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New biochars from raspberry and potato stems absorb more methane than wood offcuts and sunflower husk biochars**

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Abstract. The reduction in greenhouse gas emissions from agriculture is of particular importance at present. In recent times, biochar addition to the soil was suggested as a means of mitigating greenhouse gases emissions from arable fields. More specifically, biochars with useful properties and those produced from easily available waste materials are still being sought. In the presented experiment, the CH_4 absorption potential of four biochars incubated at 60 and 100% water holding capacity with the addition of 1% CH_4 (v/v) was investigated for 28 days at 25°C. The potato stem and raspberry stem biochars showed much higher potentials for CH_4 uptake than wood offcuts biochar and sunflower husk biochar. Potato stem and raspberry stem biochars incubated at 60% water holding capacity were characterized by a methane uptake rate of 8.01 ± 0.47 and 5.78 ± 0.17 mg CH_4-C kg^{-1} d^{-1}, respectively. The methane removal potentials of the other biochars were clearly lower. The advantage of the biochars from raspberry and potato stems over the wood offcuts biochar also results from their significantly lower production of carbon dioxide. Consequently, these materials have a high potential for agricultural use, in view of their impact on the greenhouse gas balance of the soil.

Keywords: biochar, methane, greenhouse gas removal, raspberry stems, potato stems

INTRODUCTION

Biochar may be defined as biomass that has been pyrolysed in a zero or low oxygen environment (Lehmann and Rondon, 2006). The application of biochar to soil is expected to enhance soil fertility, improve its water retention properties and increase carbon sequestration (Coomes and Miltner, 2017; Luo *et al.*, 2016). Biochar addition may also stimulate soil microbial activity and reduce the emission of greenhouse gases (GHGs) such as carbon dioxide (CO_2) and methane (CH_4) (Wu *et al.*, 2019) due to its specific properties, such as a large surface area and its high porosity value (Jeffery *et al.*, 2016; Kammann *et al.*, 2017; Sokołowska *et al.*, 2020). Oxygen in the soil environment is crucial for the functioning of microbiota and plant roots (Lehmann *et al.*, 2011; Yang *et al.*, 2017). A high degree of oxygen uptake by biochar may lead to the development of anoxic microhabitats in the soil (Ribas *et al.*, 2019). Under such conditions, methane is formed by anaerobic microbiota and released to the atmosphere rather than being removed from it (Chistoserdova and Kalyuzhnaya, 2018). Moisture levels modify the air-water conditions and a range of between 50 and 70% water holding capacity (WHC) is considered optimal for gas diffusion and soil microbiota (Walkiewicz *et al.*, 2020a). On the other hand, temporary flooding also occurs which results in a reduction in gas diffusion (Yu *et al.*, 2012). In order to mirror the variable conditions of the soil environment, we used 60 and 100% WHC. It has already been reported that the water held in the pores of the biochar may lead to a decrease in the amount of methane absorbed (Farzad *et al.*, 2007). For this reason, it is important to test biochars (especially those produced from new feedstocks) at different moisture levels.

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Biochar is increasingly used in environmental protection as a low-cost sorbent of heavy metals and hazardous gases (La *et al.*, 2018; Xiong *et al.*, 2019). Additionally, CH_4 can be removed through biochar filtration (Syed *et al.*, 2016). This gas is known for its explosive properties, which may pose a serious threat to safety in mines and landfills (Kammann *et al.*, 2017; Pytlak *et al.*, 2014), but mainly for its high infrared radiation absorption potential which results in a 28-fold higher global warming potential than CO_2 (IPCC, 2014). Nevertheless, there is an apparent deficit in studies describing the potential of biochar to remove higher than ambient CH_4 concentrations (Huang *et al.*, 2019; Syed *et al.*, 2016).

Due to the growing number of biochar applications, modifications of established products, as well as new materials for its production are being sought (Kammann *et al.*, 2017). New feedstocks could be a way to provide biochars with interesting and desirable properties (Thomazini *et al.*, 2015; Tomczyk, 2020). Another advantage of biochar is that it can be produced from waste biomass, which for various reasons is not suitable for other purposes such as feed, litter or fuel production (Qi *et al.*, 2020; Schwede *et al.*, 2017). In these circumstances, the production of biochar is economically, environmentally and ethically justifiable. For this reason, we decided to study agricultural waste from potato and raspberry stems as potential feedstock for biochar production. Potato stems are left in the fields after harvest and raspberry bushes are trimmed and discarded after each growing season. According to the FAO, in 2007 the global area used to grow potatoes amounted to around 19.3 million ha. In Europe, 7.5 million hectares were used for this purpose and the cultivation area is still increasing (Mackay, 2009). Raspberry crops are less prevalent but they have a local significance. In 2010-2012, the average global area used for raspberry production was 92,000 hectares but the amount of stem biomass harvested per hectare was considerable (Zaremba, 2014). The availability of both potato and raspberry biomass is thus high. It should be noted that the stems are often a habitat for pathogenic microorganisms and parasites and for this reason they often have to be disposed of properly (Guo *et al.*, 2019; Vincent *et al.*, 2003). Biochar production may be a beneficial way of making biohazardous plant debris safe. In this way, hazardous waste biomass may be neutralized through pyrolysis and returned safely to the environment thereby contributing to carbon sequestration and a reduction in GHG emissions.

The new aspects of our study are: i) the utilization of new agricultural waste feedstocks, ii) performing experiments on a single biochar (usually biochar with soil was under investigation), iii) comprehensive approach which included monitoring CH_4, CO_2 and O_2 exchange.

Since the ability of biochar to sequester CH_4 may depend on the feedstocks used, we hypothesize that biochars produced from raspberry and potato stems may be used to remove CH_4 from the atmosphere and that the process is moisture-dependent since a high water content may impair gas diffusion.

The aim of the study was to determine the potential of CH_4 removal as well as the accompanying CO_2 production and O_2 uptake by new biochars prepared from plant waste materials (raspberry and potato stems) in comparison with widely available biochars made from wood offcuts and sunflower husks. In addition, we studied the differences between these materials based on their physicochemical properties.

MATERIALS AND METHODS

New biochars were produced in 2018 from raspberry (Br) and potato stems (Bp) (left after crop collection) by pyrolysis (at 600 °C, for half an hour, in an N_2 atmosphere), using an LAC L15/12 electric furnace with a Ht40 AL controller, and a working volume of 15 dm^3. After pyrolysis, nitrogen flushing was maintained until the furnace cooled to room temperature. Common biochars made from wood offcuts (Bo) and sunflower husks (Bs) were produced by New Technology Trade Ltd. (Kobylany, Poland) at a temperature of 600 and 550 °C, respectively (Table 1).

All biochars were sieved with a 2 mm mesh sieve and stored in the dark at room temperature in hermetic containers. The content of the dissolved organic carbon (DOC), total carbon (TC) and nitrogen (TN), pH, oxidation-reduction potential (Eh) and bulk density were measured before incubation (Table 1). The DOC content was measured with a TOC-VCPH analyser (Shimadzu, Japan) (Yu *et al.*, 2018). The pH and Eh of the biochar were determined at a 1:5 biochar to water ratio, using a glass electrode and a redox electrode respectively (Sokołowska *et al.*, 2020; Yoo *et al.*, 2014) with a HQ40D Portable Multi Meter analyser (Hach Lange). The water holding capacity (WHC) of the tested biochars was determined according to Yoo *et al.* (2014) using the modified funnel method. The biochar C and N contents were determined using an elemental analyser (Perkin Elmer CHN 2400). The bulk density of the biochar was calculated based on its weight at 15°C, at a volume of 10 cm^3 (Özçimen and Karaosmanoğlu, 2004).

The tested biochars (5 g of air-dried biochar per sample in three replications) were weighed into 120 cm^3 glass bottles and adjusted to 60% or 100% WHC by the addition of distilled water. All samples were closed and subjected to three days of preincubation at 25°C. Next, after ventilation, the samples were closed with rubber stoppers and aluminum caps, and then the headspace was enriched with 1% CH_4 (v/v) to improve analytical precision. During the following 28 days of incubation (at 25°C, in darkness), the composition of the atmosphere (CH_4, CO_2 and O_2) above the biochar was analysed using a gas chromatograph. A GC-2014 (Shimadzu, Japan) gas chromatograph was used. It was fitted with a flame ionization detector (FID)

Table 1. Characteristics of four biochars: wood offcuts biochar (Bo), sunflower husk biochar (Bs), raspberry stem biochar (Br) and potato stem biochar (Bp)

Parameter	Biochar			
	Wood offcuts (Bo)	Sunflower husk (Bs)	Raspberry stem (Br)	Potato stem (Bp)
	Common – produced by the local company New Technology Trade Ltd., Kobylany, Poland		New – produced in the Institute of Agrophysics PAS, Lublin, Poland	
Pyrolysis temperature (°C)	600	550	600	600
C content (%)	86.13 ± 0.24	78.30 ± 0.01	74.21 ± 0.34	44.62 ± 0.02
N content (%)	0.35 ± 0.01	0.98 ± 0.03	0.90 ± 0.01	1.35 ± 0.00
C/N ratio	246.09	79.90	82.46	33.05
DOC mg dm^{-3})	214.33 ± 0.22	106.57 ± 2.77	139.70 ± 1.19	100.04 ± 0.24
pH	6.99 ± 0.01	9.19 ± 0.02	9.17 ± 0.02	9.60 ± 0.05
Eh (mV)	105 ± 0.36	-16 ± 0.17	32 ± 0.44	25 ± 0.46
Bulk density (g cm^{-3})	0.31 ± 0.01	0.35 ± 0.01	0.21 ± 0.01	0.19 ± 0.01
WHC (g H_2O g biochar $^{-1}$)	2.58 ± 0.26	2.58 ± 0.06	4.31 ± 0.16	4.45 ± 0.09

for CH_4 and CO_2 analysis and an electron capture detector (ECD) for O_2. Poraplot Q and Restek Q-bond columns (column flow – 5 cm^3 min^{-1}, split ratio 5:1, oven temp. – 30°C, injection volume – 150 µL, purge flow 3 cm^3 min^{-1}) with helium as a carrier was used to separate the gases. External standards (1% CH_4 in He; 20.9% O_2 in N_2, Air Products) were used for calibration (Walkiewicz *et al.*, 2020a, 2020b).

The methane and oxygen uptake rates were determined based on the difference between the initial and final gas concentrations on the last incubation day, and divided by the time of apparent CH_4 uptake (the lag phase for CH_4 was excluded) (Eq. (1)). The carbon dioxide production rate was calculated similarly, but in this case the difference in CO_2 concentration between the last and first incubation day was calculated due to the continuous emission of this gas (Eq. (2)) (Walkiewicz *et al.*, 2020a):

$$\mathrm{CH_4}\ uptake\ rate = \frac{C_{initial} - C_{final}}{t}, \tag{1}$$

$C_{initial}$ is the initial uptake CH_4 concentration in the headspace (mg CH_4-C kg^{-1}), C_{final} is the final CH_4 concentration in the headspace (mg CH_4-C kg^{-1}), t is the number of incubation days with CH_4 uptake.

$$\mathrm{CO_2}\ production\ rate = \frac{C_{final} - C_{initial}}{t}, \tag{2}$$

C_{final} is the final CO_2 concentration in the headspace (mg CO_2-C kg^{-1}), $C_{initial}$ is the initial CO_2 concentration in the headspace (mg CO_2-C kg^{-1}), t is the number of incubation days.

Based on the final CO_2 emission and O_2 consumption, the CO_2/O_2 ratio was calculated for each biochar separately for 60% and 100% WHC, as a measure of biochar stability.

Net GWP was calculated by making a comparison between the cumulative CH_4 and CO_2 fluxes in mg CO_2 equivalent per kg of biochar (Walkiewicz *et al.*, 2020b). In these calculations, the GWP value for CH_4 and CO_2 was considered to be 28 and 1, respectively, over a 100-year time horizon (IPCC, 2014).

The results were statistically processed with Statistica 13 software (StatSoft Inc.). A one-way ANOVA (Tukey HSD post-hoc test) was used to test the significance of the differences in CH_4 uptake and CO_2 emission rates between the tested biochars (separately for 60 and 100% WHC).

RESULTS

For the group of four biochars incubated at 60% WHC, the added methane was completely taken up by the potato (Bp) and raspberry (Br) biochars (Fig. 1a). The most efficient in terms of CH_4 removal were samples containing Bp, where after a 13-day long lag phase, the CH_4 uptake rate reached 8.01 ± 0.47 mg CH_4-C kg^{-1} d^{-1}, resulting in methane depletion within 25 days of incubation (Table 2). The incubation of Br showed a similar lag phase duration (15 days), and almost complete CH_4 removal occurred 13 days later. The methane uptake rate for the raspberry stem biochar achieved 5.78 ± 0.17 mg CH_4-C kg^{-1} d^{-1} at 60% WHC. Methane wasn't completely absorbed by sunflower husk biochar (Bs) and only *ca*. 11% (10.23 ± 3.46 mg CH_4-C kg^{-1}) of the added CH_4 was absorbed by the end of incubation (till the 28th day) after a 24 ± 2 days lag phase. The wood offcuts biochar (Bo) did not show any apparent ability for CH_4 uptake at 60% WHC. Within the applied experimental timeframes, less than 1% of the added CH_4 (0.95 ± 0.25 mg CH_4-C kg^{-1}) was removed by the wood offcuts biochar.

The tested biochars differed in the CO_2 emissions that accompanied CH_4 uptake (Fig. 1b), but special attention needs to be paid to the wood offcuts biochar. During the experiment, Bo produced several times more CO_2 than the other biochars, with an average CO_2 production rate as high as 19.98 ± 1.22 mg CO_2-C kg^{-1} d^{-1}. On the last day of incubation, CO_2 concentration in Bo was *ca*. 573 mg CO_2-C kg^{-1},

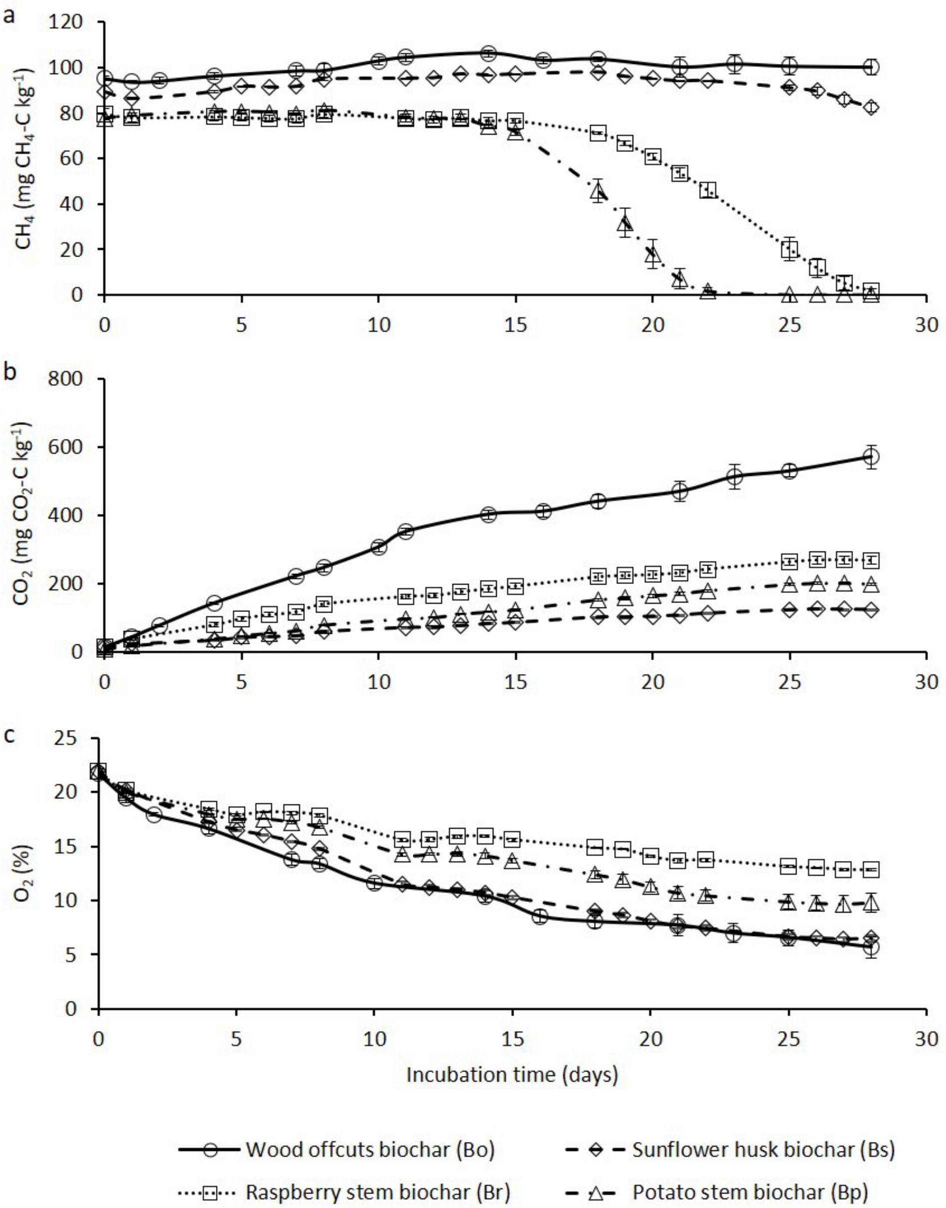

Fig. 1. Uptake of added CH_4 (1% v/v) (a), which accompanies CO_2 production (b) and O_2 uptake (c) by four biochars produced from: wood offcuts (Bo), sunflower husks (Bs), raspberry stems (Br) and potato stems (Bp) incubated at 60% WHC (avg. ± SD, n = 3).

Table 2. Methane uptake and accompanying carbon dioxide emission rate for the entire biochar incubation period with 1% CH_4 (v/v)

Biochar type	CH_4 uptake rate (mg CH_4-C kg^{-1} d^{-1})		CO_2 emission rate (mg CO_2-C kg^{-1} d^{-1})	
	60% WHC	100% WHC	60% WHC	100% WHC
Bo	$0.17^{a} \pm 0.06$	$0.33^{A} \pm 0.18$	$19.98^{c} \pm 1.22$	$21.62^{C} \pm 1.32$
Bs	$2.74^{b} \pm 0.57$	$1.51^{A} \pm 0.55$	$3.88^{a} \pm 0.08$	$2.44^{A} \pm 0.33$
Br	$5.78^{c} \pm 0.17$	$3.03^{B} \pm 0.35$	$9.05^{b} \pm 0.40$	$6.72^{B} \pm 0.16$
Bp	$8.01^{d} \pm 0.47$	$5.52^{C} \pm 0.81$	$8.39^{b} \pm 0.35$	$2.55^{A} \pm 0.04$

Different letters indicate significant differences between biochars, separately for 60% (small letters) and 100% WHC (capital letters), separately for CH_4 and CO_2, Tukey test, $p < 0.05$.

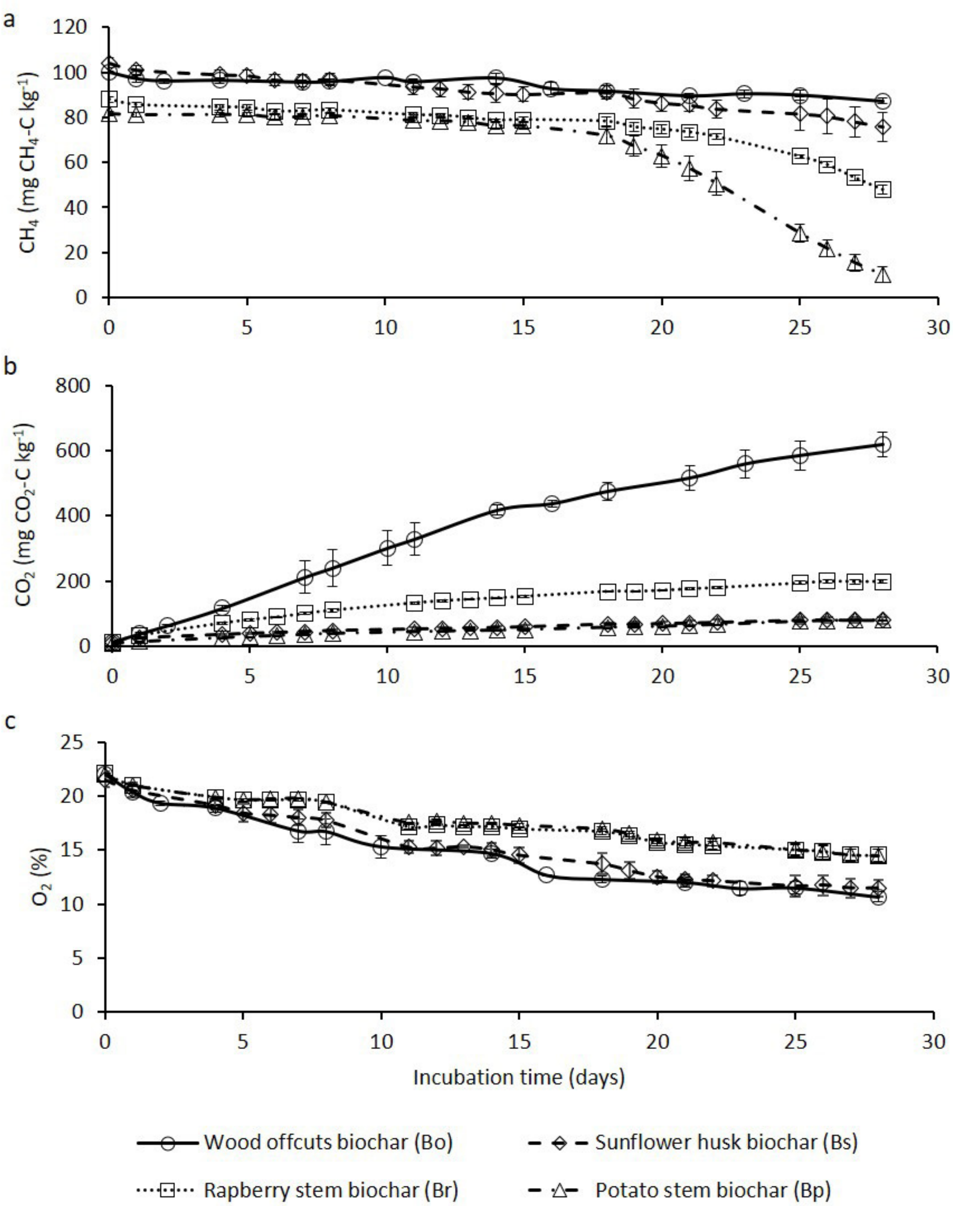

Fig. 2. Uptake of added CH_4 (1% v/v) (a), which accompanies CO_2 production (b) and O_2 uptake (c) by four biochars produced from: wood offcuts (Bo), sunflower husks (Bs), raspberry stems (Br) and potato stems (Bp) incubated at 100% WHC (avg. ± SD, n = 3).

while the CO_2 concentration determined in the other tested biochars remained below 300 mg CO_2-C kg^{-1}. The Br and Bp biochars showed similar dynamics and CO_2 production rates (respectively: 9.05 ± 0.40 and 8.39 ± 0.35 mg CO_2-C kg^{-1} d^{-1}). At 60% WHC moisture level, the production of CO_2 was definitely lowest in Bs (with a rate of 3.88 ± 0.08 mg CO_2-C kg^{-1} d^{-1}) where the final concentration of this gas didn't exceed 130 mg CO_2-C kg^{-1}.

The highest CO_2 production by Bo corresponded to its highest O_2 uptake. At 60% WHC, the differences in the O_2 uptake of new biochar were clearly visible (Fig. 1c). During incubation, the oxygen level dropped to 12.8 and 9.8% in Br and Bp respectively while for the Bs and Bo variants, the final O_2 levels were as low as 6.5 and 5.7%, respectively (v/v).

Biochars incubated at higher moisture levels (100% WHC) showed different dynamics of CH_4 uptake. Within the applied timeframes, none of the tested biochars absorbed all of the added CH_4 (Fig. 2a). The lag phases were generally longer than at 60% WHC, and CH_4 absorption was slower. Methane uptake rates in potato (Bp) and raspberry (Br) stem biochar reached values of 5.52 ± 0.81 and 3.03 ± 0.35 mg CH_4-C kg^{-1} d^{-1}, respectively (Table 2). The lag phases in the Bp and Br biochars lasted for about 16 and 18 days, respectively. The CH_4 uptake rate by Bp was highest and resulted in a reduction of 87% in the added CH_4.

Table 3. Global warming potential (GWP) contributions from CO_2 emission and CH_4 uptake by biochars (Bo, Bs, Br and Bp) incubated under 60 and 100% WHC (calculated based on GHGs data for the last incubation day)

Biochar type	Moisture WHC (%)	GWP-CO_2	GWP-CH_4	Net GWP
			(g $CO_{2(eq)}$ kg^{-1})	
Bo	60	$2.049^d \pm 0.125$	$-0.035^a \pm 0.009$	$2.014^c \pm 0.120$
	100	$2.217^C \pm 0.135$	$-0.096^A \pm 0.043$	$2.122^B \pm 0.100$
Bs	60	$0.398^a \pm 0.008$	$-0.382^b \pm 0.129$	$0.016^a \pm 0.137$
	100	$0.250^A \pm 0.034$	$-0.565^B \pm 0.204$	$-0.315^A \pm 0.217$
Br	60	$0.928^c \pm 0.041$	$-2.805^c \pm 0.082$	$-1.876^b \pm 0.085$
	100	$0.690^B \pm 0.016$	$-1.131^C \pm 0.130$	$-0.441^A \pm 0.115$
Bp	60	$0.696^b \pm 0.012$	$-2.883^c \pm 0.009$	$-2.187^d \pm 0.021$
	100	$0.262^A \pm 0.004$	$-2.440^D \pm 0.088$	$-2.178^C \pm 0.091$

Different letters indicate significant differences between biochars, separately for 60% (small letters) and 100% WHC (capital letters), Tukey test, $p < 0.05$.

Despite a lower CH_4 uptake rate than Bp, Br was also able to remove a relatively large portion of the CH_4 added (*ca.* 39% of the initial level). Clearly, less CH_4 was taken up by Bs and Bo, as at 100% WHC those biochars absorbed just 15.14 ± 5.46 mg CH_4-C kg^{-1} (*ca.* 17%) and 2.56 ± 1.14 mg CH_4-C kg^{-1} (*ca.* 3%) respectively, after quite a long lag phase duration (18 days) (Fig. 2a).

The CO_2 emissions of the new Bp and Br biochars at 100% WHC were also lower than at 60% WHC (Fig. 2b). The rate of CO_2 emission by the wood offcuts biochar (Bo) was not significantly affected by the tested moisture conditions, it showed the highest production among the tested materials (Table 2). The Br biochar was characterized by a medium CO_2 production rate (6.72 ± 0.16 mg CO_2-C kg^{-1} d^{-1}) (Table 2), but the final concentration didn't exceed 200 mg CO_2-C kg^{-1}. At 100% WHC, the tested Bp and Bs showed similarly low CO_2 production rates (Bp: 2.55 ± 0.04 mg CO_2-C kg^{-1} d^{-1} and Bs: 2.44 ± 0.33 mg CO_2-C kg^{-1} d^{-1}). For these variants, the final gas concentration was below 100 mg CO_2-C kg^{-1}. With regard to O_2 uptake, under given conditions, it was highest in the Bo and Bs incubations, with significantly lower values in Br and Bp (Fig. 2c).

The CO_2/O_2 ratio at 60% WHC had the following values: 0.65 (Bo), 0.23 (Br and Bp) and 0.19 (Bs). At 100% WHC, the CO_2/O_2 ratio was generally lower than at 60% WHC: 0.45 (Bo), 0.15 (Br), 0.07 (Bs) and 0.06 (Bp).

The values of net GWP which were calculated for each biochar under the tested moisture conditions are presented in Table 3.

DISCUSSION

Biochar is currently the focus of attention for scientists worldwide as a useful and beneficial soil additive. To date, however, most studies have been focused on gas exchange and microbial activity in biochar mixed with soil (Han *et al.*, 2016; He *et al.*, 2017; Lehmann *et al.*, 2011). Only a small group of studies have described the sole incubation of biochars. Moreover, those experiments were performed with the use of small portions of biochar (less than 1g) (Spokas and Reicosky, 2009; Thomazini *et al.*, 2015). In those studies, the uptake of CH_4 and CO_2 emissions brought about by the biochar, could usually be explained by abiotic processes (Jeffery *et al.*, 2016; Thomazini *et al.*, 2015). In our study, we presented newly developed biochars from common agricultural wastes. To the best of our knowledge, these materials had not been considered at the time of writing.

The new biochars from raspberry and potato stems were prepared under comparable temperature conditions as widely available materials produced from common feedstocks (wood offcuts and sunflower husks) (Sokołowska *et al.*, 2020; Zubkova *et al.*, 2019). Considering their potential application to soil we determined their basic physicochemical properties (Table 1). It was found that the newly produced materials may improve the soil environment by increasing C and N content, the pH value (of acidic soils) and water storage ability (especially under drought conditions); this corresponds with current, global-scale problems. With respect to the aforementioned advantages, the newly developed biochars from raspberry (Br) and potato (Bp) stems seem to be even better than the well-known wood offcuts (Bo) and sunflower husk (Bs) biochars.

According to Thomazini *et al.* (2015), CH_4 uptake by wood chip biochar (produced at 550°C) wasn't observed, while CO_2 emissions from this material were 24 mg CO_2-C kg^{-1} d^{-1} (in moisture conditions of 0.3 mL water per 1 g biochar). In our study, the wood offcuts biochar showed a similar CO_2 production rate (19.98 mg CO_2-C kg^{-1} d^{-1} at 60% WHC and 21.62 mg CO_2-C kg^{-1} d^{-1} at 100% WHC) and CH_4 uptake was also not observed. In contrast to this result, the potato stem biochar showed a three-fold lower CO_2 production rate at 60% WHC (8.39 mg CO_2-C kg^{-1} d^{-1}), while at 100% WHC this rate was nearly 10 times lower (2.55 mg CO_2-C kg^{-1} d^{-1}) than that found in the Thomazini *et al.* (2015) study. At 60% WHC, the CO_2 production rate of raspberry stem biochar (9.05 mg CO_2-C kg^{-1} d^{-1}) was at a similar level to Bp. Furthermore, potato stem and raspberry stem biochars also demonstrated a high level of CH_4 removal.

Spokas and Reicosky (2009) tested 16 different biochars in terms of CH_4 uptake and CO_2 production. Only three wet biochars (1 mL H_2O per 0.5 g biochar) from this group showed an ability for CH_4 uptake. Peanut hull biochar and corn stover biochar had an identical methane uptake rate (2.6 ± 0.6 ng CH_4 g^{-1} d^{-1}). The biochar whose feedstock was BiosourceTM showed the highest methane uptake rate of all (4.1 ± 0.9 ng CH_4 g^{-1} d^{-1}). On the other hand, those biochars exhibited a high rate of CO_2 production: peanut hull biochar 168.5 ± 23.5 µg CO_2 g^{-1} d^{-1}; corn stover biochar 162.4 ± 15.0 µg CO_2 g^{-1} d^{-1} and biochar with BiosourceTM as a feedstock produced as much as 1 022.4 ± 109 µg CO_2 g^{-1} d^{-1} (Spokas and Reicosky, 2009). In our study, the methane uptake rate of the raspberry stem biochar at 60% WHC was 5.78 ± 0.17 mg CH_4-C kg^{-1} d^{-1} (corresponding to 7 706.66 ± 226.66 ng CH_4 g^{-1} d^{-1}). The potato stem biochar at a similar moisture level showed an even higher rate at 8.01 ± 0.47 mg CH_4-C kg^{-1} d^{-1} (corresponding to 10 680 ± 626.66 ng CH_4 g^{-1} d^{-1}). Therefore, the methane uptake rates of the biochars were several thousand times higher than any biochar tested by Spokas and Reicosky (2009). It is important to note that during efficient methane absorption by biochar from raspberry and potato stems, CO_2 emissions remained at a very low level. At 60% WHC, the average CO_2 production rate from the raspberry stem biochar was 9.05 ± 0.40 mg CO_2-C kg^{-1} d^{-1} (corresponding to 33.15 ± 1.47 µg CO_2 g^{-1} d^{-1}). The biochar that was the most effective at methane removal, the one made from potato stems, showed an even lower CO_2 production rate, 8.39 ± 0.35 mg CO_2-C kg^{-1} d^{-1} (corresponding to 30.73 ± 1.28 µg CO_2 g^{-1} d^{-1}).

As yet, there are only a few studies describing the potential of biochars to remove CH_4 present at higher than ambient concentrations. However, this is particularly important when considering the use of biochar as a gas sorbent in ecosystems with increased CH_4 concentrations, such as those occurring in periodically waterlogged arable soils, paddy fields and landfills (Malyan *et al.*, 2016; Reddy *et al.*, 2014; Walkiewicz *et al.*, 2020a). For this reason, we included a widely available biochar from common feedstock (Bo) in our experiment. However, Syed *et al.* (2016) conducted a long-term incubation of biochar from pine bark (prepared by pyrolysis at 450°C) at changing CH_4 concentrations. According to that study, non-inoculated biochar was able to remove from 25% to over 80% of 10 000 ppm (1%) CH_4, but a higher effectiveness of methane removal was observed only after 100 days of incubation.

The mechanisms of effective removal of methane by raspberry and potato stem biochars haven't been elucidated yet. The pattern of CH_4 uptake in our experiment with a multi-day lag phase and a gradual decrease in CH_4 concentration may suggest biological oxidation, especially in the case of the newly produced biochars (Br and Bp). Further evidence for the microbial mechanism of the observed CH_4 oxidation may be deduced from the parallel CO_2 emission and O_2 consumption which were higher at 60% WHC (Fig. 1). These incubation conditions (including a temperature of 25°C) are widely accepted as optimal for methanotrophic bacteria (Malyan *et al.*, 2016; Skopp *et al.*, 1990; Walkiewicz *et al.*, 2020b). In fact, biochar may contribute to CO_2 emissions both biotically (*via* microbial degradation) and abiotically (*via* the release of inorganic C contained in the biochar (Gomez *et al.*, 2014; Gul *et al.*, 2015; Jones *et al.*, 2011). In the case of the exclusively physical interaction of biochar with the tested gases, higher CO_2 emissions would be expected under full saturation conditions (100% WHC). Carbon dioxide binds to oxygen-containing functional groups via hydrogen bonds (Banik *et al.*, 2018). Thus, water molecules and CO_2 are likely to adsorb to similar functional groups. As such, the direct competition for active sites between water and CO_2 molecules may be observed resulting in higher desorption rates at 100% WHC (Pytlak *et al.*, 2020). The lower bulk density of the new biochars (Br and Bp) in comparison with the well-known materials (Bo and Bs) may result in a higher degree of aeration, gas availability and surface area available for microbial colonization (Table 1). In a field experiment described by Noyce *et al.* (2016) DNA was isolated from biochar which had a long-term (four year) contact with soil. That study showed that biochar was inhabited by similar groups of microorganisms as the adjacent soil. Also, the studies on biochar inoculated with methanogenic Archaea confirm that it may be inhabited by microbes, despite the poor habitat conditions (Schwede *et al.*, 2017).

Along with the advantageous environmental effects of biochar application to soil it is important to consider some economic aspects. Biochar production under anaerobic and high temperature pyrolysis is associated with considerable costs. High energy use leads to adverse environmental consequences as it generates GHGs, mainly CO_2 (Fungo *et al.*, 2014). It should be noted, however, that biochar has the ability to remove CH_4 which (mole for mole) has a Global Warming Potential several dozen times higher than the CO_2 emitted during energy production (Wu *et al.*, 2019). CO_2 was also emitted during the incubation time and that allowed for the determination two important biochar parameters. The first is the CO_2/O_2 ratio, which may be considered as a biochar stability parameter. A low

CO_2/O_2 ratio indicates higher biochar stability. Accordingly, it may be assumed that biochar from Bp and Bs (at 100% WHC) were the most stable, while the one originating from Bo showed the lowest stability under both moisture levels. Moreover, CO_2 production during biochar incubation were more variable than O_2 uptake, which was similar to the results observed by Almeida *et al.* (2019). The climate change mitigation potential of biochars, may be expressed as the changes in the global warming potential (GWP) of the gases which are either adsorbed or released during incubation. It was observed that the effect of biochars on CH_4 and CO_2 exchange depended on the feedstock type and moisture level. At 60% WHC, the change in net GWP in the headspace of potato (Bp) and raspberry (Br) biochar incubations was negative and amounted to -2.187 and -1.876 g CO_2(eq) kg^{-1}, respectively. These values resulted from the great potential of the new biochars to adsorb CH_4. For the sunflower husk biochar (Bs) incubations, net GWP was close to zero (0.016 g CO_2(eq) kg^{-1}) while for the wood offcuts biochar (Bo) it was positive (2.014 g CO_2(eq) kg^{-1}) which was a consequence of the highest CO_2 production and minimal CH_4 absorption. At 100% WHC, net GWP in incubations with Bp was characterized by similar negative values (-2.178 g CO_2(eq) kg^{-1}) as at lower moisture levels. That confirmed usefulness of Bp, especially for waterlogged ecosystems emitting CH_4 into the atmosphere. At higher moisture levels, in the Br and Bs headspaces, net GWP was still negative, yet lower, not exceeding -0.5. At both moisture levels studied, Bo incubations were characterized by a strongly positive net GWP (2.122 g CO_2(eq) kg^{-1}) value. The negative net GWP values (Table 3) and relatively high Br and Bp stability under both moisture levels could be the economic and environmental justification for the application of new biochars. Furthermore, the positive effects of soil enrichment with biochar are long-lasting and apply to many areas, *i.e.* fertility, hydrological and aeration conditions which result in increased crop productivity and a reduced necessity for agrotechnical practices. The trade-offs of economic profits and a reduction in GHG emissions should be included in the evaluations of the consequences of biochar application.

Therefore, it is important to continue research with biochars from new materials produced at lower temperatures in order to find optimal pyrolysis parameters to combine the lowest possible economical costs with maintained or even improved expected properties.

CONCLUSIONS

1. The methane uptake of four biochars was evaluated in a lab experiment. The results showed that two new biochars (from potato and raspberry stems) were able to efficiently remove added 1% CH_4, especially at 60% water holding capacity.

2. The high CH_4 consumption presented by the new biochars has great potential compared to common biochars from wood offcuts or sunflower husks and this could be a way of managing agricultural waste.

3. The advantage of new biochars from raspberry and potato stems over wood offcuts biochar is their significantly lower production of carbon dioxide, yet high methane absorption potential. At 60% water holding capacity, as well as at 100% water holding capacity, the potato stem biochar still showed the highest CH_4 uptake rates with relatively low CO_2 emission and O_2 uptake. Hence the potato stem biochar may be a good choice in ecosystems characterized by relatively high methane concentrations, such as periodically flooded and waterlogged areas, landfills or paddy fields.

4. Based on the CO_2/O_2 ratio, the biochars from sunflower husks and potato stems (at 100% water holding capacity) were the most stable, between the materials tested.

5. As a consequence, it is reasonable to carry out both short-term and long-term studies concerning the various sorptions and emissions of gases by these biochars. It should also be considered whether the observed greenhouse gas dynamics are dependent on physical or biological factors. Knowledge concerning the properties of biochars which enhance methane removal could be used to increase the filtration potential of these highly promising materials

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