biosolid mix sieved <5.6 mm	(low VS) DW, AD vs TD	N.A.	−15 % (*52.0 vs 44.0*)	−81 % (*11.4 vs 2.2*)	+111 % (*27.0 vs 57.0*)	High VS content biosolids were less stable; may explain lower *Min-N*.
				(high VS) DW, AD vs TD	N.A.	−20 % (*51.0 vs 41.0*)	−86 % (*12.2 vs 1.7*)	+383 % (*6.0 vs 29.0*)	
2	Min-N (% of organic N)	30 °C, 84 days, 50 % WHC. Four soils.	Air-dried and sieved <2 mm	AD vs TD	120	+3 % (*60.6 vs 62.3*)	+118 % (*1.7 vs 3.7*)	+4 % (*18.2 vs 18.9*)	Mean of four different soils
					180	+5 % (*60.6 vs 63.6*)	+53 % (*1.7 vs 2.6*)	−12 % (*18.2 vs 16.1*)	
		10 °C, 84 days, 50 % WHC. Four soils.	Air-dried and sieved <2 mm	AD vs TD	120	+3 % (*60.6 vs 62.3*)	+118 % (*1.7 vs 3.7*)	+65 % (*8.4 vs 13.8*)	
					180	+5 % (*60.6 vs 63.6*)	+53 % (*1.7 vs 2.6*)	+46 % (*8.4 vs 12.2*)	
3	Min-N (% of organic N)	126 day, 70 % of field capacity.	Oven-dried at 40 °C (24 h), sieved <2 mm.	DW vs TD	N.A.	+3 % (*25.0 vs 25.7*)	−39 % (*1.8 vs 1.1*)	+38 % (*33.0 vs 45.7*)	
4	Min-N (% of organic N)	Soil from same site as for this study. 190 day incubation	Moist soil sieved to 4 mm	AD vs TD (2.1 % to 35 % dry matter)	N.A.	−36 % (*70.2 vs 44.8*)	−79 % (*31.4 vs 6.7*)	N.A. (*~0.0 vs 19.0*)	Digested biosolids of low dry matter content did not mineralise any N
Field experiments									
5[a]	PAN (% of total N)	Mean of 2 years. Coarse loamy soil.	Surface biosolid application. Forage grass grown.	DW, AD vs TD	N.A.	−7 % (*58.7 ± 4.9 vs 54.3 ± 6.0*)	−80 % (*11.3 ± 1.2 vs 2.3 ± 0.7*)	−6 % (*38.3 ± 1.7 vs 36.0 ± 4.6*)	Mean of three types of DW, AD and TD
	Fraction N uptake[a] (% of total N)	Mean of 2 years. Coarse loamy soil.	Surface biosolid application. Forage grass grown.	DW, AD vs TD	N.A.	−7 % (*58.7 ± 4.9 vs 54.3 ± 6.0*)	−80 % (*11.3 ± 1.2 vs 2.3 ± 0.7*)	+18 % (*56.5 + 2.8 vs 66.3 + 0.9*)	
6	Min-N (% of organic N)	Sampling 149 days after addition. Loamy texture soil.	Vegetation removed, soil tilled to 25 cm. Surface biosolid application. Grass mix grown.	DW, AD vs TD	N.A.	−5 % (*46.6 vs 44.5*)	−50 % (*6.8 vs 3.4*)	−48 % (*23.0 vs 12.0*)	Inorganic N values only given in paper. Min-N calculated here from these inorganic N values
7	Min-N (% of organic N)	90 days. Two soil types	Crop killed by herbicide. Biosolids applied to soil and mixed by hand. Soil left bare.	DW, AD vs TD (silty clay soil)	N.A.	−43 % (*60.3 vs 34.3*)	−95 % (*9.2 vs 0.5*)	+122 % (*14.2 vs 31.5*)	
				DW, AD vs TD (sandy silt loam soil)	N.A.	−43 % (*60.3 vs 34.3*)	−95 % (*9.2 vs 0.5*)	+94 % (*20.4 vs 39.6*)	

References: 1. (Smith and Durham 2002), 2. (Matsuoka et al. 2006), 3. (Silva-Leal et al. 2013), 4. (Yoshida et al. 2015), 5. (Cogger et al. 2004), 6. (Tarrasón et al. 2008), 7. (Rigby et al. 2009). *PAN* plant-available N, i.e. the proportion of N from the biosolids present in the harvested portion of the plant divided by the proportion of N present when the same amount of inorganic N was added, and fraction N uptake is the fraction of available N taken up into the harvested portion of the plant (Cogger et al. 2004). *Min-N* mineralisable organic N fraction in the biosolids. Biosolid types: *DW* dewatered, *AD* anaerobically digested, *TD* thermally dried, *VS* volatile solids. 'N.A.' indicates that the parameter was not reported. Reference numbers are defined underneath the table

[a] As the undried and TD biosolids in this study came from different WWTPs, they did not make a direct comparison between biosolids. Therefore, the averages of several undried and TD biosolids were compared

LD70 only (−12.4 ± 2.0 %, Fig. 2b). Min-N was negative or insignificantly different from 0 in all laboratory-dried biosolid treatments (Fig. 2b). Our results are in agreement with Rouch et al. (2011) who suggested that biosolids in soils maintained at near-saturated conditions had a lower net mineralisation than those in field-moist soil. Nitrogen mineralisation has been observed to increase with water content to pF 1 and above (Paul et al. 2003), although another study identified an 'optimum' water content for N mineralisation (between 57 and 89 % water-filled pore space, depending on the soil), above which it decreases (Sleutel et al. 2008). At such high water content conditions, denitrification will likely prevail at least in hot spots of microbial activity, and hence the low min-N is likely to be a result of denitrification losses of the N mineralisation in more aerobic parts of the soil matrix (Wulf et al. 2002).

Our results for min-N at pF 2 were high, but within the range of values found elsewhere in the literature (Rigby et al. 2016); however, most studies have observed greater min-N in thermally dried biosolids compared to undried biosolids (Table 2). The values presented in the literature range from 0 to 33 % for dewatered or AD biosolids, and from 12 to 57 % for thermally dried biosolids, which vary widely according to experimental and environmental conditions (Table 2). However, there were no consistent trends with drying temperature, drying conditions, or biosolid properties in these studies that would help to explain the differences found in this study with the general trends of N mineralisation with dried biosolids in the literature.

Generally, other studies have found that thermally dried biosolids contain more min-N than the raw or AD biosolids they come from. However, there are exceptions. Tarrasón et al. (2008) did not observe greater soil NH_4^+ or NO_3^- concentrations following the addition of dried biosolids compared to the addition of AD biosolids. In a field study, Cogger et al. (2004) found that thermal drying of biosolids did not affect plant-available N, but did increase the fraction of N uptake in the first two harvests after application (Table 2). Neither of these studies attempted to explain these findings.

Overall, it was concluded that thermal drying reduced the inorganic N content of biosolids and did not increase the availability of the N in the dried product. Therefore, thermally dried biosolids provided less available N to soil. From the perspectives of those farmers who readily accept AD biosolids as an alternative nutrient source, there is no agronomic advantage in choosing thermally dried biosolids to use as an N fertiliser (however, there still may be logistical and practical reasons, e.g. lower weight, easier handling and spreading).

Carbon mineralisation

Rates of C mineralisation, measured as CO_2 production from soil and biosolids, were significantly greater at the start of the incubation (Fig. 3a, b). In the first 7 days, soil CO_2 emissions occurred at the fastest rate at both pF 2 and pF 1, and then the rate of increase was lower by day 16 at both moisture contents (below 50 μg CO_2-C g^{-1} day^{-1}), which was not significantly different from the control. At pF 2 between day 42 and day 120, S-AD increased its rate of CO_2 emissions relative to earlier time periods and produced the most CO_2 of all the treatments (Fig. 3a). This suggested that drying (below 190 °C) may affect the temporal release pattern of C by increasing mineralisation soon after soil addition.

Cumulative production of CO_2-C from the biosolids as a percentage of their total C (CO_2%) over 120 days was taken as a measure of C mineralisation (Table 3). At pF 2, CO_2% was the greatest in the S-AD and S-FD treatments and drying did not increase the C mineralisation of sewage biosolids. CO_2% was lower in biosolids at the highest drying temperatures, at 13.6 ± 0.5 % and 8.9 ± 2.8 % for S-LD190 and S-LD250, respectively. These two treatments also had the lowest CO_2% at pF 1 (Table 3). Over all the biosolid-amended treatments, CO_2% was greater at pF 1 than at pF 2 ($p < 0.05$), suggesting that C mineralisation at pF 2 was somewhat moisture limited.

The CO_2 data clearly showed that biosolids dried at the highest temperatures (190 and 250 °C) had the lowest CO_2% and so were more recalcitrant than those dried at lower temperatures, supporting the findings of Matsuoka et al. (2006). It is known that organic material dried at high temperatures (>170 °C) may cause the agglomeration of particles and the creation of recalcitrant chemical bonds (Bougrier et al. 2006). These include Maillard reactions, in which melanoidins (brown, high molecular weight heterogeneous polymers formed from sugars and amino acids at high temperatures) are created that are almost impossible to degrade (Carrère et al. 2010; Ariunbaatar et al. 2014). The lower CO_2% from the S-LD190 and S-LD250 treatments at pF 2 clearly confirmed this finding (Table 3) and corresponded with the observed decline in min-N at the higher temperatures. The higher drying temperatures clearly reduced decomposability and mineralisation of the biosolids; changes in biochemical composition should be further investigated to confirm whether the abovementioned reactions could explain this increase in recalcitrance.

Soil N_2O emissions

There was an initial 'burst' of soil N_2O emissions in the first 10 days following amendment at both pF 2 and pF 1 (Fig. 3c, d). The initial rapid increase in N_2O production lasted longer at pF 1 than in soil at pF 2; at this higher water content, N_2O production of >1 μg N_2O-N g^{-1} day^{-1} was observed as late as day 42, e.g. for S-LD190 (Fig. 3c, d), while N_2O production rates at pF 2 were less than 0.25 μg N_2O-N g^{-1} day^{-1} by day 24. Between day 42 and 120, S-AD emitted the most N_2O (Fig. 3c), suggesting that thermal drying changed the temporal

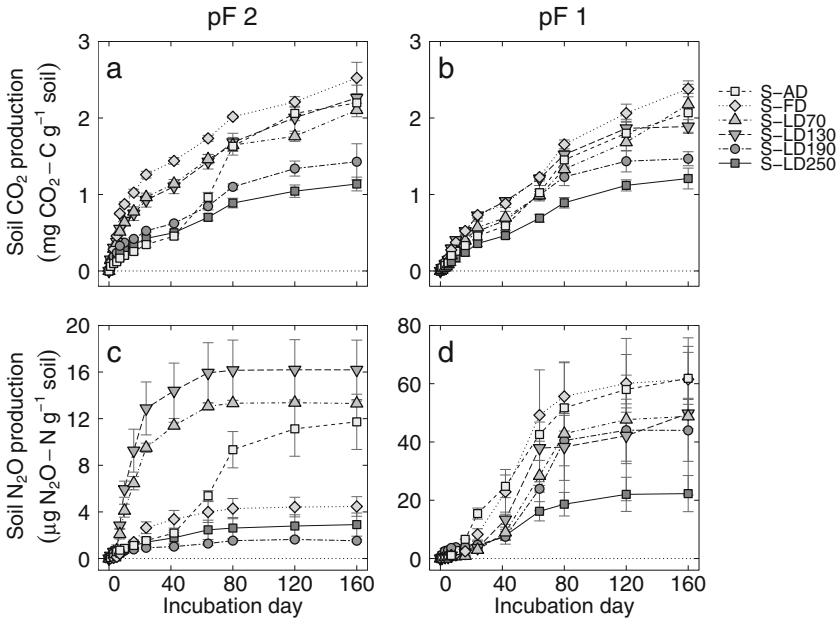

Fig. 3 The effect of biosolids on soil **a**, **b** N_2O and **c**, **d** CO_2 production during the incubation in soil wetted to pF 2 (**a**, **c**) or pF 1 (**b**, **d**). *Points* indicate mean, *bars* denote standard error. The *treatment letters* signify the following: S-AD = soil + dewatered AD biosolids, S-FD = soil + WWTP-dried biosolids, and S-LD70, S-LD130, S-LD190, and S-LD250 = soil + laboratory-dried AD biosolids dried at 70, 130, 190, or 250 °C, respectively. The *horizontal dotted lines* indicate 0

dynamics of N_2O emissions by increasing short-term release (with biosolids dried below 190 °C). Overall, soil N_2O production was greater at pF 1 than at pF 2 (Table 3), which was expected as denitrification is generally much more active at higher water contents (Senbayram et al. 2012).

Cumulative production of N_2O-N as a percentage of total biosolid N (N_2O%) was calculated over 120 days (Table 3). For soil maintained at pF 2, N_2O% ranged from 0.29 to 1.64 %. At this moisture content, the N_2O% for S-AD was in between the other treatments (Table 3). For the thermally dried treatments, N_2O% was greatest in S-LD70 and S-LD130 (which was also significantly higher than S-AD), whereas it was significantly lower for S-LD190, S-LD250, and S-FD (Table 3). N_2O% was in general much greater at pF 1 than at pF 2, between 2.3 and 6.1 %. At pF 1, biosolid type or drying treatment had no significant effect on N_2O%. Therefore, our third hypothesis, that N_2O emissions would be lower in soils amended with higher drying temperature biosolids, was only confirmed at pF 2 but not at pF 1 (Table 3). We could not explain the inconsistent trends in N_2O% with thermal drying, or with drying temperature.

The N_2O% found for most of the biosolids in our study at pF 2 was close to the IPPC Tier 1 emission factor of 1 % for fertilisers (values ranged from 0.17–1.79 %, Table 3, De Klein

Table 3 The cumulative production of N_2O-N and CO_2-C from biosolids (control soil values subtracted) as a percentage of total organic + inorganic N in biosolids (for N_2O-N) and as a percentage of total C (for CO_2-C) over 120 days from biosolids addition

Soil moisture status	Treatment	N_2O-N production (% of total N)	CO_2-C production (% of total C)
pF 2	S-AD	1.04 (0.21) b	27.3 (0.5) a
	S-FD	0.44 (0.09) c	28.6 (0.4) a
	S-LD70	1.36 (0.03) ab	21.6 (0.4) c
	S-LD130	1.64 (0.29) a	25.1 (1.0) b
	S-LD190	0.17 (0.01) c	13.6 (0.5) d
	S-LD250	0.29 (0.11) c	8.9 (0.4) e
pF 1	S-AD	5.44 (0.46) a	29.8 (0.8) b
	S-FD	6.06 (1.05) a	32.8 (0.6) a
	S-LD70	4.87 (3.08) a	27.2 (0.6) c
	S-LD130	4.27 (1.06) a	29.5 (0.6) b
	S-LD190	4.79 (1.18) a	21.9 (0.7) d
	S-LD250	2.34 (0.65) a	17.0 (0.4) e

Values indicate mean (+/− standard error). Letters indicate a significant difference between treatments of the same soil water status ($p < 0.05$). S-AD = soil + dewatered AD biosolids, S-FD = soil + WWTP-dried biosolids, and S-LD70, S-LD130, S-LD190, and S-LD250 = soil + laboratory-dried AD biosolids dried at 70, 130, 190, or 250 °C, respectively

et al. (2007)). N_2O% at pF 1 was much greater but was comparable to organic fertiliser N_2O emission factors in areas of high precipitation (Lesschen et al. 2011).

The influence of drying process

It was clear from the min-N, CO_2, and N_2O results that the material dried at the WWTP (FD) was quite different from the laboratory-dried products (LD70–250). In this study, the results for min-N and N_2O% were sometimes different between WWTP and laboratory thermally dried biosolids at similar drying temperatures (70–200 °C, Fig. 2 and Table 3), which suggested that drying temperature was just one of multiple factors that affected min-N.

The laboratory drying process is different from that of a large-scale WWTP drying system in many ways. For example, WWTP thermal drying involves continuous moving and mixing of biosolids and exposure to varying temperatures along the process and, as a consequence of this, differences in the final dry matter content of the product. These factors may influence the physical and chemical properties of biosolids and the changes in the physical structure of the dried product may be different from that of the laboratory-dried sludge produced under constant and more or less static conditions (Bennamoun et al. 2013).

Conclusions

Thermal drying of anaerobically digested biosolids reduced its inorganic N content and did not increase its N mineralisation. Thermal drying temperature had a significant negative effect on C and N mineralisation and N_2O/CO_2 emissions; in soils at field capacity, biosolids dried at 190 °C or 250 °C had the lowest N mineralisation, N_2O production, and CO_2 production, indicating that the biosolid organic matter had become more recalcitrant.

Overall, thermal drying provided no advantage in terms of optimising N availability from biosolids to soil. These findings are in contrast to several studies that observed increased N availability following biosolid thermal drying. Further studies need to confirm these findings with dried biosolids sourced from other waste water treatment plants in different soil types, and to characterise the effects of drying on biosolid physical and chemical properties.

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