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Hydrochar from dairy sludge as phosphorus fertiliser affects greenhouse gas emissions and maize yield

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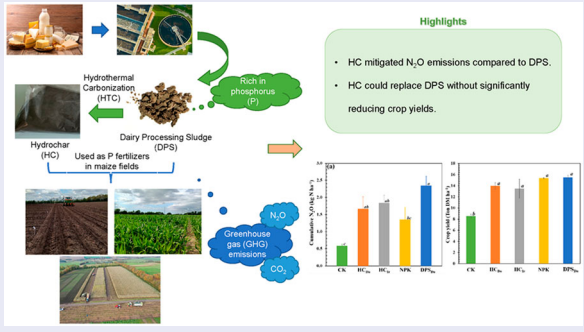
ABSTRACT

Dairy processing sludge is a phosphorus (P) rich waste with a high potential to replace mineral phosphorus fertiliser in crop production, with possible enhancement of greenhouse gas emissions to the environment. Hydrothermal carbonisation is a technology that transforms the sludge into a hydrochar. The objective of this study is examining P availability of two hydrochars produced from Danish and Irish dairy sludge and their influence on greenhouse gas emissions and maize yields. The trial assessed (i) Danish dairy sludge; (ii) hydrochar derived from Danish sludge; (iii) hydrochar made from Irish dairy sludge; (iv) mineral phosphorus fertiliser; and (v) control. Emissions of nitrous oxide and carbon dioxide, soil pH, mineral nitrogen contents and crop yields were measured. Treatment with Danish dairy sludge had significantly higher cumulative nitrous oxide emissions while the emissions from both hydrochars were not significantly different compared to mineral phosphorous feriliser. Statistical modelling showed that temperature, soil nitrate content, interactions both between temperature and precipitation, and between soil moisture and precipitation were drivers for nitrous oxide emissions. There was no difference in emissions among all treatments when scaled for yield. Hydrochar may alleviate the enhanced nitrous oxide emissions in soil without constraining P availability and maize crop yields.



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Bio-based fertiliser; Dairy manures; Environment; Hydrothermal carbonisation; Soil; STRUBIAS

Abbreviations

CK	Control, untreated soil
DM	Dry matter
DPS	Dairy processing sludge
DS	Dried sludge
GHG	Greenhouse gas
GHG_I	GHG intensity
GWP	Global warming potential
GWP_t	Total global warming potential
HC_{Da}	Hydrochar produced with a Danish DPS
HC_{Ir}	Hydrochar produced with an Irish DPS
HTC	Hydrothermal carbonization
NPK	Application of mineral nitrogen, phosphorus and potassium fertilizers

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OM	Organic matter
DPS_{Da}	Application of untreated DPS with mineral nitrogen and potassium fertilizers
SOC	Soil organic carbon
SOM	Soil organic matter
STRUBIAS	STRUvite, BIochar, AShes

Introduction

The European Commission approved a series of policy initiatives (named the European Green Deal) in 2020 to make the European Union (EU) climate neutral by 2050 (European Commission 2021). The deal is focused on achieving 55% reduction of greenhouse gas emissions (GHG) by 2030 compared to 1990 levels and improvement of economies without increasing resource consumption (European Commission 2021). Agriculture is one of the major sources of GHG emissions, contributing 66% of the global emission of nitrous oxide (N_2O) gas (Davidson and Kanter 2014). The high global warming potential (GWP) of N_2O and its contribution to stratospheric ozone depletion and global warming are the negative consequences of agricultural practices (IPCC 2019).

Phosphorus (P) is a vital nutrient for plants and food production. Its sources are limited and are confined in certain geographic locations and thus need to be imported into many countries (Zou et al. 2022). To reduce imports, recycling of P present within agricultural wastes is encouraged (FAO 2022). In 2019 and 2020, there were around 2.42 and 2.45 million tons of dairy processing sludge (DPS) produced from European milk production, leading to ca. 12,680 and 12,840 tons of total P retained in the DPS (Hu et al. 2021). Since DPS is an agricultural waste low in heavy metal content and rich in P, it can replace mineral P fertilisers in crop production (Ashekuzzaman, Fenton, et al. 2021; Ashekuzzaman, Forrestal, et al. 2021; Hu et al. 2021; López-Mosquera and Carral 2000), along with its derived secondary products (e.g. struvite, biochar and ashes (STRUBIAS)) (Shi, Fenton, et al. 2022). However, DPS can have drawbacks such as high transportation and storage costs due to its high water content (Sommer and Knudsen, 2021) and easily degradable organic matter content which may form anaerobic hotspots after application, leading to enhancement of N_2O emissions through coupled nitrification-denitrification (Petersen et al. 1991).

Hydrothermal carbonisation (HTC) is a promising technology that could contribute to the efficient management of organic waste (Smith et al. 2023). It works by pressure cooking organic slurries in their water to enable coalification reactions, leading to dehydration and aromatisation of the organic carbon. When applied to DPS under optimal conditions, it reduces the volume of DPS by aiding dewatering and removing oxygen present in the DPS. A combination of dehydration and aromatisation should result in an increasingly recalcitrant C, which has the potential to enhance carbon sequestration and mitigate GHG emissions after applying to the soil (Luo et al. 2023). Previously, hydrochar produced from a range of feedstocks has been used as fertilisers (Bargmann et al. 2014; Khosravi et al. 2022), however, crop yields and GHG emissions vary due to the nature of the feedstocks, processing conditions, soil and environmental conditions.

The objectives of this study were: (a) to assess the effects of DPS and DPS-derived hydrochars on GHG emissions from maize fields; (b) to determine the possible drivers of emissions from maize fields treated with DPS and hydrochars; and (c) to examine the effects of DPS and derived hydrochars on maize crop yields. For that, a field experiment was conducted on sandy loam soil under maize crops for one year. Effects of DPS and DPS-derived hydrochars on GHG emissions and maize yields were compared in reference to mineral fertilisers and untreated control.

Materials and methods

Characteristics of DPS and derived hydrochar

A Danish DPS (DPS_{Da}) and two DPS-derived hydrochars (HC_{Da} and HC_{Ir}) were used in this field trial. The DPS_{Da} was collected from a local dairy industrial wastewater treatment plant at Videbæk, Denmark (Picture is in Supplementary Materials). For HC_{Da}, the DPS was processed in a continuous HTC reactor at Aarhus University (Picture can be found in Supplementary Materials). About 500 kg of DPS was mixed with water to give a slurry with a DM (dry matter) of 15% and pH was corrected to pH 5 using hydrochloric acid to reduce oil formation and promote carbonisation. The slurry was then processed at 50 kg h^{-1}, with a residence time of approximately 60 min at 225°C. The hydrochar was recovered from the slurry using a drum filter with 100 µm mesh before being dried at 70°C, mixed and homogenised. A mass yield of 58% was estimated based on mass balances and supporting experiments carried out in a 2000 ml Parr reactor operated in comparable conditions. The HC_{Ir} was produced at the University of Limerick utilising the DPS received from a local dairy industrial wastewater treatment plant at Limerick, Ireland, using a 7500 ml Parr reactor, with a processing temperature of 180°C and a resonance time of 120 min. The characteristics of two DPS and derived hydrochars are presented in Table 1.

Table 1. Characteristics of two dairy processing sludge (DPS) and derived hydrochars.

	Danish (Da) DPS	Hydrochar from Da-DPS (HC_{Da})	Irish (Ir) DPS	Hydrochar from Ir-DPS (HC_{Ir})
DM (% total weight)	20.4	–	19.3	–
Total C (% DM)	35.7	38.2	48.7	57.1
Total N (% DM)	5.8	6.3	4.9	11.2
Total P (% DM)	4.3	7.1	5.7	9.4
NH_4^+-N (g kg^{-1} DM)	9.1	–*	5.1	–*
pH	7.8	5.0	7.6	6.8
Al (mg kg^{-1} DM)	1149.0	3662.2	6115.6	7958.6
Ca (mg kg^{-1} DM)	46,771.3	68,053.2	49,205.4	67,989.9
Fe (mg kg^{-1} DM)	97,426.1	133,444.0	128,740.7	177,286.1
K (mg kg^{-1} DM)	10,694.9	5143.3	15,256.4	13,486.9
Mg (mg kg^{-1} DM)	5844.7	8338.9	2874.7	3722.5
Mn (mg kg^{-1} DM)	204.5	362.0	4321.4	3210.5
Zn (mg kg^{-1} DM)	169.2	214.0	136.0	186.1

*: The NH_4^+-N contents in both hydrochars were negligible.

Study site and applications

The experiment was started on 11th May 2021 in a maize field at Foulum (56°50′ N, 9°57′ E), Denmark (Pictures are available in Supplementary Materials). The soil was a sandy loam (7.3% clay, 6.5% silt, 47% fine sand, and 39.2% coarse sand), with pH of 6.0, 1.47 mg kg^{-1} NH_4^+-N, 5.48 mg kg^{-1} NO_3^--N, and 10.0 g kg^{-1} total soil organic carbon (SOC) (Pedersen et al. 2022). Daily air temperatures, precipitation, and soil temperatures at 10 and 30 cm depths during the experiment were collected from a meteorological station at Foulum (Figure 1).

There were five treatments with triplicates in the experiment: (1) application of HC_{Da} together with mineral N and potassium (K) fertilisers, (2) application of HC_{Ir} together with mineral N and K fertilisers, (3) application of untreated Danish DPS together with mineral N and K fertilisers, designated as 'DPS_{Da}', (4) application of mineral N, P and K fertilisers, designated as 'NPK', and (5) untreated soil control, designated as 'CK'. The DPS, HC_{Da} and HC_{Ir} were treated as bio-based P fertilisers and compared with a mineral P fertiliser. The details of mineral fertilisers, application rates of N, P and K and actual applied amounts of fertiliser products are presented in Table 2.

The treatments were laid down in a completely randomised design in a total of 15 plots, with a gross size of 15 m × 6 m (comprising 8 rows) for each plot. Mouldboard ploughing (0–25 cm) was conducted before fertiliser application for all the plots in order to break large soil aggregates and loose the soil to achieve a great seedbed for sowing. During the application, the DPS, HC_{Da} and HC_{Ir} were applied manually on the soil surface with 30 kg P ha^{-1} based on their total P contents (Table 2), followed by incorporating them into the soil through tillage with rotor harrows to a depth of 5–10 cm. Mineral fertiliser (N, P, K) application was carried out by an automatic fertiliser spreader to ensure fertilisers applied 5 cm beside and 5 cm below where maize seeds would be placed.

Silage maize (*Zea mayz* L.) seeds were drilled 5 cm into the soil maintaining 75 cm row and 13 cm crop spacing. Maize crops were harvested with a plot harvester for all plots (2nd Nov 2021), and subsamples of fresh chopped crops were dried at 60°C for 72 h, (adapted from Pedersen et al. 2022) to determine dry biomass yields.

GHG emission measurements

Greenhouse gas (N_2O, CO_2 and CH_4) emission measurements were carried out with the static chamber technique from 11th May 2021 to 20th September 2021. During that time, samples were taken for 23 sampling times, with 4 sampling occasions in the first week, followed by 2 sampling occasions per week for 4 weeks, and then once per week for 9 weeks until 9th August 2021. The final 2 samples were obtained on 27th August and 20th September 2021. The measurement method was the same as Nair et al. (2020). In brief, the collars were inserted prior to the experiment on the rows of each plot, where maize seeds were sown. During gas sampling plastic-made static chambers (35 cm L × 25 cm W × 20 cm H) were placed on stainless steel collars, and immediately, chambers and collars were tightened with straps. On each sampling occasion, headspace gas inside the chamber was mixed 3–4 times with a 10 ml syringe and hypodermic needle injected via a septum on the chamber, followed by collecting and transferring the gas to a pre-evacuated 6 mL exetainer (Labco, High Wycombe, UK). In total four samples were collected within an hour of closure i.e. at 0, 20, 40 and 60 min.

When maize was grown taller than the chamber's height (from July 2021) an open top and bottom plastic extension (35 cm L × 25 cm W × 40 cm H) was applied between the collar and chamber to help accommodate the crop. Each sampling occasion was carried out between 10:00-13:00, since it was reported as optimal time for minimising influences of sampling bias and diurnal temperature (Ashiq et al. 2020). The concentrations of N_2O, CO_2 and CH_4 in gas samples were analysed with an Agilent 7890 (Agilent, Nærum,

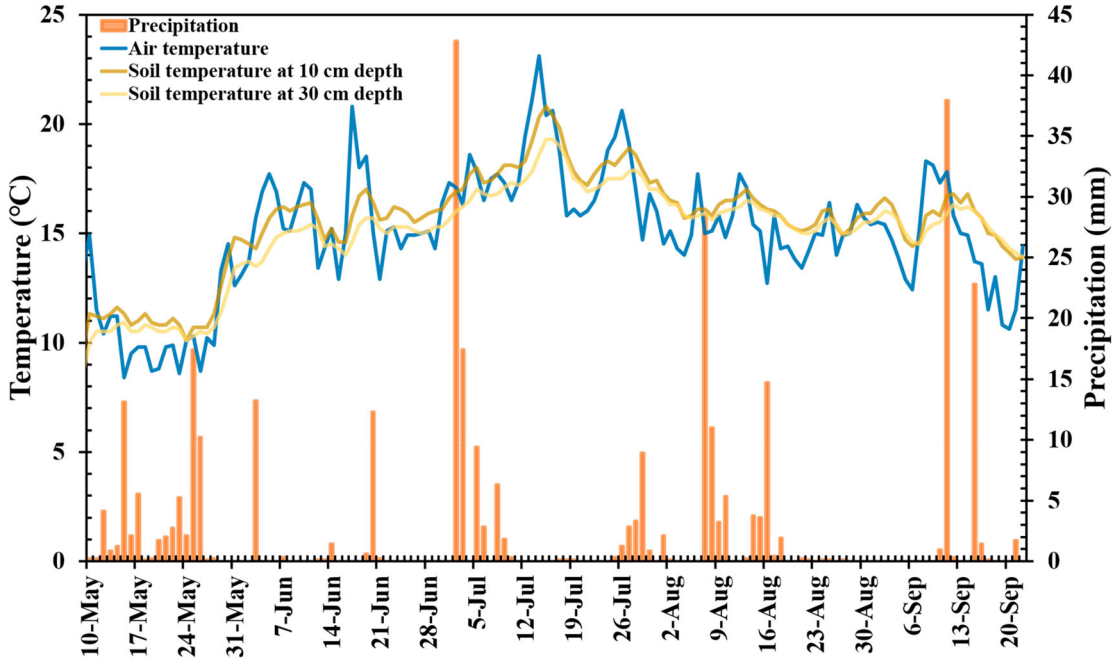

Figure 1. Temporal changes of air and soil temperatures and precipitation during the experiment.

Denmark) gas chromatograph as described by Petersen et al. (2012).

Flux calculations

GHG fluxes were calculated by a free package HMR in R (Pedersen et al. 2010). Cumulative emissions of GHG were calculated by the integration of GHG fluxes with time. For a better comparison of effects of different GHGs under a unified criterion, cumulative N_2O emissions were converted to the 100-year global warming potential (GWP) of N_2O assuming a CO_2 equivalent heating potential of 273 kg CO_2 per kg N_2O (IPCC 2022). Since CH_4 fluxes were negligible during the experiment, it is not included in the calculations. Total GWP (GWP_t) was calculated with Equation (1) (IPCC 2022):

$$GWP_t = CE_{CO2} + 273 \times CE_{N2O} \quad (1)$$

where CE_{CO2} and CE_{N2O} were cumulative emissions of CO_2 and N_2O during the experiment, respectively. The yield-scaled N_2O emissions (YE_{N2O}) for linking agronomic productivity to N_2O emissions, were calculated with Equation (2) (Mosier et al. 2006; Yang et al. 2020):

$$YE_{N2O} = 273 \times CE_{N2O}/CY \quad (2)$$

Table 2. Treatments and amounts of fertilisers applied in the experiment.

Treatment	Abbr.	Nitrogen (N) application rate (kg N ha^{-1})	Actual[1] N fertiliser[2] addition (kg ha^{-1})	Phosphorus (P) application rate (kg P ha^{-1})	Actual P fertiliser[3] addition (kg ha^{-1})	Potassium (K) application rate (kg K ha^{-1})	Actual K fertiliser[4] addition (kg ha^{-1})
Danish DPS + mineral N & K fertilisers	DPS_{Da}	130	457[5]	30	3876	165	660
Hydrochar (HC) from a Danish DPS + mineral N & K fertilisers	HC_{Da}	130	481	30	421	165	660
Hydrochar (HC) from an Irish DPS + mineral N & K fertilisers	HC_{Ir}	130	481	30	320	165	660
Mineral N, P and K fertilisers	NPK	130	481	30	170	165	660
Untreated (no fertiliser addition)	CK	0	0	0	0	0	0

1: Actual amount of fertiliser addition was calculated by the application rate divide by the percentage of active ingredient (i.e. N, P or K) in the fertiliser.
2: Nitrogen fertiliser was applied in calcium ammonium nitrate (CAN, 27% N).
3: Phosphorus fertilisers were applied in bio-based fertilisers (i.e. HC_{Da}, HC_{Ir}, DPS) and triple superphosphate (TSP, 17.6% P, as NPK), and bio-based fertilisers were calculated in respective total *P* contents (referred to Table 1).
4: Potassium fertiliser was applied in Patenkali (25% K).
5: The actual addition of N fertiliser was deducted with the amount of NH_4^+-N in the added DPS (equivalent to 24 kg ha^{-1} mineral N fertiliser).

where CY represented maize crop yields (kg). The direct emission factors (EF_d) of N_2O induced by different treatments were calculated with Equation (3):

$$EF_d = 100 \times (CE - C_0)/F_N \quad (3)$$

where CE was cumulative emission of N_2O (kg N ha^{-1}) from respective treatment, C_0 was cumulative N_2O emission (kg N ha^{-1}) from CK treatment, and FN was the N fertiliser application rate (kg N ha^{-1}).

Soil sampling and analyses

Soil was sampled from plots avoiding the area inside and close to the gas sampling collars at the following time intervals: twice per week in May, once per week in June, once per two weeks in July, and once per four weeks from August until the end of experiment (20th September 2021). On each sampling occasion, soil samples were collected from six random places in each plot with an auger (2 cm diameter, 20 cm depth). Collected soil samples were stored in sealed plastic bags and carried to the laboratory with ice boxes (at 0 °C). The soil was then well mixed and passed through 2 mm sieves prior to subsampling for soil moisture and pH measurement (1:4 w/w in 1M KCl) on the same day as sampling. The soil moisture was measured gravimetrically by drying the soil at 105°C for 24 h. The mineral N contents were measured on soil extraction by adding 10 g soil to 40 ml 1 M KCl solution, shaking the mixture end-over-end for 30 min, filtering it with 1.6 µm microfiber filters (VMR, Sweden) and storing the filtrate at −20°C until measurement. The concentrations of soil NH_4^+-N and NO_3^--N were determined with standard colorimetric analyses on a Spectroquant Photometer NOVA 60A (Merck KGaA, Darmstadt, Germany).

Data analyses

Statistical analyses were performed using R-software version 4.1.2 (R Core Team 2022). Model assumptions (normality and homogeneity of variance) were tested by diagnostic plots of residuals. The daily and cumulative N_2O and CO_2 emissions were log-transformed to meet model assumptions. The data were analysed by linear mixed effect (*lme*) model under *nlme* package using the restricted likelihood (REML) method. For daily N_2O and CO_2 emissions, the autocorrelation between measurements was considered using the function CorAR1. Pairwise comparisons between treatments were evaluated by the estimated marginal mean (*emmeans*) function. The *p*-values were adjusted by Tukey's HSD method, with the hypothesis rejection threshold of 0.05.

Main and interaction effects of soil and environmental variables such as temperature, precipitation, soil moisture, pH, NH_4^+-N and NO_3^--N contents on N_2O emissions were analysed with multiple regression analysis. During analysis, all possible two-way interactions of variables with respect to N_2O emissions were examined for meaningful interpretation. We developed a full model during analysis which was reduced using backward selection removing non-significant interaction terms ($p > 0.05$) to make the final model.

Results and discussion

Temperatures and precipitation

Daily mean values for air temperatures during the sampling period (12th May–20th September 2021) ranged between 7.6 and 23.1°C, with the highest temperature in July and lowest temperature in May (Figure 1). Rainfall was typical for the summer season with one maximum daily precipitation of 43 mm on 2nd July 2021 (Figure 1). Cumulated precipitation during the experimental period was 348 mm. Soil temperatures followed the same trends as the air temperature and ranged between 8.2 and 20.8°C at 10 mm depth and between 8.0 and 19.3°C at 30 mm depth.

Soil moisture, pH and mineral N dynamics

Gravimetric soil moisture (Figure 2) was above 16% at the beginning of the experiment. During the growing season, the lowest soil moisture content was below 10% in mid-July with high temperature. Although soil moisture showed differences in treatments, the differences were not significant ($p > 0.05$), implying that the soil moisture decrease could be due to the temperature increase as well as the enhanced water consumption by maize growth.

Soil pH decreased significantly ($p < 0.05$) on 17th May 2021 compared to that on previous days (all treatments were below pH of 4.5 except NPK) and increased again in the following week (Figure 2). In all plots, the pH varied between 5 and 7 over experimental period, which implies that HC addition might not be the main driver for soil pH changes. Previously, there was a study showing that beet-root-chips-derived hydrochar (pH of 4.10) application increased soil pH and it was ascribed to mitigation of acidic metabolites due to proton-depleting reductive activities of soil microorganisms (Rillig et al. 2010), however, that was not found here due to possible background soil buffering capacity.

In the 'fertilised plots', the concentrations of NH_4^+-N in soil were high from May to June, with the highest concentrations occurred in NPK and DPS_{Da} plots (ca. 35 mg kg^{-1} dry wt.) and decreased to a low range

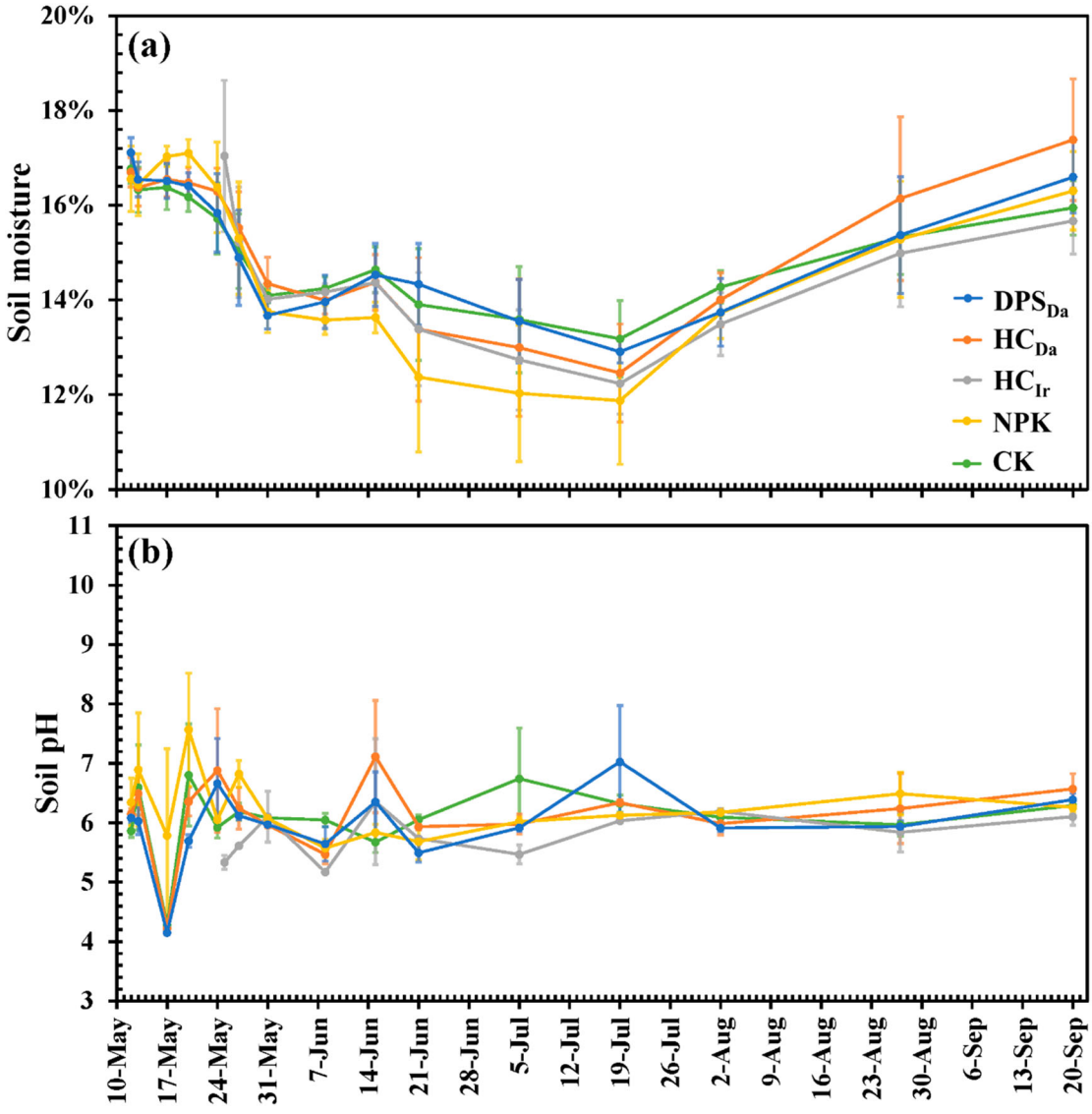

Figure 2. Temporal changes of soil moisture and pH with standard error of the mean (SEM) during the experiment. $n = 3$. The legend shows DPS (Dairy Proceeding Sludge), HC (Hydrochar (Da: Denmark, Ir: Ireland)), NPK (mineral fertiliser,) and CK (Control).

after mid-June (Figure 3(a)). The soil NO_3^--N content increased up to 118 mg kg^{-1} after fertilisation and started to decline shortly thereafter (Figure 3(b)). The NH_4^+-N and NO_3^--N concentrations peaking at the beginning of the experiment could be attributed to the release of N fertiliser added to all plots except the control, and the decreases might be due to plant uptake, nitrification of NH_4^+ and denitrification of NO_3^-, as well as possible NO_3^- leaching. The NO_3^--N concentration increased again from 31st May to 21st June, and then reached the background level. Evidence of denitrification is present with high levels of N_2O produced during this period (Figures 3 and 4(a)). The higher contents of NO_3^--N in two HC treatments compared to DPS_{Da} and NPK during June could be attributed to mineral N retention by physical and chemical sorption of hydrochar (Luo et al. 2023). It seems that inorganic N contents in HC treatments decreased probably due to the slow release of N and possible plant uptake (Taghizadeh-Toosi et al. 2012).

GHG emissions

Previous studies showed that dairy manure or slurry sharply increased N_2O emissions within a week of application (Hunt et al. 2019; Leytem et al. 2019). Treated dairy effluent had greater net GHG emissions than urea in a semiarid field trial with maize crops (Lombardi et al. 2022). It was reported that dairy manure and inorganic N fertilisation enhanced GHG emissions while biochar amendment together with the fertilisation reduced the emissions (Ashiq et al. 2020; Hu et al. 2023). In this study, the two highest N_2O emission events were in the DPS_{Da} plot on the 31st of May with

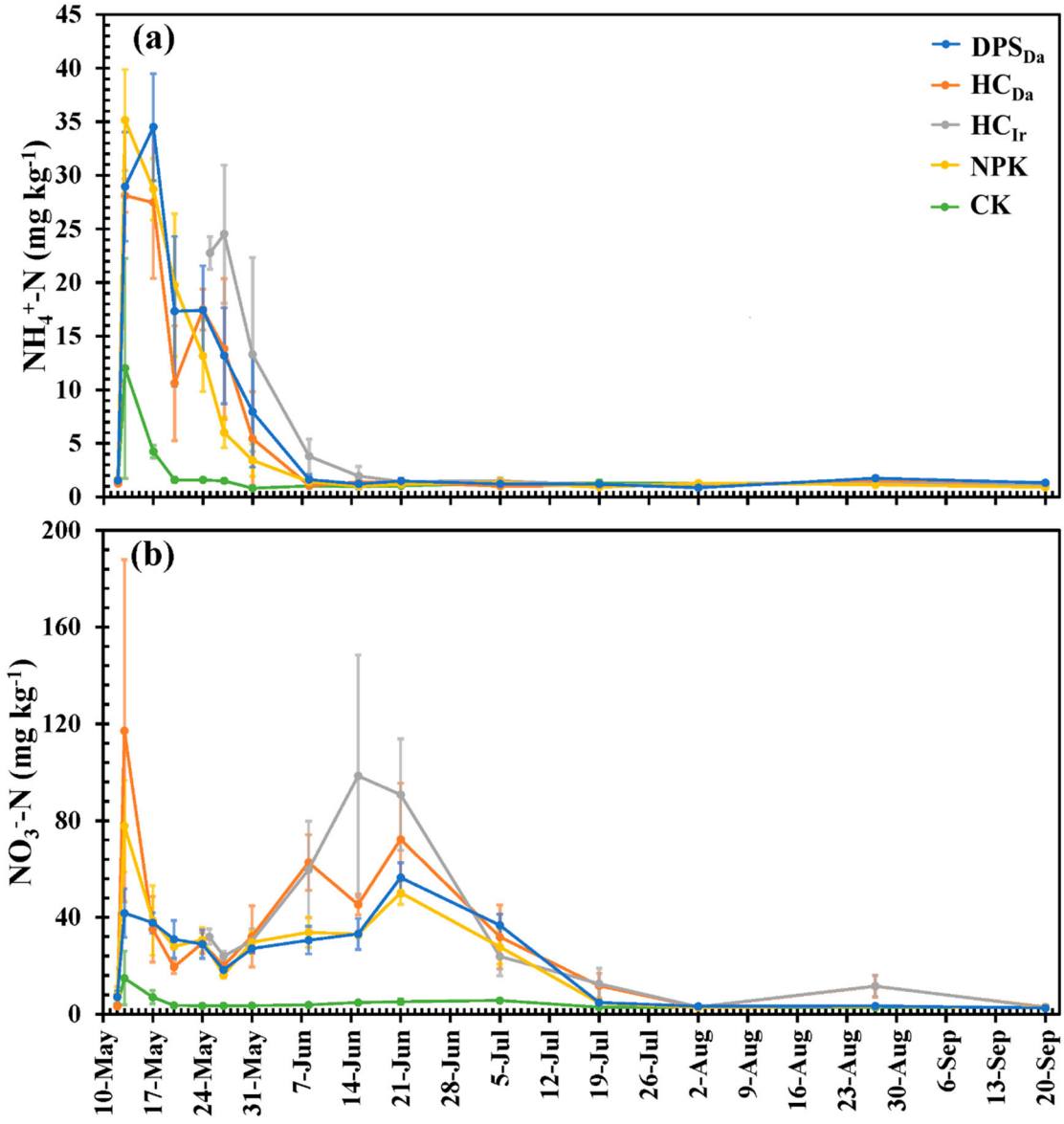

Figure 3. Temporal changes of soil NH_4^+ and NO_3^- contents with standard error of the mean (SEM) during the experiment. $n = 3$. The legend shows DPS (Dairy Proceeding Sludge), HC (Hydrochar (Da: Denmark, Ir: Ireland)), NPK (mineral fertiliser,) and CK (Control).

1.35 mg N_2O m^{-2} h^{-1} and in the HC_{DA} plot on the 5th of July (1.3 mg N_2O m^{-2} h^{-1}). The first peak was attributed to nitrification of NH_4^+, and the second peak was mainly due to denitrification, and warming and enhanced precipitation stimulated the processes. All fertilised plots had several small peaks in mid-May and June (Figure 4a). After July, N_2O fluxes for all treatments were in low ranges because inorganic N contents were depleted.

Cumulative N_2O emissions from DPS_{Da} treated plots were highest (a mean of 2.34 kg N_2O-N ha^{-1}) followed by the other plots in descending order of HC_{Ir}, HC_{Da}, NPK and CK. The mean cumulative N_2O emissions of HC_{DA} and HC_{Ir} were 29.1% and 21.6% lower than that from DPS_{Da}, although there was no statistical difference. The emissions from NPK were lower ($p < 0.05$) than that from DPS_{Da}, but not significantly different from HC_{DA} and HC_{Ir}. This could be due to the organic matter content in DPS_{Da}, which might have contributed to anaerobic hot-spots for N_2O production, while HCs either alleviated the formation of hot-spots, or attributed to the NO_3^- retention (Schimmelpfennig et al. 2014). The latter was indicated by the higher NO_3^--N contents in HCs than in DPS_{Da} plots. Other potential reasons could be plant uptake, N immobilisation and reduced activities of nitrifying and denitrifying enzymes with hydrochar application (Wang et al. 2015).

The multiple regression analysis for N_2O emissions with environmental and soil variables (Table 3) indicated that temperature and soil NO_3^--N were the main driving factors ($p < 0.05$) for N_2O emissions. Furthermore, the

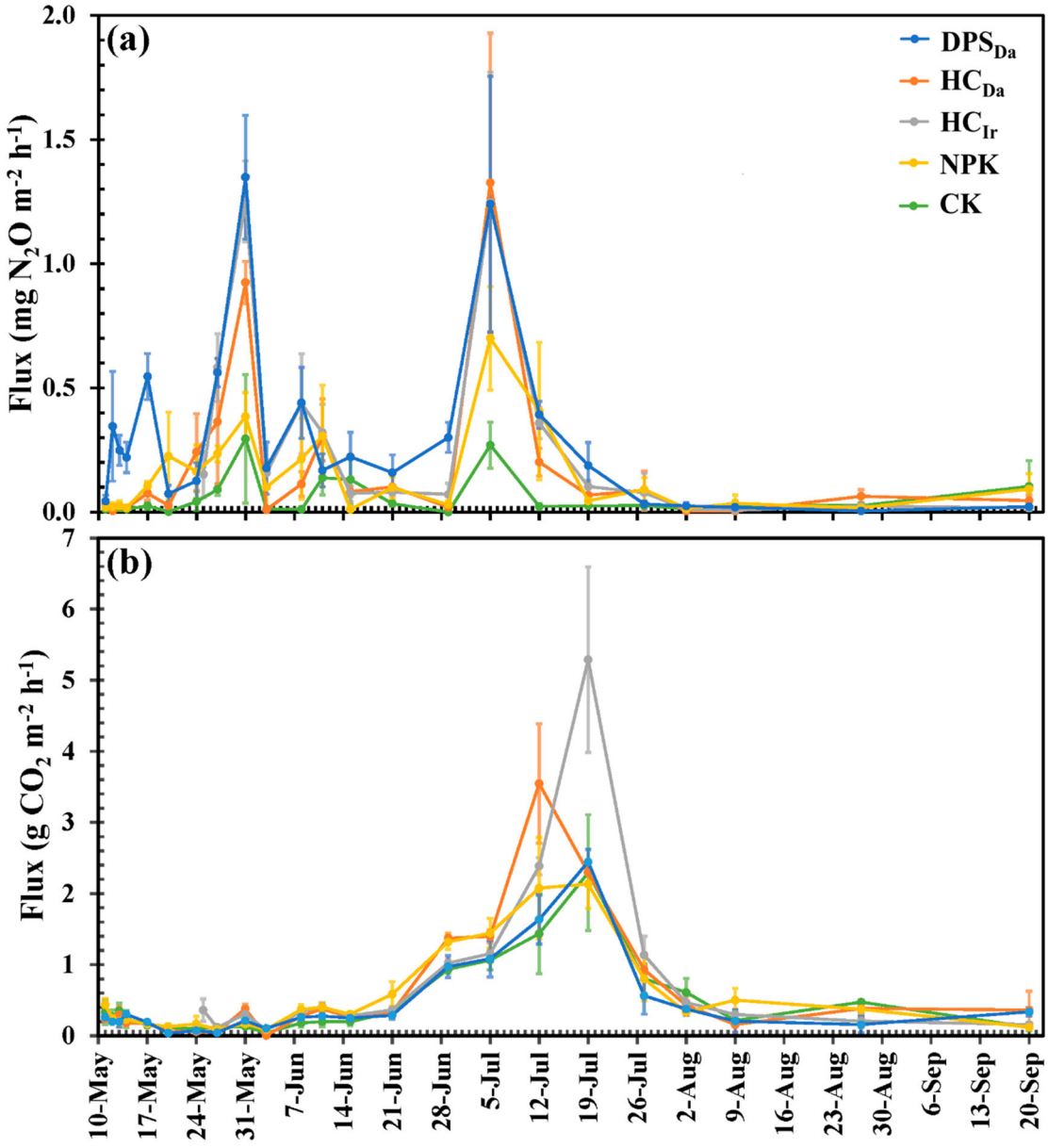

Figure 4. Temporal changes of N_2O and CO_2 fluxes with standard error of the mean (SEM) during the experiment. $n = 3$. The legend shows DPS (Dairy Proceeding Sludge), HC (Hydrochar (Da: Denmark, Ir: Ireland)), NPK (mineral fertiliser,) and CK (Control).

Table 3. The multiple regression analysis for N_2O emissions correlated with environmental and soil variables.

Variables	numDF	denDF	F value	*p*-value	Coefficient
Intercept	1	200	900.9165	<0.0001	−2.7856
Soil moisture	1	200	2.6469	0.1053	12.8776
pH	1	200	1.9031	0.1693	−0.1425
NH_4^+-N	1	200	1.7912	0.1823	0.0202
NO_3^--N	1	200	4.3131	0.0391*	0.0058
Temperature	1	200	22.5104	<0.0001**	0.0756
Precipitation	1	200	1.7255	0.1905	−0.9483
Soil moisture*Precipitation	1	200	14.9258	0.0002**	1.7399
Soil moisture*Temperature	1	200	0.8773	0.3501	−0.7672
Temperature*Precipitation	1	200	19.0858	<0.0001**	0.0500
Soil moisture* NO_3^--N	1	200	0.0247	0.8753	−0.0198

** indicates the respective variable has a strong significant effect (*p*-value < 0.005); * indicates the respective variable has a significant effect (*p*-value < 0.05).

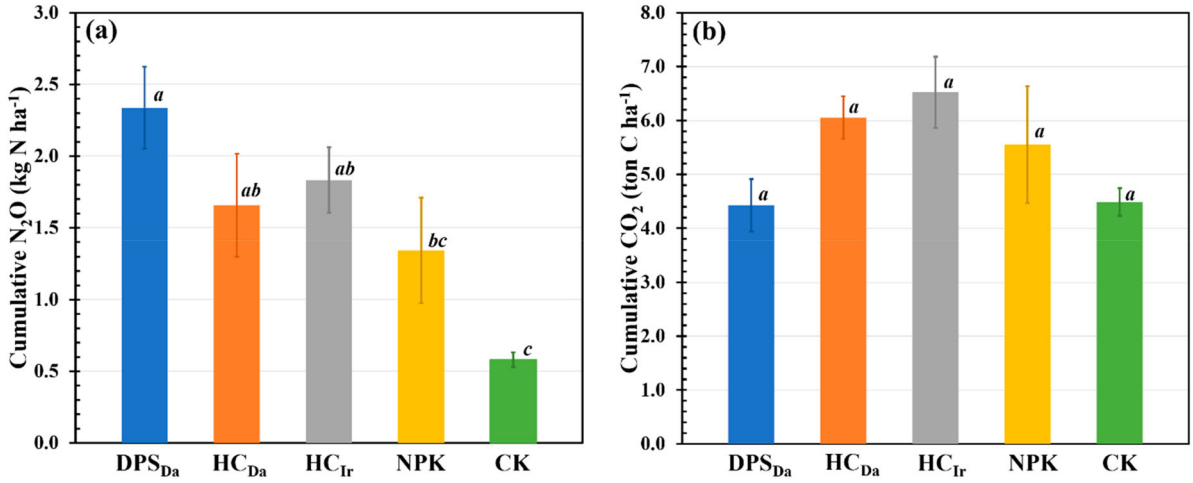

Figure 5. Cumulative emissions of N_2O and CO_2 with standard error of the mean (SEM) during the experiment. $n = 3$. Different letters indicate significant differences by Tukey HSD test ($p < 0.05$) between treatments. The X axis shows DPS (Dairy Proceeding Sludge), HC (Hydrochar (Da: Denmark, Ir: Ireland)), NPK (mineral fertiliser,) and CK (Control).

interaction between soil moisture and precipitation and the interaction between temperature and precipitation were also strongly ($p < 0.05$) and positively related with N_2O emissions, suggesting that N_2O was mainly produced via denitrification processes.

Treatments affected temporal CO_2 fluxes ($p < 0.05$). Highest cumulative CO_2 emission (Figure 5b) was 6.52 ton CO_2-C ha^{-1} from the HC_{Ir} plots, and in descending order of HC_{DA}, NPK, CK and DPS_{Da}. Hydrochar application increased CO_2 emissions in this study and is in line with some studies having municipal digested sludge (Ebrahimi et al., 2022); beet root and bark chips (Kammann et al. 2012); and corn silage (Malghani et al. 2015) as feedstocks for producing hydrochar. The CO_2 fluxes (Figure 4b) peaked in July, and could be ascribed to the high temperature stimulated C decomposition and respiration. In a meta-analysis presented in Yang et al. (2022), it was found that the combination of increased temperature and precipitation had more significant effects on CO_2 emissions compared to the individual effect of higher temperature or enhanced precipitation. The higher CO_2 emissions from HC treatments in this study might be attributed to a large amount of oxygen-containing compounds (Fuertes et al. 2010; Sevilla et al. 2011) and a labile C pool (Malghani et al. 2013) presented in hydrochar. Those labile compounds could be from residual processed water in the hydrochar which had not been washed as well as the complex feedstock which had not been fully aromatised, and they were highly degradable and enhanced soil respiration (Malghani et al. 2013 & 2015), contributing to higher CO_2 emissions. This also implies less potential for carbon sequestration by hydrochar compared to biochar from pyrolysis, which is in line with the perspective of Luo et al. (2023).

Crop yields, total GWP, yield-scaled N_2O emissions and N_2O emission factors

The highest crop yields were recorded for DPS_{Da}, followed by NPK, HC_{DA}, HC_{Ir} and CK in descending order (Table 4). The crop yields for DPS_{Da} were almost the same as for NPK, while HC_{DA} and HC_{Ir} had slightly lower crop yields compared to the former two ($p > 0.05$). From this study, we did not see obvious negative effects of HC treatments on crop yields. There are conflicting impacts of application of HC on plant growth in literature (e.g. Busch et al. 2012; and de Jager and Giani 2021). But in general, it has been reported HC inhibitory effect disappeared when the hydrochar was aged and

Table 4. Crop yields, total global warming potential (GWP_t), yield-scaled N_2O (YE_{N2O}) emissions and N_2O direct emission factors (EF_d) for all treatments. DPS (Dairy Proceeding Sludge), HC (Hydrochar (Da: Denmark, Ir: Ireland)), NPK (mineral fertiliser,) and CK (Control).

Treatment	Crop yield (ton DM ha^{-1})	GWP_t (ton $CO_{2eq.}$ ha^{-1})	YE_{N2O} (ton $CO_{2eq.}$ ton DM^{-1})	EF_d
DPS_{Da}	15.52 ± 0.36 ^{b}	18.24 ± 1.59 ^{a}	129.80 ± 17.41 ^{a}	1.35 ± 0.25 ^{a}
HC_{Da}	13.96 ± 0.59 ^{ab}	23.62 ± 1.75 ^{a}	104.18 ± 27.09 ^{a}	0.83 ± 0.24 ^{a}
HC_{Ir}	13.47 ± 1.70 ^{ab}	25.49 ± 2.62 ^{a}	119.77 ± 19.38 ^{a}	0.96 ± 0.21 ^{a}
NPK	15.35 ± 0.11 ^{b}	21.52 ± 4.28 ^{a}	75.34 ± 21.06 ^{a}	0.59 ± 0.28 ^{a}
CK	8.53 ± 0.34 ^{a*}	16.95 ± 0.98 ^{a}	59.06 ± 7.72 ^{a}	–

*: Different letters indicate the differences between respective treatments are significant.

dried, and this was due to the reduction of volatile phytotoxic substances (e.g. formic or acetic acid) contained in the fresh hydrochar. Some literature also reported long C-chain aliphatic compounds would be degraded to short C-chain phytotoxic volatile substances via HTC processes (Jandl et al. 2013). Hydrochar treated by aging or washing may be a solution for alleviating the potential negative effects.

In this study, total GWP (GWP_t), yield-scaled N_2O emissions (YE_{N2O}) and N_2O direct emission factors (EF_d) were calculated (Table 4) to evaluate overall GHG impacts of DPS and derived hydrochar application on maize fields (IPCC 2022). There was no difference ($p > 0.05$) between treatments for GWP_t and YE_{N2O}. As for the N_2O EF_d, DPS_{Da} had the highest value (1.35) with HC_{Ir}, HC_{DA}, and NPK in descending order. Hagemann et al. (2017) showed that biochar reduced N_2O emissions from a field fertilised with mineral N by 63% in the third year after application. Therefore, further research on the effects of replacing DPS with derived hydrochar is needed particularly for longer period than one year, and to avoid enhancing adverse environmental effects and negative impact on crop production.

Conclusions

In this one-year experiment, the application of two DPS-derived hydrochars (HC_{DA} & HC_{Ir}) to a maize field decreased N_2O emissions compared to emissions from DPS_{Da}. Temperature, soil NO_3^--N content, and interactions between soil moisture and precipitation and between temperature and precipitation were drivers for N_2O emissions. There was no significant difference in CO_2 emissions between the treatments, but as an average HC_{DA} and HC_{Ir} increased cumulative CO_2 emissions compared to DPS_{Da}. The HC treatments did not significantly decrease maize crop yields compared to DPS_{Da} and NPK treatments in this trial. The DPS and derived hydrochars did not show significant effects on GWP_t, YE_{N2O} and N_2O EF_d compared to mineral fertilisers, while two HCs had higher GWP_t but lower YE_{N2O} and N_2O EF_d compared to DPS_{Da}. Based on the results, the potential of DPS-derived hydrochar as P fertiliser replacement for maize crops and its environmental effects should be further evaluated for longer than one year study herein.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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