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1 **Adsorption and Desorption of Nitrous Oxide on Raw and Thermally Air-Oxidized Chars**

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Abstract.

Addition of biomass chars (biochar) to soil reportedly suppresses emissions of nitrous oxide (N_2O), a potent greenhouse and ozone-depleting gas, but the causes and endurance of the effect are unclear. To determine whether adsorption may play a role, adsorption isotherms of N_2O were constructed at 273 K on outgassed samples of anoxically-prepared wood-derived chars (300 -700 °C) and on a subset briefly reheated in air at 400 °C. Sorption by the chars was greater and more reversible than sorption by soils or soil mineral phases. Adsorption by chars increased with pyrolysis temperature after post-pyrolysis air oxidation. The Langmuir maximum capacity correlates well with the CO_2 -determined (but not N_2 -B.E.T.-determined) surface area. At environmentally realistic partial pressures in soil, N_2O adsorption correlates with CO_2 adsorption, and is found to predominate in the micropores (<1.5 nm), especially ultramicropores (< 0.7 nm). Neither adsorption nor adsorption reversibility was affected by coating the char with soil organic matter extract. It is concluded that char added at levels above 1% in soil would act as a strong and reversible sink for N_2O , and could be responsible for the temporary nature of emission suppression observed in some cases.

Keywords: biochar; black carbon; greenhouse gas; geosorbent; soil organic matter.

Graphical Abstract

(Size: 2.70 in. wide and 1.75 in. height)

1. Introduction.

Nitrous oxide (N_2O) is a potent greenhouse (IPCC 2014) and stratospheric ozone-depleting gas (Ravishankara et al. 2009). It has a global warming potential 300 times greater than that of CO_2 , and can persist for up to 150 years (IPCC 2007). It is thought to be the single most important ozone-depleting substance (Ravishankara et al. 2009). While naturally occurring due to the global nitrification-denitrification cycle in soils and oceans (Bremner 1997)— N_2O is a byproduct of stepwise ammonium oxidation or nitrate reduction—the atmospheric concentration of N_2O has increased considerably since the 18th century and the rate of increase has accelerated since 1975 (Machida et al. 1995, USEPA 2015). The rise in N_2O emissions is due mainly to human activities, including fuels combustion, waste management, and the use of synthetic nitrogen fertilizers. Human activities now account for ~40% of total emissions (USEPA 2016). In the United States, agricultural soil management is the most important source of anthropogenic N_2O , contributing 79% of total emissions in 2014 (USEPA 2015). Extensive research has been conducted on ways to reduce greenhouse emissions from agricultural soils in order to mitigate global warming and its impacts.

Char is a component of environmental black carbon resulting from wildfires or intentional fires set to clear the land or remove crop residue (Skjemstad et al. 1999, Lehmann and Joseph 2009, Schmidt and Noack 2000, Skjemstad et al. 2002). It is widespread in soils (Skjemstad et al. 1999, Lehmann and Joseph 2009, Schmidt and Noack 2000, Skjemstad et al. 2002), and may comprise 30% or more of total soil organic carbon in some places (Mao et al. 2012, Glaser et al. 2001). A great deal of interest has emerged recently in the application of engineered char (biochar) as a soil additive for improving soil quality (Laird 2008, Basso et al. 2012, Lehmann and Joseph 2015) and fertility (Jeffery et al. 2011, Hammond et al. 2013, Chan

et al. 2008, Pandit et al. 2018) and reducing greenhouse gas emissions (Jeffery et al. 2011, Hammond et al. 2013, Chan et al. 2008, Woolf et al. 2010, Glaser et al. 2002, He et al. 2018). Char resists abiotic and biotic degradation compared to non-pyrogenic natural organic matter (Zimmerman 2010, Spokas et al. 2014), and thus represents a long-term sink for carbon (Kuhlbusch and Crutzen 1995, Glaser and Amelung 2003). Studies have shown that amending soil with biochar in many cases can reduce N₂O emissions, at least over the short term (Cayuela et al. 2014, Kammann et al. 2017, Verhoeven et al. 2017, He et al. 2017, Spokas 2013). The causes are still unresolved, however (Kammann et al. 2017). Chars may affect soil nitrification and denitrification processes by interacting directly with soil bacteria and fungi (Lehmann et al. 2011); by altering soil pH (Cayuela et al. 2014, Van Zwieten et al. 2010), aeration, or moisture content (Rogovska et al. 2011, Yanai et al. 2007); or by affecting the bioavailability of nutrients (Van Zwieten et al. 2010, Kameyama et al. 2012, Mukherjee and Zimmerman 2013, Chen et al. 2015). The char body may also act as an electron shuttle that facilitates electron transfer to soil denitrifying organisms (Cayuela et al. 2013), or participate in chemical redox reactions directly with N₂O (Quin et al. 2015). Such mechanisms may be interdependent and time variant, making them difficult to untangle. Some studies suggest that reduction of N₂O emission after biochar addition is only temporary. Spokas found that weathering of three different biochars in fields at 22 Mg/ha for three years negated the suppression of N₂O production initially observed in the laboratory (Spokas 2013). By contrast, Hagemann et al. found that N₂O emission was still reduced three years after application of a beechwood biochar at 60 Mg/ha (Hagemann et al. 2017a). In a meta-analysis of 91 studies, He et al. found a mean of 31% reduction in N₂O emissions and observed that the response ratio of test to control was not statistically dependent on experimental duration (He et al. 2017). Nevertheless, an examination of their Fig. S4 shows

weaker suppression in experiments lasting more than ~100 d. In another meta-analysis (Verhoeven et al. 2017), a trend of reduced N₂O mitigation was observed for studies lasting longer than ~1 year. Those authors stated that “The sustained N₂O mitigation potential of biochar is an open question.” (Verhoeven et al. 2017)

Due to its porous nature, char or biochar (hereafter, referred to interchangeably as BC) in soil may act as an adsorptive sink of N₂O, influencing its soil-to-air transport as well as its functions in the biological nitrogen cycle. Adsorption studies of N₂O by carbonaceous materials, however, are rare in the literature (Cornelissen et al. 2013, Peng et al. 2009). Adsorption of N₂O on activated carbon was found comparable to adsorption of CO₂ (Peng et al. 2009). Cornelissen et al. observed much stronger adsorption of N₂O on biochars than on alumina, silica or iron oxide at relative pressures (p/p_0) in the range ~0.001–0.023 and under anhydrous conditions, suggesting that adsorption by biochars could potentially account for the reported suppression of N₂O emissions in biochar-amended soil (Cornelissen et al. 2013). Quin et al. suggested that adsorption to BC might have contributed to the retention of N₂O injected into a sterile BC-amended soil column relative to the soil-only column (Quin et al. 2015).

We were prompted to undertake this study by questions regarding the sustained N₂O mitigation potential of biochar mentioned above, and by the recognition that a detailed understanding of the factors governing adsorption of N₂O by BC is essential toward the goal of fully defining the roles of BC in generation, emission, and conversion of N₂O in soil systems. The physical-chemical properties of BC that govern adsorption are controlled by the biomass precursor, pyrolysis conditions, surrounding soil conditions, and prior effects of weathering in soil. We selected a manageable few of these variables for study here. Adsorption and desorption isotherms of N₂O were constructed at relative partial pressures p/p_0 ranging from 10⁻⁶ to 0.03 at

273 K on BCs made anoxically from two sources, hardwood and pecan shells, in comparison with isotherms for soils and soil constituents, including sand, clays, and soil humic substances. Adsorption was investigated as a function of surface area and pore size, heat treatment temperature (HTT) and the presence or absence of air during heating (Lattao et al. 2014, Li et al. 2002, Karanfil and Dastgheib 2004, Xiao and Pignatello 2015). Air is present during open burning, and air may be introduced into biochar pyrolysis reactors. Thermal air oxidation can affect the adsorptive properties of BC. Previously, we found that brief post-pyrolysis air oxidation (PPAO) of BCs generally increased adsorption of nonionic and ionizable organic compounds by several-fold (Xiao and Pignatello 2016, Xiao et al. 2017). The increase was attributed to pore reaming—the combined process of pore enlargement and pore clearing caused by oxidative etching of pore walls and outgassing of entrained molecules and their gaseous oxidation products. The reversibility of N₂O adsorption was also addressed. Reversibility is an important consideration because most of the surface area of BC particles is present in micropores and mesopores that are directly inaccessible to microbes. The presence of dissolved natural organic matter during sorption may affect adsorptivity of BC toward N₂O (Pignatello et al. 2015a). Natural organic matter molecules transferred to BC surfaces during the aging process in soil is known to suppress sorption of organic compounds via competition for sorption sites and blockage of pores (Pignatello et al. 2015a). Therefore, we determined the effects on adsorption of N₂O after prior exposure of the BC to aqueous solutions of soil organic matter. Lastly, based on our results we evaluated the question of whether biochar added to soil can reduce N₂O emissions at relevant concentrations by providing an adsorptive sink.

2. Methods and materials.

Maple wood BCs were made by heating shavings at six different HTTs from 300 °C to 700 °C for 2 h under a flow of N₂, as previously described(Cao et al. 2012) (named M300 through M700). Pecan shell BCs were obtained from the U.S. Department of Agriculture, Agricultural Research Service and were made anoxically at 400 °C or 500 °C (named PS400 or PS500). Pine wood BC was made anoxically at 500°C for 8 h (PW500). PPAO was carried out by heating 0.1 g of M400 or PS500 samples in uncapped 60-mL flat-bottom screw-cap glass vials (28 mm diameter, 139 mm height) at 400 °C placed in a muffle furnace open to the air. They are named M400-xx or PS500-xx, where xx is the PPAO time in minutes.

Lockwood soil (Cheshire fine sandy loam; course-loamy, mixed, mesic Typic Dystrochrepts) was collected from the surface horizon at the CAES Lockwood farm in Hamden, Connecticut, USA. It contains 59% sand, 34% silt, 6% clay, and 1.2% organic carbon (OC). The dominant clay mineral is illite. Montmorillonite SWy-1 and kaolinite KGa-1b were purchased from the Clay Minerals Society (Purdue University, West Lafayette, IN). Ottawa sand was from Fisher Scientific. Pahokee peat (a high organic matter reference soil), Pahokee peat humic acid (PPHA), and Suwanee River fulvic acid (SRFA) were purchased from the International Humic Substances Society (St. Paul, MN). Amherst soil HA was extracted from Amherst soil (Lu and Pignatello 2004, Sander et al. 2006).

Adsorption and desorption of gases on BCs and the other geosorbents were measured volumetrically on an Autosorb-1 (Quantachrome, Boynton Beach, FL) after sample outgassing at 493 K for a time needed to pass the instrument test (Kwon and Pignatello 2005, Braidă et al. 2003). Adsorption of N₂O was conducted at 273 K. Pore size distribution, pore volume, and surface area were determined from the N₂ (77 K) and CO₂ (273 K) adsorption isotherms (Echeverria et al. 1999, Garrido et al. 1987, Thommes et al. 2012). Analysis of the high-

resolution N₂ adsorption isotherm (relative pressure, $p/p^0 = 10^{-6}$ –1) using nonlocal density functional theory and assuming slit-shaped pores with graphitic walls generated pore size distribution in the range 15–60 Å (mainly within the mesopore range). Nitrogen surface area was calculated from an 11-point subset of the isotherm using the B.E.T. (Brunauer-Emmitt-Teller) equation. Analysis of the CO₂ isotherm ($p/p^0 = 10^{-6}$ –0.029) using DFT and Monte Carlo methods yielded pore surface area and pore size distribution up to 14.7 Å (within the micropore range, as defined by the International Union of Pure and Applied Chemistry). Table 1 provides the porosities and surface areas for all BCs and the two soils.

Adsorption isotherms of N₂O were fit to the Langmuir model:

$$C_{\text{adsorbed}} = \frac{S_{\text{LM}} K_{\text{L}} (p / p_0)}{1 + K_{\text{L}} (p / p_0)} \quad (1)$$

where p is pressure, p_0 is the vapor pressure at 273 K (30.46 bar), and S_{LM} (mol/kg) and K_{L} are the Langmuir maximum capacity and affinity coefficients, respectively, obtained by nonlinear regression of experimental data weighted by the dependent variable. Table 2 lists the Langmuir parameters of all the geosorbents.

In addition, adsorption isotherms of N₂O and CO₂ on the BCs were fit to the linear (Henry's law) model for data in the low pressure range up to p/p_0 of 1×10^{-3} :

$$C_{\text{adsorbed}} = K_{\text{H}} (p / p_0)$$

where K_{H} (mol/kg) is the Henry constant.

The contribution of BC amendment to N₂O adsorption in a hypothetical soil containing raw or PPAO-treated M400, kaolinite, sand, and soil organic matter (reference Pahokee peat HA) was estimated by the Monte Carlo method using the equation:

$$F(\Gamma_{\text{adsorption}}) = \frac{F(f_{\text{BC,adsorption}}) \times F(C_{\text{BC,adsorption}})}{\Sigma_{\text{adsorption}}} \quad (2)$$

where F represents the frequency and $\Gamma_{\text{adsorption}}$ is the ratio of N₂O adsorption by the BC component to the total adsorption by the hypothetical soil $\Sigma_{\text{adsorption}}$, given by:

$$\Sigma_{\text{adsorption}} = F(f_{\text{BC}}) \times F(C_{\text{BC,adsorption}}) + F(f_{\text{kaolinite}}) \times F(C_{\text{kaoliniteadsorption}}) + F(f_{\text{sand}}) \times F(C_{\text{sand,adsorption}}) + F(f_{\text{om}}) \times F(C_{\text{om,adsorption}}) \quad (3)$$

where f is the fraction of each soil component and $C_{\text{adsorption}}$ is the observed N₂O adsorption (mol/kg) on the geosorbents. The values of $F(f)$ are provided in Table S1 of the Supplementary data. An arbitrary, but environmentally-relevant N₂O p/p_0 of 1.1×10^{-5} (Liengaard et al. 2013) was chosen for the estimates.

The effect of humic acid coating on BC adsorption of N₂O was investigated with Amherst HA. A stock solution of 400 mg OC L⁻¹ (determined on a TOC-5000, Shimadzu) was prepared by dissolving the isolate in NaOH (0.1 mol/L) and adjusting the pH to 7 with HCl. A PW500 BC sample (0.5 g) was pre-wetted with 25 mL deionized water for 24 h. Then 25 mL of the stock solution was added, and the mixture was re-equilibrated for another 24 h on an end-over-end shaker. Subsequently, the mixture was evaporated to dryness on a rotary evaporator at 40 °C under aspirator pressure, resulting in a final nominal OC concentration of 20 mg OC (g BC)⁻¹, assuming all the HA coated the char. The process was performed twice in succession for a second 0.5 g sample of PW500 (two-times coated), and three times in succession for a third 0.5 g

sample (three-times coated) giving nominal OC contents of 40 and 60 mg OC (g BC)⁻¹, respectively.

3. Results and discussion

3.1. Adsorption and adsorption reversibility.

Fig. 1 shows the adsorption and desorption isotherms of N₂O for the raw maple and pecan BCs, and Fig. 2 for the other geosorbents constructed at 273 K. Adsorption of N₂O by the BCs generally increased with HTT and was typically much greater than adsorption by the other geosorbents, with the exception of the organic matter samples, PPHA and SRFA, which are comparable to the lower-HTT BCs. Adsorption of N₂O by the non-BC geosorbents follows the order, PPHA $\approx$ SRFA > montmorillonite > Pahokee peat soil > kaolinite > Lockwood soil > sand. The Langmuir model fits each data set well on the basis of the R_{adj}^2 (Table 2). The Langmuir S_{LM} for the raw BCs ranges from 1.4 to 4.2 mole/kg (Table 2). This may be compared with the S_{LM} of the four biochars prepared by Cornelissen et al. anoxically from softwoods, which, after conversion of units, ranged from 0.91 to 2.75 mole/kg at 273 K (Cornelissen et al. 2013). The S_{LM} for the BC sorbents trends positively with HTT and increases with PPAO treatment time up to 30 min.

Hysteresis in all the BC isotherms is very weak (Fig. 1), indicating that adsorption of N₂O is essentially reversible. By contrast, hysteresis in the isotherms of the non-BC geosorbents, except for montmorillonite, is pronounced (Fig. 2). One-fifth to one-fourth of the maximum N₂O taken up by those geosorbents appears resistant to desorption at extremely low pressures and after cumulatively long desorption times. The small net adsorption observed during the initial

steps of the desorption cycle is evidence that diffusion limitation is at least one cause of hysteresis. The possibility that the irreversibility is due to chemisorption or conversion to non-gaseous products cannot be excluded.

Table 2 provides the measured and Langmuir-computed adsorption of N_2O on all the geosorbents at the environmentally-realistic p/p_0 of 1.1×10^{-5} . At this low pressure the Langmuir model tends to overestimate adsorption on sand, clays and peat, and to underestimate adsorption on the BCs. However, the general trends of increasing computed adsorption with HTT and PPAO time among the BCs, as well as the order in adsorption among the other geosorbents, are substantially the same as for the S_{LM} . Fig. 3 shows that at p/p_0 of 1.1×10^{-5} the measured adsorption of N_2O by M400 is between 6-times and 84-times greater than adsorption by the non-BC geosorbents, and adsorption by M700 is between 20-times and 260-times greater than adsorption by the non-BC geosorbents. Measured adsorption at p/p_0 of 1.1×10^{-5} among the non-BC geosorbents follows the order, PPHA $\approx$ SRFA $>$ montmorillonite $>$ kaolinite $>$ Pahokee peat $\approx$ Lockwood soil $>$ Ottawa sand, which is the same as the order in S_{LM} except for the reversal between Pahokee peat and kaolinite.

3.2. Effects of thermal air oxidation.

Thermal PPAO treatment of BCs significantly increased adsorption of both N_2O (Table 2 and Fig. 4) and CO_2 (Fig. S3, Supplementary document). For example, adsorption of N_2O by M400 increased by a factor of two after PPAO treatment for 30 or 40 min. The increase in adsorption after PPAO is consistent with previous results for organic compound adsorption from aqueous solution (Xiao and Pignatello 2016, Xiao et al. 2017). Pore size analysis (Xiao and Pignatello

2016) showed that PPAO treatment of raw M400 increases the N₂ BET surface area from 34 m²/g to as much as 565 m²/g and the CO₂-accessible surface area from 370 m²/g to as much as 895 m²/g (Table 1). Changes in pore size distribution of the micropore (< 15 Å) and small mesopore (20-60 Å) regions of the M400 upon PPAO treatment reported previously (Xiao and Pignatello 2016) can be visualized in Fig. S4 of the Supplementary document. PPAO increases ultramicroporosity (< 7 Å), supermicroporosity (7–20 Å), and mesoporosity (Table 1). The changes in surface area and pore size are attributable to pore reaming (Xiao and Pignatello 2016). Pore reaming has a greater effect on N₂ than on CO₂ and N₂O adsorption due to hindrance of N₂ diffusion in ultramicropores at cryogenic temperatures (see Section 3.4).

After PPAO treatment the isotherms of N₂O develop slight hysteresis which tended to increase with treatment time (Fig. 4). The increased hysteresis after PPAO is unlikely due to chemisorption because: a) the BC is converted to a more oxidized state, whereas the standard reduction potential of N₂O is 1.766 V; and b) hysteresis increases for CO₂, as well (compare Fig. 4 with Fig. S3).

3.3. Comparison of N₂O adsorption with CO₂ adsorption.

The adsorption-desorption isotherms of CO₂ at 273 K are shown for the raw maple and pecan BCs and for the Lockwood and Pahokee peat soils in Figures S1 and S2, respectively, of the Supplementary data. Henry's law constants K_H in the low pressure range ($p/p_0 < 1 \times 10^{-3}$) for all BCs (raw and PPAO-treated) are supplied for N₂O in Table 2 and for CO₂ in Table S2. A comparison of the isotherms reveals that adsorption of N₂O and CO₂ by a given BC are comparable. Figure 5 shows the strong free energy correlation between N₂O and CO₂ adsorption (log-scale plot of Henry's parameters), with a slope of 1.136 ($R^2 = 0.808$). Carbon dioxide is expected to undergo weaker dispersion interactions with the carbon surface (Yang 1987) due to

its smaller size (van der Waals length, 0.407 nm compared to 0.459 nm for N₂O) (Hirschfelder et al. 1954), but to engage in stronger quadrupolar interactions (Bastin et al. 2008, Bae et al. 2009) due to its more negative quadrupole moment (-14.3×10^{-40} compared to -11.03×10^{-40} Coulomb·m for N₂O (Coriani et al. 2000, Watson et al. 1997, Chetty and Couling 2011)). In addition, the smaller-size CO₂ molecules may experience less exclusion in the ultramicropores (< 0.7 nm). Evidently, these effects collectively cancel out such that N₂O adsorption closely parallels CO₂ adsorption.

Like N₂O adsorption, CO₂ adsorption is essentially reversible on the raw BCs but hysteretic on the two soils. Carbon dioxide isotherms were not obtained for the minerals or organic matter standards.

3.4. Correlations between N₂O adsorption and changes in physical properties.

Adsorption of N₂O was probed as a function of surface area or pore size distribution considering the raw and PPAO-treated BC sorbents together. The S_{LM} correlates well with CO₂ surface area ($R^2 = 0.86$; Fig. 6a). The slope corresponds to 5.8×10^{-3} mmol/m², which can be compared with the van der Waals projected molecular surface area of N₂O of about 0.115 nm², or about 14.4×10^{-3} mmol/m² if closely packed. Thus, N₂O if closely packed would occupy about 40% of the incremental increase in CO₂ surface area. In contrast with CO₂ surface area, the relationship between S_{LM} and N₂ B.E.T. surface area is more complex (Fig. 6b): below ~50 m²/g the correlation is poor, whereas above ~250 m²/g S_{LM} increases linearly with N₂ B.E.T. surface area. A reasonable explanation for the pattern in Fig. 6b is as follows. Nitrogen diffusion through narrow micropores is kinetically hindered at 77 K (Braidà et al. 2003, Echeverría et al. 1999,

Garrido et al. 1987, Thommes et al. 2012); thus, N₂ may not access all surface area available to N₂O at the higher temperature of 273 K in these pores. The points below ~50 m²/g, with the exception of M400-5, correspond to samples prepared anoxically and not PPAO-treated. PPAO widens pores through reaming. The widening of pores increases N₂ diffusivity and greatly increases N₂ B.E.T. surface area. Thus, it is likely that the cluster of points below ~50 m²/g in Fig. 6b is an artifact of nitrogen diffusion limitations, meaning that absent this artifact they would have been shifted to the right where they may have better correlated with S_{LM}. The K_L correlates poorly both with CO₂ surface area ($R^2 = 0.23$) and N₂ B.E.T. surface area ($R^2 = 0.04$).

The S_{LM} correlates well with total microporosity ($S_{LM} = 16.9 \times (\text{microporosity}) + 0.87$; $R^2 = 0.826$). The slope corresponds to 16.9 mmol/cm³, which is close to the liquid density of N₂O (at 21.1 °C) of 17.5 mmol/cm³ (AirProducts). This suggests that essentially all of the incremental increase in microporosity is filled by N₂O. The S_{LM} does not correlate very well with mesoporosity ($R^2 = 0.520$). Moreover, including a term for mesoporosity does not improve the correlation between S_{LM} and microporosity, a result that contrasts with results we obtained for triazine herbicides and an estrogen (Xiao and Pignatello 2016, Xiao et al. 2017), which showed that adsorption correlated best with a linear combination of terms for microporosity and mesoporosity. Evidently, as N₂O is much smaller than these organic compounds, N₂O adsorption is not much affected by mesoporosity. The Langmuir K_L of N₂O does not correlate with either microporosity ($R^2 = 0.17$) or mesoporosity ($R^2 = 0.04$).

We further looked at the influence of pore size distribution on adsorption of N₂O by the BCs at more environmentally-relevant pressures, i.e., below p/p_0 1×10^{-3} . The Henry's parameter K_H correlates better with total microporosity ($R^2 = 0.766$) than with total mesoporosity ($R^2 = 0.326$), and better with ultramicroporosity ($R^2 = 0.744$) than with supermicroporosity ($R^2 = 0.47$).

Correlations of observed low-pressure adsorption with porosity in different pore slices within the micro- and mesopore regions at p/p_0 values of 0.5, 1.1, and 2.0×10^{-5} are shown in Fig. S5. The standard error in R^2 (represented by the bars) was generally small. The R^2 value peaks for slices in the ultramicropore region ($R^2 \sim 0.45-0.6$) and then in one narrow slice in the supermicropore region (14–15 Å; $R^2 \sim 0.51$), and is considerably lower in the other pore slices. The correlation of CO_2 adsorption at an environmentally relevant pressure of CO_2 (p/p_0 of 1.1×10^{-4}) (Robbins 1986) with porosity is also superior for pore slices in the ultramicropore region than the supermicropore region (Fig. S6, Supplementary document). Overall it is concluded that low-pressure adsorption of N_2O correlates better with microporosity than mesoporosity, and better with ultramicroporosity than supermicroporosity of BC.

3.5. Effect of natural organic matter.

Fig. 7 shows that depositing one to three coats of soil HA on PW500 has no significant effect on the adsorption/desorption isotherm of N_2O , either in terms of magnitude or hysteresis. Spokas (Spokas 2013) suggested that a reduction in sorption potential for inorganic forms of N due to pore clogging was one possible reason biochar lost its ability to suppress N_2O after field aging, but provided no data in support of this or any other cause. Numerous studies have reported declines in surface area of BCs, often accompanied by suppression of organic compound adsorption, after aging in soil or exposure to humic substances (Pignatello et al. 2015b). In one case suppression was kinetic rather than thermodynamic (Hale et al. 2009) Recently, Hagemann et al. (Hagemann et al. 2017b) reported a 64% decline in mesopore surface area (mainly in the 1.25 – 1.45 nm range) and an 18% decline in micropore surface area (mainly in the 0.65– 0.85 nm range) after composting a biochar with manure and green waste, although they did not

investigate sorption of any particular compound. Based on the results of the present study, it is reasonable to conclude that N₂O molecules are small enough that they occupy different adsorption domains than SOM molecules, or that SOM molecules are ineffective at blocking N₂O from entering pores, or both.

3.6. Contribution of BC to N₂O retention in soil.

Monte Carlo simulations were performed to estimate the contribution of raw or PPAO-treated BC to overall retention of N₂O in a hypothetical soil. The soil contained by weight, 1–10% raw M400 or M400-30, 1–30% clay (kaolinite), 10–70% sand, and 1–10% Pahokee peat humic acid. The simulations consider all possible combinations of independent variables (see Table S1 in the Supplementary document), and the peak of this frequency distribution curve represents the most probable value of the dependent variable within the ranges of the independent variables (Xiao et al. 2015). As illustrated in Fig. 8, the frequency curve shifts toward greater contribution of BC to overall sorption for the thermally air-oxidized BC. Considering frequencies above 5%, the raw BC would contribute ~60–85%, while the PPAO-treated BC would contribute ~80–92% of overall N₂O adsorption in this hypothetical soil. The dominance of BC was verified experimentally for a mixture (unaged) of 5% by weight of PW500 in Lockwood soil (Figure S7). The BC-soil mixture adsorbed ~6.8 times as much N₂O as the soil alone at $p/p_0 \sim 1 \times 10^{-5}$, and ~1.9 times as much at $p/p_0 \sim 1 \times 10^{-3}$. The results show that, whether thermally air oxidized or not, BCs can be significant adsorptive sinks of N₂O in soil.

With some assumptions we may estimate partitioning of N₂O at realistic pressures in a typical soil at 273 K, using the strongest adsorbing char M400-40 as example (Table 2).

Consider a 1-m³ parcel of a soil similar to Lockwood soil having a bulk porosity of 25% and a skeletal particle density of 2.2 g/cm³. Consider a second 1-m³ parcel of the same soil mixed with 10% by volume M400-40 (assumed skeletal density of 1.1 g/cm³), and having same bulk porosity. Both parcels lie under an atmosphere of air containing N₂O at $p/p_0 = 1.1 \times 10^{-5}$. The gas phase of each parcel would contain 2.61 mmol N₂O. Based on the measured adsorption (Table 2), the solids would contain 215 mmol N₂O without M400-40, and 1070 mmol N₂O with M400-40. Thus, the gas phase would contain 1.20% of the total N₂O without M400-40, but only 0.244% with M400-40. These estimates ignore competitive sorption by water, which could be considerable, and likely differ among the soil components. Adsorption of the small organic molecule, bromomethane by an activated carbon was reduced by about one order of magnitude in a water-flooded condition compared to the dry condition (Hsieh and Pignatello 2017). If water competition decreases adsorption of N₂O by BC and soil components equally by an order of magnitude, the percent of N₂O in the gas phase would be 10.9% and 2.39% of total N₂O for the parcel without and with M400-40, respectively. Nevertheless, these calculations suggest that most N₂O will be sorbed to soil components, and that char enrichment or biochar amendment would substantially increase N₂O sorption.

4. Conclusions and Implications.

Overall, our results show that on a mass basis N₂O adsorption by the tested BCs far exceeds N₂O adsorption by soil mineral fractions, and, except for the lowest temperature chars, exceeds adsorption by soil organic matter. Cornelissen et al. (Cornelissen et al. 2013) studied sorption of N₂O and CO₂ to four biochars and two activated carbons in comparison to uncharred pinewood, Pahokee peat, alumina, fumed silica, and silica gel, and they calculated isosteric heats of sorption.

They found that sorption of N₂O to the carbonaceous materials was comparable to sorption of CO₂ and greater than sorption to peat and, especially, the minerals. Our results are in qualitative agreement with theirs on these general findings.

This study advances our understanding of the adsorptive function of BC with respect to N₂O. We show that adsorption is not only greater, but less hysteretic on BCs than on other major soil components. This means that BC will be both a strong and reversible sink for N₂O in soils. We show that biomass pyrolysis in the presence of air increases the magnitude and slightly decreases the reversibility of N₂O adsorption. This has implications for soils containing fire-derived chars as well as soils amended with biochars that had been exposed to hot air during at least some stages of their production. We show that the maximum adsorption capacity correlates better with CO₂-measured surface area than with N₂ B.E.T surface area, and at realistic N₂O pressures correlates best with microporosity, especially ultramicroporosity. That adsorption of N₂O and CO₂ are of similar magnitude and correlate well in the environmentally-relevant low pressure range suggests that CO₂ adsorption can be used as a surrogate for N₂O adsorption. The fact that pore/surface physical properties seem to account for N₂O adsorption trends (section 3.4) is in line with the molecule's apolar nature (dipole moment, 0.166 D) and inability to strongly hydrogen bond. Nevertheless, a role for surface chemistry in N₂O adsorption cannot be ruled out with the present data set.

Cornelissen et al. calculated that N₂O suppressions reported in the literature were far less than the Langmuir maximum capacities of their biochars (Cornelissen et al. 2013). However, capacity is reached only at unrealistically high partial pressures. We show that at environmentally-realistic N₂O pressures, biochar applied to soils at customary rates would dominate sorption of N₂O, especially biochars pyrolyzed in the presence of air. We also show

that the deposition of organic matter substances on biochar has no effect on its subsequent adsorption of N_2O . Like the Cornelissen study (Cornelissen et al. 2013), adsorption was conducted in the absence of water, which will compete for N_2O adsorption domains. Nevertheless, it is likely that water will be less competitive at sites in chars than in soil organic matter and minerals, since the dominant interaction of N_2O is van der Waals forces, and the chars are more hydrophobic than soil organic matter and soil minerals. If true, in the presence of water chars will dominate sorption of N_2O relative to soil even more than predicted by Fig. 7. The study of Quin et al. (Quin et al. 2015) on columns of soil-BC mixtures supports the hypothesis that BC sorbs significant quantities of N_2O in the presence of water in proportion to the fractional content of BC.

Adsorption enhancement of N_2O by BC may explain the temporary nature of N_2O emission suppression by biochar reported in some studies. BC may represent a significant reservoir for N_2O and a buffer for biological transformations in soil. The following scenario can be supposed for a parcel of soil, assuming constant physicochemical conditions and microbial activity. Application of biochar initially causes a sharp decrease in the pore space concentration (air plus water) of N_2O via adsorption, resulting in a sharp decrease in N_2O diffusion to the atmosphere and reaching some minimum value. With continued microbial activity producing N_2O , the biochar, soil components, and pore space concentrations gradually increase in tandem dictated by the quasi-equilibrium partitioning among them, and atmospheric emission accordingly gradually recovers to its original level.

Apart from any impact on net emissions to the atmosphere, BC likely plays a fundamental role in the bioavailability of N_2O to microorganisms in the nitrogen cycle through its strong adsorptive properties. Nitrifying and denitrifying bacteria are incapable of penetrating

430 pores smaller than their diameters ($\sim 10^3$ nm) where virtually all N_2O in/on BC will be located.
431 Therefore, BC may act as a reversible reservoir that buffers the concentration of N_2O with
432 respect to this bacterial community (see Abstract graphic). This study contributes knowledge
433 toward understanding that role.

434

435 **Abbreviations used:**

436 BC, char or biochar

437 B.E.T., Brunauer-Emmitt-Teller theory of multilayer adsorption of non-interacting gases

438 HA, humic acid

439 HTT, heat treatment temperature

440 PPAO, post-pyrolysis air oxidation

441 PPHA, Pahokee peat humic acid

442 SRFA, Suwanee River fulvic acid

443 U.S., United States

444

445 **Notes**

446 The authors declare no competing financial interest.

447

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453

454 **Supplementary data**

455 Supplementary data related to this article include distribution of parameters used in the Monte
456 Carlo simulation, pore size distributions of the chars, adsorption-desorption isotherms of carbon
457 dioxide, correlations of nitrous oxide and carbon dioxide adsorption with pore size slices, and
458 adsorption in soil versus biochar-soil mixture and can be found on the on-line version.

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Table and Figure Captions

Table Captions

Table 1. Surface areas and porosities of the biochars and soils of this study.

Table 2. Langmuir and Henry’s parameters of N₂O adsorption isotherms and the measured and computed adsorption at relative pressure p/p_0 of 1.1×10^{-5} .

Figure Captions

Figure 1. Adsorption and desorption isotherms of N₂O at 273 K for the temperature series of six maple chars and two pecan chars.

Figure 2. Adsorption and desorption isotherms of N₂O at 273 K for the non-BC geosorbents.

Figure 3. Ratio of dry weight-based measured adsorption of N₂O at p/p_0 of 1.1×10^{-5} on M400 (a) or M700 (b) relative to other geosorbents.

Figure 4. Adsorption and desorption of N₂O at 273 K on original and thermally air-oxidized M400 (5–40 min).

Figure 5. Correlation between Henry’s adsorption parameters for N₂O and CO₂ adsorption ($p/p_0 < 10^{-3}$) on raw and PPAO-treated chars.

Figure 6. Langmuir maximum capacity (S_{LM}) of N₂O as a function of CO₂ surface area (a) or N₂ B.E.T surface area (b) for raw and PPAO-treated chars.

Figure 7. Adsorption/desorption of N₂O on PW500 BC coated with Amherst soil HA.

Figure 8. Monte Carlo simulation of the adsorption of N₂O attributable to raw (M400) or 30-min air-oxidized (M400-30) char mixed in a hypothetical soil.

Table 1. Surface areas and porosities of the biochars and soils of this study.

	CO ₂ surface area (m ² /g)	N ₂ B.E.T. surface area (m ² /g)	Ultramicroporosity (3–7 Å) (cm ³ /g)	Supermicroporosity (7–14.7 Å) (cm ³ /g)	Microporosity (3–14.7 Å) (cm ³ /g)	Mesoporosity (15–60 Å) (cm ³ /g)
Lockwood soil	15	8	0.003	0.002	0.005	0.004
Pahokee peat	83	4	0.009	0.026	0.036	0.001
PS350	211	2	0.042	0.024	0.065	0.0004
PS400	271	1	0.055	0.025	0.080	0.0004
PS500	387	1	0.080	0.031	0.11	0.0002
M300	164	4	0.023	0.041	0.064	0.002
M350	269	5	0.048	0.040	0.088	0.002
M400	370	34	0.072	0.040	0.11	0.009
M500	511	281	0.11	0.041	0.15	0.068
M600	591	364	0.12	0.039	0.16	0.033
M700	629	276	0.13	0.034	0.17	0.038
M400-5	435	41	0.083	0.046	0.13	0.035
M400-10	592	335	0.12	0.061	0.18	0.11
M400-20	732	417	0.14	0.083	0.22	0.16
M400-30	742	565	0.15	0.11	0.26	0.13
M400-40	895	415	0.14	0.17	0.31	0.052

PS: pecan shell; MP: maple wood. MP BC400_5: maple wood 400 °C biochar treated by AO at 400 °C for 5 min.

Table 2. Langmuir and Henry parameters of N₂O adsorption isotherms and the measured and computed adsorption at relative pressure p/p_0 of 1.1×10^{-5} .

	Langmuir S_{LM} , mole/kg at 0 °C	Langmuir K_L	R_{adj}^2	Adsorption of N ₂ O (mol/kg) at p/p_0 of 1.1×10^{-5}		Henry's K_H (mol/kg) ^c
				Measured	Computed ^a	
Ottawa Sand	0.12 ± 0.005	54.2 ± 4.2	1.0	5.1×10^{-5}	7.2×10^{-5}	
SWy-1 montmorillonite	1.3 ± 0.02	26.7 ± 0.8	1.0	2.5×10^{-4}	3.8×10^{-4}	
KGa-1b kaolinite	0.6 ± 0.02	48.6 ± 3.6	1.0	1.6×10^{-4}	3.2×10^{-4}	
Lockwood soil	0.2 ± 0.008	50.5 ± 3.4	1.0	1.3×10^{-4}	1.1×10^{-4}	
Pahokee peat	0.8 ± 0.03	36.3 ± 2.3	1.0	1.4×10^{-4}	3.2×10^{-4}	
PPHA	2.5 ± 0.08	28.2 ± 2.2	1.0	6.7×10^{-4}	7.8×10^{-4}	
SRFA	3.8 ± 0.03	12.4 ± 0.9	1.0	5.3×10^{-4}	5.2×10^{-4}	
PS400	1.4 ± 0.02	141.3 ± 0.9	1.0	4.9×10^{-3}	2.1×10^{-3}	232 ± 8
PS500	2.0 ± 0.02	185 ± 8	1.0	1.2×10^{-2}	4.1×10^{-3}	404 ± 14
M300	1.9 ± 0.06	65.4 ± 5	1.0	2.1×10^{-3}	1.3×10^{-3}	172 ± 2
M350	2.6 ± 0.09	71.6 ± 6	1.0	2.9×10^{-3}	2.0×10^{-3}	276 ± 9
M400	2.8 ± 0.08	90.7 ± 7	1.0	4.3×10^{-3}	2.8×10^{-3}	334 ± 7
M500	3.1 ± 0.07	83.5 ± 5	1.0	4.9×10^{-3}	2.8×10^{-3}	330 ± 6
M600	4.7 ± 0.1	130 ± 9	1.0	1.3×10^{-2}	6.8×10^{-3}	759 ± 23 ^c
M700	4.2 ± 0.08	153 ± 11	1.0	1.3×10^{-2}	2.5×10^{-3}	764 ± 2 ^c
M400-5	3.5 ± 0.04	186 ± 8	1.0	1.2×10^{-2}	7.1×10^{-3}	699 ± 14
M400-10	4.0 ± 0.05	170 ± 8	1.0	1.5×10^{-2}	7.5×10^{-3}	752 ± 10
M400-20	4.7 ± 0.05	138 ± 5	1.0	1.3×10^{-2}	7.1×10^{-3}	668 ± 19
M400-30	5.6 ± 0.09	129 ± 6	1.0	1.7×10^{-2}	8.0×10^{-3}	834 ± 7
M400-40	5.3 ± 0.07	174 ± 8	1.0	2.1×10^{-2}	1.0×10^{-2}	1005 ± 14
PW500	2.6 ± 0.02	225 ± 66	1.0	1.2×10^{-2}	6.1×10^{-3}	619 ± 19
PW500+ 2% Amherst soil HA ^b	2.7 ± 0.02	205 ± 6	1.0	1.2×10^{-2}	5.7×10^{-3}	
PW500 + 2% Amherst soil HA (2nd time)	2.7 ± 0.02	194 ± 6	1.0	1.1×10^{-2}	5.7×10^{-3}	
PW500 + 2% Amherst soil HA (3rd time)	2.8 ± 0.03	219 ± 8	1.0	1.3×10^{-2}	6.7×10^{-3}	
PW500 + 5% Amherst soil HA	2.6 ± 0.02	220 ± 8	1.0	1.2×10^{-2}	6.3×10^{-3}	
<i>a</i> : computed from Langmuir fits; <i>b</i> : Amherst soil HA. PS: pecan shell. M: maple wood. M BC400_5: maple wood char made at 400 °C and subsequently treated by AO at 400 °C for 5 min. PW: pine wood. R_{adj}^2 : coefficient of determination adjusted for degree of freedom (Xiao et al., 2013). ^c ± standard error; $R^2 > 0.976$ in all cases.

Fig. 1. Adsorption and desorption isotherms of N₂O at 273 K for the temperature series of six maple chars and two pecan chars.

Fig. 2. Adsorption and desorption isotherms of N_2O at 273 K for the non-BC geosorbents.

Fig. 3. Ratio of dry weight-based measured adsorption of N₂O at p/p_0 of 1.1×10^{-5} on M400 (a) or M700 (b) relative to other geosorbents.

Fig. 4. Adsorption and desorption of N_2O at 273 K on thermally air-oxidized M400 (0–40 min).

Figure 5. Correlation between the Henry’s adsorption parameters for N₂O and CO₂ adsorption ($p/p_0 < 10^{-3}$) on raw and PPAO-treated chars.

Figure 6. Langmuir maximum capacity (S_{LM}) of N_2O as a function of CO_2 surface area (a) or N_2 B.E.T surface area (b) for raw and PPAO-treated chars.

Figure 7. Adsorption/desorption of N_2O on PW500 BC coated with Amherst soil HA.

Fig. 8. Monte Carlo simulation of the adsorption of N₂O attributable to raw (M400) or 30-min air-oxidized (M400-30) char mixed in a hypothetical soil.

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