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## **Análisis agronómico y ambiental del uso de biocarbón como enmendante de suelo**

Tesis para optar al grado de Doctor en Ciencias de la Agronomía

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## ABREVIATURAS Y NOMENCLATURA

### Abreviaturas y nomenclatura en idioma español

- C: Carbono
- CT: Carbono total
- CO: Carbono orgánico
- O: Oxígeno
- H: Hidrógeno
- CO<sub>2</sub>: Dióxido de carbono
- CH<sub>4</sub>: Metano
- N<sub>2</sub>O: Óxido nitroso
- IBI: Iniciativa Internacional del Biocarbón
- P: Fósforo
- K: Potasio
- Ca: Calcio
- Mg: Magnesio
- CIC: Capacidad de intercambio catiónico
- sBC*<sub>+100</sub>: C añadido con el biocarbón estable por más de 100 años en el suelo
- BC*<sub>+100</sub>: % de C en el biocarbón que se almacena durante 100 años
- GEI: Gases de efecto invernadero
- IPCC: Panel Intergubernamental de Cambio Climático (por sus siglas en inglés)
- Al: Aluminio
- MO: Materia orgánica

### Abreviaturas y nomenclatura en idioma inglés

#### CAPÍTULO II

- GHG: Greenhouse gas
- BC: Biochar

CEC: Cation exchange capacity

Si: Silicon

WHC: Water holding capacity

BC-chicken: Chicken manure biochar

BC-cow: Cow manure biochar

BC-pig: Pig manure biochar

C<sub>org</sub>: Organic C

GWP: Global warming potential

FDA: Fluorescein diacetate

CO<sub>2</sub>-eq: CO<sub>2</sub> equivalent

### **CAPÍTULO III**

CaCO<sub>3</sub>-eq: CaCO<sub>3</sub> equivalent proportion

SOM: Soil organic matter

OC: Organic carbon

Cox: Oxidizable carbon

Cnox: Non-Oxidizable carbon

TC: Total carbon

EWBC: Eucalyptus wood residue biochar

DMBC: Dairy manure biochar

PMBC: Pig manure biochar

PLCM: Poultry litter carbonaceous material

WFPS: Water-filled pore space

ECD: Electron capture detector

FID: Flame ionization detector

IC: Inorganic C

EC: Electrical conductivity

### **CAPÍTULO IV**



PM: Pig manure

PMB: Pig manure biochar

DM: Dairy manure

DMB: Dairy manure biochar

Efs: Emission factors

$N_2O$  Ef:  $N_2O$  Emission factors

$CD_{rate}$ : C decomposition rate

$\Delta C$  stocks: Changes in soil C stocks

$GWP_{(\Delta C \text{ stocks})}$ : Global warming potential avoided according to changes in soil C stocks

$GWP_{(net)}$ : Net global warming potential



## RESUMEN

Los enmendantes de suelo tienen como objetivo la modificación de propiedades físicas, químicas y/o biológicas del suelo para mejorar su funcionalidad, ya sea para la producción de alimentos o con motivaciones medio-ambientales. En la actualidad, frente al crecimiento exponencial de la población y, por tanto, la demanda de alimentos, la intensificación sostenible del sector agropecuario se ha convertido en una necesidad de primer orden. Un reto adicional es el recrudecimiento del cambio climático, el cual requiere del uso de enmendantes que sean ambientalmente amigables. En este sentido, la pirólisis de estiércol para producir biocarbón y aplicarlo como enmendante de suelo aparece como alternativa para el uso de residuos, promoviendo la economía circular.

El objetivo de este trabajo fue evaluar el impacto ambiental y agronómico de la aplicación de biocarbón proveniente de estiércol como enmendante de suelos de origen volcánico. La investigación se llevó a cabo en la Universidad de Concepción, y consistió en tres ensayos. El Ensayo 1 se realizó a escala de laboratorio, mientras que los Ensayos 3 y 4 se realizaron bajo condiciones de campo. El Ensayo 1 evaluó el efecto del biocarbón producido a partir de diferentes residuos agrícolas (estiércol de pollo, cerdo y vaca) sobre emisiones de gases de efecto invernadero (GEI) y propiedades químicas y biológicas del suelo en diferentes suelos de pradera (suelos volcánicos y no volcánicos). El Ensayo 2 evaluó los efectos de biocarbones producidos desde residuos ganaderos y madereros sobre la productividad del *Sorghum sudangrass* (*S. bicolor* × *S. bicolor* var. Sudanese), la calidad del suelo y las emisiones de CO<sub>2</sub> y N<sub>2</sub>O. Finalmente, el Ensayo 3 comparó el potencial de calentamiento global inducido por la adición de estiércoles animales pirolizados y sin pirolizar. En los Ensayos 2 y 3 se usaron dosis de 1% biocarbón: suelo, equivalentes a 11 t ha<sup>-1</sup>. Todos los biocarbones fueron producidos por pirólisis lenta (500 a 550 °C).

En condiciones de laboratorio los biocarbones de estiércol aumentaron el pH (0,9 ± 0,5, en promedio) y disminuyeron la actividad de la β-glucosidasa en suelos de origen volcánico y no volcánico. Las emisiones de GEI variaron dependiendo de la materia prima del biocarbón. Sin embargo, el biocarbón de

ganado lechero indujo flujos más bajos de CO<sub>2</sub> y CH<sub>4</sub> que el resto de los enmendantes, probablemente debido a la disminución de la actividad de la β-glucosidasa. En condiciones de laboratorio y campo, el carbono total (CT) del suelo aumentó significativamente ( $p \leq 0.05$ ) con la adición de biocarbón de cerdo y ganado lechero, mientras el biocarbón de guano de ave no tuvo ningún efecto respecto al suelo control. En condiciones de campo, los biocarbones de estiércol modificaron propiedades claves para suelos volcánicos, aumentando el pH entre 0,19 y 0,73 unidades, así como el P y K disponibles. La intensidad de estos efectos varió en función de la materia prima del biocarbón. Sin embargo, todos los biocarbones de estiércol aumentaron significativamente ( $p \leq 0.05$ ) el rendimiento del forraje entre 6,9 y 10,8 t ha<sup>-1</sup> respecto al suelo sin enmendar. Aunque el biocarbón leñoso resultó más efectivo para incrementar el C no oxidable del suelo, los tres biocarbones de estiércol aumentaron el C oxidable (entre 6,4% y 27%), posiblemente asociado al aumento de los rendimientos.

El Ensayo 3 mostró que las emisiones de CO<sub>2</sub> en campo fueron 8,35% y 63% del C añadido con estiércoles pirolizados y sin pirolizar, respectivamente, indicando que la pirólisis aumenta la estabilidad del C del estiércol. El factor de emisión de N en forma de N<sub>2</sub>O de los estiércoles fue de 0,27%. Sin embargo, los biocarbones produjeron emisiones negativas respecto al suelo sin enmendar. El aumento del C del suelo y la mitigación de emisiones de N<sub>2</sub>O produjo potenciales de calentamiento global negativos, representando entre 3,95 y 4,96 toneladas de CO<sub>2</sub> equivalentes evitadas por hectárea, debido a la adición de biocarbón de estiércol al suelo.

Se concluye que el uso de biocarbón de estiércol como enmendante de suelos volcánicos tiene potencial para mejorar el rendimiento agronómico de cultivos forrajeros, a la vez que favorece el almacenaje de C en el suelo y evita emisiones de GEI. Por lo tanto, su producción y aplicación es una práctica agronómica y ambientalmente factible y eficiente para el reciclado de nutrientes contenidos en los estiércoles de granja.



## ABSTRACT

Soil amendments are intended to modify the physical, chemical and/or biological properties of the soil, improving its functionality for food production or environmental purposes. Nowadays, due to the exponential growth of the population and high food demand, the sustainable intensification of the agricultural sector has become a priority. In addition, there is an increasing need for more eco-friendly amendments as climate change aggravates. In this sense, the pyrolysis of manure to produce biochar, and its application as a soil amendment is an alternative that allows the use of waste, promoting the circular economy.

The objective of this study was to evaluate the environmental and agronomic impact of the application of biochar derived from manure as a soil amendment in volcanic soils. The research was conducted at the University of Concepción and consisted of 3 trials. Trial 1 was conducted under laboratory conditions, while Trials 2 and 3 were performed under field conditions. Trial 1 evaluated the effect of biochar produced from different types of farm waste (chicken, pig and cow manures) on greenhouse gas (GHG) emissions, and soil chemical and biological properties in different grassland soils (volcanic and non-volcanic soils). Trial 2 evaluated the effects of biochar produced from livestock and wood residues on *Sorghum sudangrass* (*S. bicolor* × *S. bicolor* var. Sudanese) productivity, soil quality, and CO<sub>2</sub> and N<sub>2</sub>O emissions. Finally, Trial 3 compared the global warming potential induced by the addition of pyrolyzed and unpyrolyzed animal manures. For Trials 2 and 3, doses of 1% biochar: soil, equivalent to 11 t ha<sup>-1</sup>. All biochars were produced by slow pyrolysis (500 to 550 °C).

Under laboratory conditions, soil pH increased with the application of manure biochars (0.9 ± 0.5, on average) and the β-glucosidase activity decreased in volcanic and non-volcanic soils. GHG emissions varied depending on biochar feedstock. However, biochar derived from cow manure induced lower CO<sub>2</sub> and CH<sub>4</sub> fluxes than the other amendments, probably due to the decreases in β - glucosidase activity. Under laboratory and field conditions, soil total carbon (TC) increased significantly ( $p \leq 0.05$ ) with the addition of pig and cow manure

biochar, while chicken manure biochar had no effect compared to the control soil. Under field conditions, the manure biochars modified key properties of volcanic soils, increasing the pH between 0.19 and 0.73 units, as well as available P and K. The intensity of these effects varied depending on the biochar feedstock. However, all manure biochars significantly ( $p \leq 0.05$ ) increased forage yield between 6.9 and 10.8 t ha<sup>-1</sup> compared to unamended soil. Although the woody biochar was more effective in increasing non-oxidizable soil C, all three manure biochars increased oxidizable C (between 6.4% and 27%), possibly due to higher forage yields.

Trial 3 showed that field emission of CO<sub>2</sub> were 8.35% and 63% of the C added with pyrolyzed and unpyrolyzed manures, respectively, which indicates that pyrolysis increases manure C stability. The N<sub>2</sub>O-N emission factor from manures was 0.27%. However, biochars produced negative emissions compared to unamended soil. The increase in soil C and mitigation of N<sub>2</sub>O emissions produced negative global warming potentials, representing between 3.95 and 4.96 tons of CO<sub>2</sub> equivalent avoided per hectare due to the addition of manure biochar to the soil.

The use of manure biochar as an amendment of volcanic soils has the potential to improve the agronomic yield of forage crops, while favoring soil C stock and reducing GHG emissions. Therefore, biochar application is an agronomically and environmentally viable practice for the recycling of nutrients from farm manure.

# CAPÍTULO I

## INTRODUCCIÓN Y OBJETIVOS

### 1. INTRODUCCIÓN

#### 1.1. *Generalidades del biocarbón*

El uso de biocarbón en suelos agrícolas se remonta a una práctica ancestral desarrollada en Brasil, que dio lugar a las "Tierras Oscuras del Amazonia" o "Terra preta do Indio"(Mann, 2002; Marris, 2006). En la actualidad, la producción de biocarbones y su aplicación como enmendantes de suelo, incluyendo los co-beneficios medioambientales que generan, adquiere cada vez mayor relevancia dentro de la comunidad científica (IPCC, 2019; Lehmann y Joseph, 2015; Paustian et al., 2016).

El biocarbón es resultado de la carbonización de biomasa en condiciones de bajo oxígeno o sin oxígeno, y temperaturas sobre los 250 °C; definiéndose como el residuo sólido obtenido de la descomposición térmica o pirólisis de residuos orgánicos, con alto potencial para su aplicación al suelo como parte de un proyecto agronómico y/o medioambiental (Lehmann y Joseph, 2015; Paustian et al., 2016). El proceso de pirólisis genera además del biocarbón (fase sólida), co-productos tales como el bioaceite y gas no condensado. Estos co-productos pueden ser usados en la producción de energía y la proporción en que se obtienen depende de la temperatura y el tiempo de pirólisis (Mahinpey et al., 2009).

Dentro de las principales características del biocarbón está el alto contenido de carbono orgánico (CO), y mayor área superficial y porosidad que los materiales que le dan origen (Hassan et al., 2020). Su estructura, predominantemente aromática y heterogénea, está formada por macromoléculas condensadas que disminuyen sus contenidos de oxígeno (O) e hidrógeno (H) después de la pirólisis (Lehmann and Joseph, 2015; Stylianou et al., 2020). De hecho, la Iniciativa Internacional del Biocarbón (IBI) establece que para que un material sea considerado biocarbón debe tener un contenido de CO mayor al 10% y su radio molar H:CO debe estar por debajo de 0,7 (IBI- International Biochar Initiative, 2013). Además del enriquecimiento en C, los biocarbones

generalmente tienen altos contenidos de ceniza y contienen nutrientes como fósforo (P), potasio (K), calcio (Ca), y magnesio (Mg) (Camps-Arbestain et al., 2015, 2017; Wang et al., 2012b)

Las propiedades del biocarbón son variables y dependen principalmente de las condiciones de operación durante la pirólisis, así como de la composición de la biomasa elegida como material de origen (Calvelo Pereira et al., 2011; Enders et al., 2012; Hassan et al., 2020; Stylianou et al., 2020). Algunos biocarbones son ricos en constituyentes minerales, que se originan a partir de la materia prima (Singh et al., 2010). Estos constituyentes mejoran significativamente la alcalinidad del biocarbón otorgándoles mayor potencial de encalado (Vassilev et al., 2013). Los biocarbones derivados de estiércol suelen tener mayor poder fertilizante y de encalado, aportando nutrientes disponible al suelo y a las plantas (Camps-Arbestain et al., 2017; Subedi et al., 2016; Wang et al., 2012b, 2014), mientras los biocarbones derivados de material leñoso son pobres en constituyentes minerales pero ricos en C (Hassan et al., 2020). La temperatura de pirólisis influye en propiedades del biocarbón como su estabilidad (W. Li et al., 2019), independientemente de la materia prima usada, los biocarbones producidos a altas temperaturas tienen valores más bajos de C degradable química o térmicamente (Calvelo Pereira et al., 2011), lo que genera una menor tasa de descomposición del C una vez añadidos al suelo (Gascó et al., 2016).

## **1.2. Beneficios de la producción y/o aplicación de biocarbón al suelo**

Aunque el biocarbón tiene numerosos efectos positivos potenciales (Abagandura et al., 2019; Abbruzzini et al., 2019; Zhang et al., 2019a), debido a la variabilidad en sus propiedades resulta imposible que todos los beneficios se produzcan de forma simultánea y con igual intensidad, por lo que compensaciones asociadas a los diferentes usos de biocarbón suelen ocurrir (Jeffery et al., 2015; W. Li et al., 2019; Zhang et al., 2019a). De manera general, las principales motivaciones para la producción de biocarbón y/o su posterior aplicación al suelo se pueden resumir en 5:

- I. Producción de energía (Gaunt and Lehmann, 2008; Mahinpey et al., 2009).

- II. Remoción de contaminantes desde suelo o agua (Hassan et al., 2020; Stylianou et al., 2020; Zhang et al., 2019a).
- III. Mejoramiento de suelo (Abbruzzini et al., 2019; Alcívar et al., 2018; Jeffery et al., 2017, 2011; Liu et al., 2013; Muñoz et al., 2019) y rendimiento de cultivos (Jeffery et al., 2017, 2015, 2011; Ye et al., 2020).
- IV. Mitigación del cambio climático (Cayuela et al., 2015, 2014, 2013; IPCC, 2019; Zimmerman et al., 2011).
- V. Manejo de residuos (Gascó et al., 2016; Grutzmacher et al., 2018; Subedi et al., 2016).

La producción de energía en los procesos de pirólisis se asocia a la materia prima usada y a las condiciones de la pirólisis. Procesos pirolíticos lentos a menores temperaturas (250 a 750 °C) propician la producción de biocarbón disminuyendo la fracción de bioaceites y gas de síntesis que pueden ser recogidos y usados con fines energéticos (Jeffery et al., 2015). Gaunt y Lehmann, 2008 informaron que la pirólisis lenta para producir biocarbón reduce la producción de energía en aproximadamente un 30%, en comparación con pirólisis rápidas optimizadas para la producción de biocombustibles; sin embargo, en términos de reducción de emisiones el efecto del biocarbón sobre el almacenamiento de C del suelo podría equilibrar esta disminución. Por lo tanto, resulta necesario continuar investigando en la cuantificación de las compensaciones que inevitablemente se producen entre la producción de energía y de biocarbón con fines agrícolas y/o ambientales (Jeffery et al., 2015).

El potencial del biocarbón en la gestión de contaminantes depende de su superficie específica, grupos funcionales y porosidad (Zhang et al., 2019a). Hassan et al., 2020 ha resumido que: altas temperaturas generan biocarbones de gran porosidad y cantidad de sitios activos aromáticos, que pueden ser empleados para la adsorción de contaminantes orgánicos; mientras que los producidos a bajas temperaturas generalmente adsorben contaminantes inorgánicos por interacción electrostática e intercambio de iones debido a su abundancia de grupos funcionales (Hassan et al., 2020).

Aunque la producción de energía asociada a la pirólisis y el potencial del biocarbón en la remoción de contaminantes son motivaciones con gran repercusión en los estudios ambientales actuales, en este trabajo se aborda con mayor profundidad el potencial del biocarbón como mejorador de suelo y rendimiento de cultivos, y como estrategia para mitigar el cambio climático y manejar residuos ganaderos.

### **1.2.1. El biocarbón en el mejoramiento del suelo y rendimiento de cultivos**

La adición de biocarbón como enmendante puede mejorar propiedades físicas, químicas y biológicas del suelo, estas mejoras se asocian a las características del biocarbón, dosis y tipo de suelo al que se aplica (Brassard et al., 2018; Garbuz et al., 2020). La modificación de propiedades físicas (por ej. capacidad de almacenamiento de agua y porosidad del suelo) es más probable a altas dosis de aplicación,  $\geq 30 \text{ t ha}^{-1}$  (Herath et al., 2013; Kammann et al., 2011), mientras cambios químicos (pH, nutrientes disponibles, CIC) y biológicos en el suelo (diversidad y actividad) han sido reportados incluso a bajas dosis,  $\leq 10 \text{ t ha}^{-1}$  (Brassard et al., 2018; Garbuz et al., 2020).

El biocarbón puede aumentar el rendimiento de los cultivos fundamentalmente a través de su potencial para encalar el suelo y/o el nivel de nutrientes disponibles que aporta (Abbruzzini et al., 2019; Jeffery et al., 2017, 2011; Liu et al., 2013); sin embargo, como se expresó anteriormente, el biocarbón es un material heterogéneo y sus características son variables y dependientes de los materiales de origen y las condiciones de pirólisis (Singh et al., 2010). En este sentido, resulta indispensable la determinación de la capacidad de encalado y fertilizante del biocarbón cuando se aplica al suelo con fines agrícolas (Camps-Arbestain et al., 2015; Balwant Singh et al., 2017; Wang et al., 2012b, 2014).

De manera general, se ha estimado que el biocarbón aumenta el rendimiento, en promedio, entre el 9% y el 17%, especialmente cuando biocarbones ricos en nutrientes (como los provenientes de residuos de cosecha o estiércol) se añaden a suelos ácidos que limitan la productividad de los cultivos (Jeffery et al., 2017, 2011; Liu et al., 2013; Ye et al., 2020). Jeffery et al., 2017 en un meta

análisis encontró que los rendimientos aumentan solo con la adición de biocarbón en suelos tropicales, pobres en nutrientes y de bajo pH, mientras que en los suelos de otras latitudes podía incluso afectarse el rendimiento por sobre encalado. Este autor considera que biocarbones con pH de dos unidades superior al suelo, puede incrementar el pH por encima del óptimo para la fertilidad, sin embargo, en este estudio se consideraron tasas de aplicación, en promedio, de 30 t ha<sup>-1</sup>. Más recientemente, otro meta análisis que incluyó estudios con menores dosis (entre 5 y 20 t ha<sup>-1</sup>) encontró que tasas inferiores a 10 t ha<sup>-1</sup> no tienen efecto en el rendimiento, pero no se encontraron efectos negativos a ninguna dosis de aplicación (Ye et al., 2020). En general, los biocarbones ricos en nutrientes han mostrado mayores efectos sobre el rendimiento de los cultivos (Jeffery et al., 2011; Ye et al., 2020), no obstante, Garbuz et al., 2020 encontró que incluso biocarbones con pocos nutrientes tienen efectos positivos en la productividad de suelos volcánicos, lo que se relacionó a los cambios en las comunidades biológicas del suelo y a su poder de encalado.

### **1.2.2. Biocarbón: almacenamiento de C del suelo y emisiones de CO<sub>2</sub>**

Recientemente, el reporte especial de cambio climático incluyó la producción y adición al suelo de biocarbón como una de las medidas efectivas para enfrentar la crisis ambiental (IPCC, 2019). La asociación del término “biocarbón” con la mitigación del cambio climático es un concepto que surge fundamentalmente ligado a la idea de que la pirólisis produce compuestos de C estables (Sohi et al., 2010), que pueden ser almacenados por largos periodos de tiempo en el suelo (Whitman et al., 2015). De hecho, el valor de almacenaje de C constituye una de las categorías de clasificación del biocarbón más estudiadas (Zimmerman et al., 2011). El “*Protocolo de C estable de IBI*” con el cual se clasifica el biocarbón según su potencial para aumentar los contenidos de C del suelo, emplea la metodología desarrollada por Budai et al., 2013 donde se estima la fracción de CO del biocarbón que se mantiene estable por más de 100 años. Este protocolo se basa en la aromaticidad que el radio molar H:CO concede al biocarbón, considerándose que la fracción de C estable por más de 100 años en el suelo ( $sBC_{+100}$ ) es el resultado de la multiplicación de los

contenidos de CO del biocarbón por su porcentaje de almacenamiento durante 100 años ( $BC_{+100}$ ) ecuación 1.

$$sBC_{+100} = CO * BC_{+100} \quad (1)$$

En la Tabla 1 se muestra la relación entre el radio molar H: CO del biocarbón, su aromaticidad y los valores de corte propuestos por IBI para determinar el porcentaje de carbono estable.

Tabla 1. Radio molar H : CO, porcentaje de aromaticidad y valores de corte del carbono estable por más de 100 años en el Protocolo de C estable de IBI (**Fuente:** Adaptado de Camps-Arbestain et al., 2015).

H: CO	Aromaticidad	BC <sub>+100</sub> (IBI)
mol mol <sup>-1</sup>	%	%
0.4	92	70
0.5	87	50
0.6	81	50
0.7	74	50

El balance de CO en los suelos es un proceso complejo, que se rige por el equilibrio entre las entradas de C y los flujos de CO<sub>2</sub> emitidos durante los procesos de descomposición (Lal, 2018a; Powlson et al., 2013). Aunque el biocarbón puede tener un largo tiempo de residencia en el suelo, no es un material inerte (Budai et al., 2013; Lehmann and Joseph, 2015; Powlson et al., 2013) y su fracción de C lábil puede ser rápidamente mineralizada induciendo emisiones de CO<sub>2</sub> (Bruun et al., 2012), ya sea por su propia descomposición o por el cebado positivo (efecto priming positivo) de las fracciones de CO preexistentes en el suelo. Por lo tanto, independientemente de la aromaticidad estimada a partir del radio H: CO, otros factores como el tipo de suelo donde se aplica el biocarbón deben valorarse para determinar la permanencia del C que se añade al suelo (Herath et al., 2015; Muñoz et al., 2019).

La presencia de C inorgánico en el material pirolizado, fundamentalmente cuando se aplica en suelos ácidos, es otro de los factores que puede inducir



emisiones de CO<sub>2</sub> tras la adición de biocarbón (Maestrini et al., 2015; Muñoz et al., 2019; Sheng and Zhu, 2018). Mientras que biocarbones con relaciones C:N altas y bajos índices de C oxidable vs C no oxidable propician la estabilidad del C que se añade al suelo con el biocarbón (Calvelo Pereira et al., 2011; P Cely et al., 2014; Grutzmacher et al., 2018).

### **1.2.3. El biocarbón y las emisiones de N<sub>2</sub>O del suelo**

El potencial de calentamiento global del N<sub>2</sub>O es 265 veces mayor que el del CO<sub>2</sub> (basado en un horizonte de tiempo de 100 años), lo que lo convierte en uno de los más importantes GEI (IPCC, 2019; Myhre et al., 2013). Otro de los co-beneficios ambientales de la aplicación de biocarbón al suelo es precisamente su efecto en la reducción de las emisiones de N<sub>2</sub>O (Cayuela et al., 2014; Cayuela et al., 2015; Hangs et al., 2016) generando una alternativa para atenuar el impacto de la agricultura sobre el calentamiento global (Wang et al., 2013).

El efecto del biocarbón sobre las emisiones de N<sub>2</sub>O es muy variable y depende de (i) la producción del biocarbón (materia prima y condiciones de pirólisis); (ii) las propiedades inherentes al biocarbón (relaciones C:N, H:OC, efecto de encalado, contenido de N); y (iii) el entorno pedoclimático al que queda expuesto el biocarbón (contenido de C y N del suelo, pH, densidad aparente y condiciones climáticas) (Cayuela et al., 2013, 2014, 2015; Z. Wang et al., 2013).

En promedio, una reducción de las emisiones de N<sub>2</sub>O del suelo de 28 ± 16% ha sido reportada bajo condiciones de campo, mientras que en condiciones controladas de laboratorio estos valores alcanzan una reducción de 54 ± 3% (Cayuela et al., 2015). Contrario a estos resultados, se ha observado que los biocarbones con alto contenido de N mineral (como los derivados de estiércol) pueden incrementar las emisiones de N<sub>2</sub>O del suelo (S. Li et al., 2019); sin embargo, los estudios del potencial de mitigación de los biocarbones de estiércol deberían evaluar también las inevitables emisiones de las materias primas sin pirolizar (Van Zwieten et al., 2015).

#### **1.2.4. Biocarbón como alternativa de manejo de residuos ganaderos**

Debido a la demanda de alimentos, los residuos ganaderos han crecido exponencialmente en las últimas décadas y su manejo se ha convertido en un problema medioambiental de escala global (Guo et al., 2020; Shakoore et al., 2021; Zhou et al., 2017). De hecho, se estima que la ganadería en Sudamérica excreta cinco veces más N que el excretado en 1860, aumentando drásticamente las emisiones de N<sub>2</sub>O por este concepto (Zhang et al., 2017). Según el Panel Intergubernamental de Cambio Climático (IPCC, por sus siglas en inglés), la agricultura y la ganadería tienen un potencial de mitigación de entre 2,3 a 9,6 Gt CO<sub>2</sub> eq año<sup>-1</sup>, jugando un importante rol en la reducción del calentamiento global para el 2050 (IPCC, 2019).

El re-uso del estiércol en la agricultura brinda una alternativa para transferir C y N y mejorar la calidad física, química y biológica del suelo (Lupwayi et al., 2014; Maillard and Angers, 2014; Mangalassery et al., 2019; Qin et al., 2021). Sin embargo, debido a los procesos de descomposición, los estiércoles pueden ser rápidamente mineralizados a CO<sub>2</sub> (Grutzmacher et al., 2018; Zhang et al., 2021), facilitando procesos como la nitrificación y/o desnitrificación, que incrementan las emisiones antropogénicas de N<sub>2</sub>O (Meyer et al., 2021; Zhou et al., 2016, 2014). De esta forma, los beneficios asociados a las ganancias de C por la adición de estiércol al suelo pueden verse disminuidos por la inducción de emisiones de GEI (Zhou et al., 2017). No obstante, estas emisiones también ocurren si el estiércol no es adicionado al suelo, debido a la descomposición desde los centros de almacenamiento sólido (Chadwick et al., 2011). Lo cual indica que mejores prácticas de manejo del estiércol son necesarias para convertirlos en materiales más estables o resistentes a la descomposición microbiana (Zhang et al., 2017, 2021).

La pirólisis es una alternativa que permite convertir bio-residuos en nuevos productos de valor agregado, reduciendo el volumen y concentrando nutrientes, fundamentalmente cuando se dispone de una elevada cantidad de biomasa con difícil disposición final (Lehmann and Joseph, 2015). Los estiércoles animales logran una alta polimerización, aromatización y carbonización tras la pirólisis (Gascó et al., 2016; Grutzmacher et al., 2018; Stylianou et al., 2020),

por lo tanto, los biocarbones de estiércol podrían utilizarse con fines medioambientales como el aumento de las reservas de C del suelo (Stylianou et al., 2020; Subedi et al., 2016). Adicionalmente, la pirólisis evita emisiones de CO<sub>2</sub> y N<sub>2</sub>O producto de la descomposición que naturalmente ocurre desde los residuos ganaderos (Gascó et al., 2016; Grutzmacher et al., 2018; Lehmann y Joseph, 2015). Sin embargo, el proceso de pirólisis puede ser costoso (El-Naggar et al., 2019); por lo tanto, el potencial de mitigación del biocarbón de estiércol debe demostrarse en contraste con prácticas convencionales de menor costo, como la aplicación directa de estiércol al suelo.

### **1.3. Los suelos volcánicos y el biocarbón**

Los Andosoles representan aproximadamente 0,84% de la superficie terrestre mundial (aproximadamente 124 millones de hectáreas) (Shoji et al., 1993), sin embargo contienen 1,8% del C global del suelo (Takahashi and Dahlgren, 2016). Los suelos volcánicos presentan bajas tasas de respiración y sus contenidos de CO tienen largos tiempos de residencia en el suelo (Doetterl et al., 2015), debido a que la materia orgánica (MO) queda protegida contra la descomposición microbiana a través de su interacción con constituyentes inorgánicos de bajo orden (Kleber et al., 2015; Kögel-Knabner et al., 2008).

De hecho, exceptuando los materiales carbonizados, las fracciones de C del suelo más estables son las contenidas en complejos órgano-minerales, resultado de la asociación química de la MO con superficies minerales y cationes metálicos (Heckman et al., 2018; Kleber et al., 2015, 2007; Kögel-Knabner et al., 2008). Este es el caso de algunos suelos ácidos, como los de origen volcánico (Takahashi and Dahlgren, 2016), donde el aluminio (Al) es capaz de formar complejos con ligandos orgánicos, aumentando la preservación de la MO. Sin embargo, se ha observado que aumentos bruscos de pH pueden favorecer la formación preferente de hidróxidos de Al y el debilitamiento de los puentes de protones entre los ligandos orgánicos (Newcomb et al., 2017; Shen et al., 2018a).

Diversos autores han reportado la vulnerabilidad de los complejos órgano-Al a la adición de enmiendas químicas como la cal y los fertilizantes de P

(Miyazawa et al., 2013; Shen et al., 2018a; Verde et al., 2010). El aumento en la concentración de ligandos  $\text{OH}^-$  aumenta la capacidad de desplazar a los ligandos orgánicos previamente unidos al Al, volviendo a la MO más susceptibles a la descomposición microbiana (Miyazawa et al., 2013). Este proceso no solo reduce la cantidad de complejos orgánicos de Al (Miyazawa et al., 2013; Verde et al., 2010), sino que también amortigua el pH del sistema mediante la formación de nuevas asociaciones Al-OH (Shen et al., 2018a). Por otra parte, el fosfato actúa de forma similar, ya que compite con ligandos orgánicos por los cationes de Al, quedando inmovilizado el P y más susceptible a la descomposición la MO (Kleber et al., 2015; Shen et al., 2018a).

Este fenómeno sugiere que la manipulación del P y el pH del suelo pueden tener marcados efectos sobre el C almacenado en suelos volcánicos, por lo que estudios detallados deberían ser desarrollados ante prácticas de manejo que supongan encalado y/o adición de enmendantes ricos en P (Miyazawa et al., 2013; Shen et al., 2018a; Verde et al., 2010). Aunque varios estudios han investigado el efecto del biocarbón sobre propiedades claves en suelos volcánicos (Herath et al., 2015; Koga et al., 2017; Stylianou et al., 2020; Yamamoto et al., 2019), hasta la fecha, resultan escasos los datos a escala de campo sobre el efecto de biocarbones ricos en nutrientes y de alto potencial de encalado, sobre las concentraciones de C del suelo y la productividad. En Chile más del 60% de los suelos con potencial agronómico tienen origen volcánico (Besoain, 1985), por lo que su inclusión dentro de los suelos que se enmienden con biocarbón podría ofrecer un amplio potencial para almacenar C a largo plazo.

## **2. HIPÓTESIS**

La aplicación de biocarbón de estiércol como enmendante de suelos volcánicos podría disminuir el potencial de calentamiento global de los sistemas de producción ganaderos y agrícolas, siendo factible agronómica y ambientalmente.

### 3. OBJETIVO GENERAL

Evaluar el impacto ambiental y agronómico de la aplicación de biocarbón proveniente de estiércol como enmendante de suelos de origen volcánico.

### 4. OBJETIVOS ESPECÍFICOS

- Cuantificar, a escala de laboratorio y campo, el efecto de biocarbones producidos de residuos ganaderos sobre emisiones de gases de efecto invernadero y el almacenamiento de C del suelo.
- Evaluar el uso del biocarbón sobre propiedades claves del suelo y su efecto en la productividad del sorgo forrajero.
- Evaluar el efecto de la pirólisis lenta sobre la estabilidad del estiércol como enmendante de suelo.

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## RESULTADOS Y DISCUSIÓN

### CAPÍTULO II

**Title: Variation of greenhouse gases fluxes and soil properties with addition of biochar from farm-wastes in volcanic and non-volcanic soils**  
(artículo publicado en *Sustainability*, 27/03/2019)

#### **Abstract**

The decomposition of organic wastes contributes to greenhouse gas (GHG) emissions and global warming. This study evaluated the effect of biochar (BC) produced from different farm wastes (chicken, pig and cow manures) on greenhouse gas emissions and soil chemical and biological properties in different grassland soils (volcanic and non-volcanic soils). A 288-day laboratory experiment was carried out, monitoring CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emissions and evaluating total C, soil pH, microbial biomass and enzymatic activity in three grassland soils. The results varied depending on the soil type and feedstock of BC produced. BC-cow decreased emissions of CO<sub>2</sub> and CH<sub>4</sub> fluxes for volcanic and non-volcanic soils, probably due to decreases in  $\beta$ -glucosidase activity. Biochars from cow and pig manures increased soil C content, favouring the persistence of C into the soil at 288-days of incubation. Soil pH increased with the application of BC in the soils.

**Keywords:** Greenhouse gases; Biochar; Farm wastes; Microbial biomass; Total Carbon

#### **1. Introduction**

Soil organic carbon is a key factor that influences both crop productivity and soil functions. However, its role in the mitigation of greenhouse gas emissions has not been fully determined. C-sequestration refers to an increase in soil organic C content caused by a change in land use or management, which can help to mitigate GHG emissions. Paustian et al. [1] have indicated that the potential for climate change mitigation requires the implementation of innovative strategies involving local knowledge to abate GHG emissions.

An alternative to increase soil organic C is through farm wastes or exogenous organic matter (e.g., slurry, manure and others). An alternative fate of the residue needs to be accounted as net transfer of C from the atmosphere to the soil; the repeated application of exogenous organic matter has been shown to increase soil organic C over time but the increase tends to level off as soil organic C content increases [2]. However, these farm wastes tend to have an important fraction of labile C, which rapidly mineralizes in the first time of decomposition (registered as CO<sub>2</sub> emissions). Therefore, rapidly mineralizable organic materials with less content of C could be a better alternative to increase net C-sequestration and reduce GHG emissions.

Biochar from organic wastes produces a C-rich product, which is chemically and biologically more stable than its original C sources, deliberately applied into the soil with the purpose of improving soil properties [3]. In this sense, DeLuca et al. [4] compiled diverse studies where show the capacity of BCs to modified soil nutrient transformation as ammonification and nitrification, availability of phosphorous and sulphur. Van Zwieten et al. [5] used BC from papermill waste and determined change in diverse soil properties as increases in soil pH, CEC and total C, likewise a decrease in Aluminium availability in a Ferrosol. Another interest way to understand the contribution of BC modifying soil properties is according to study of Houben et al. [6] and Li et al. [7] who used BC produced from a Si (silicon)-accumulator plant (*Miscanthus*), demonstrating that BC- Si enriched supplied Si bioavailable and promote the Si biological cycle. On the other hand, changes in soil physical properties have been evaluated with the use of BCs, Laird et al. [8] demonstrate that BC from lignocellulosic materials reduced bulk density and increase water holding capacity (WHC) among other parameters, increasing the soil quality; however, Masiello et al. [9] shown different and contrasting results respect the WHC response until BC application, depending of soil type.

In terms of C accumulation in soils, Lehmann et al. [10] compiled diverse studies that evaluated the persistence of BC in soils, reporting variations between 6-4419 years of mean residence time of BC due to a wide variety of pyrogenic organic materials evaluated in different experiments and conditions.

Persistence is relevant for the framework of BC use for environmental management.

Different studies have reported variations in GHG emission due to BC applications [11–18]; Pokharel et al. [19] have indicated that the reduction of GHG emissions from forests and grassland soils resulted from a decrease in the extracellular soil enzyme activities and microbial biomass with the addition of pine sawdust BC. However, meta-analyses show variable results respect to soil GHG emissions, where diverse factors as length of experimental studies, BC properties and application rate, soil texture and crop fertilization vary the response of soils at BC application [20,21]. For that, are necessary more studies over diverse soils (including volcanic soils) and climate conditions to reduce uncertainly for estimate GHG emissions and consider at BC as an alternative to reduce the global impact of agriculture on climate change.

Chile has a north-south climatic gradient (precipitation and temperature) with cooler and wetter regions in the south, which has a strong influence on the soil organic C distribution all across the country. Padarian et al. [22] generated a map with the spatial distribution of soil C for Chile, determining an increase in the north-south gradient; and highlighting the relevance of volcanic soils (Andosols) in increasing soil organic C content. It is important to note that 50-60% of soils with agronomic potential in Chile are of volcanic origin; mainly distributed in Mediterranean and temperate oceanic climate conditions [23]. The climatic and geochemical factors have a key role in C-stabilization in these soils [24]. However, as described by Muñoz et al. [25] these soils are more sensitive to temperature, with a high potential for C mineralization increase with increases in environmental temperature. This is relevant information to consider in the current scenario of climate change.

## **2. Materials and Methods**

### **2.1. Soils**

The studied soils correspond to grassland soils of Central-South Chile and these correspond to three soil orders and classified by Stolpe [26]. The soils were named by their respective soil series: Bulnes soil is developed on fine

alluvial sedimentary materials, classified as thermic duric Argixerolls of the Mediterranean Humid climate zone, located in the Ñuble Region (36°340S, 72°060W); Cauquenes soil is an Alfisol developed on granitic material, classified as Ultic Palexeralfs under Mediterranean arid climate, it is located in the Cauquenes Province (Maule Region; coordinates 35°570S, 72°190W); and Collipulli soil is developed on ancient volcanic ash, classified as Mesic Xeric Paleumults, this soil is localized in Araucanía Region (37°570S 72°260W), south of Chile. Climatic data and soil properties of the sites are shown in Tables 1 and 2. The top 0.10 m of soils were collected in triplicates during autumn 2016, having 20 subsamples for each soil sample.

**Table 1.** Soils characterization.(**Source:** Own elaboration)

Soils	Climate	Soil Taxonomy	Parental material	Clay content (%)
Bulnes	Mediterranean humid	Thermic Duric Argixerolls <sup>1</sup>	Ancient volcanic ash, devolved on a fluvio glacial substrate, highly decomposed, with the presence of grave. <sup>1</sup>	29.2
Cauquenes	Mediterranean arid	Fine, mixed, active, mesic, Ultic Palexeralfs <sup>1</sup>	Granite and/or granodiorite <sup>1</sup>	39.0
Collipulli	Mediterranean humid	Very fine, halloysitic, mesic Xeric Paleumults <sup>1</sup>	Old ash volcanic <sup>1</sup>	45.7

<sup>1</sup>Stolpe [26]

**Table 2.** Soils characterization. (**Source:** Own elaboration)

Soils	Total C (%)	Total N (%)	pH	SB (cmol kg <sup>-1</sup> ) <sup>1</sup>	Olsen P (mg kg <sup>-1</sup> )	Al sat. (%) <sup>2</sup>
Bulnes	2.84	0.25	5.4	7.93	7.4	0.07
Cauquenes	1.45	0.13	5.7	3.93	3.9	0.14
Collipulli	2.80	0.17	5.4	8.51	21	1.05

<sup>1</sup> Sum of bases; <sup>2</sup>Aluminum saturation

## **2.2. Feedstock**

Farm wastes were obtained from local farms of the Biobío and Ñuble regions of Chile; these consisted of: (a) chicken manure, (b) cow manure and (c) pig manure. The material was collected once in November of 2016, approximately 100 kg per each one (wet weight basis). The waste material was air-dried at ambient temperature for 2 weeks, stirred periodically to homogenize and sieved at 5 mm. Subsequently, the material was oven dried at 60 °C to reduce water content to less than 20%.

## **2.3. Pyrolysis Process**

Slow pyrolysis process with highest heating temperature of 500 °C (during 2 h) was applied for farm wastes, the final yield of chicken, pig and cow manure was 82%, 42% and 41%, respectively. The gases produced through the pyrolysis process were trapped using a condenser and an electrostatic precipitator. It was produced 3 types of BC according with feedstock: BC-chicken, BC-cow and BC-pig. The BC produced was sieved through a 250 µm mesh and kept at ambient temperature in desiccators until used.

## **2.4. Chemical and Physical Characterization of Dry Manure and BCs**

Total C and N of feedstock were analysed by dry combustion in an elemental analyser (Truspec CN, LECO, St. Joseph, MI, USA). The elemental C, N, H compositions of BCs were done (Elementar Analysensysteme GmbH, Hanau, Germany). Inorganic C of BCs was done by titrimetric method [27,28]. The organic C ( $C_{org}$ ) of BC was then estimated by difference between total C minus inorganic C [29]. The pH and contents of nitrate, ammonium, available phosphorus and potassium content were analysed according to protocols for compost [30]. The chemical and physical properties of the different feedstocks and BCs produced are showed in Table 3.

**Table 3.** Characterization of feedstocks and BCs. (Source: Own elaboration)

Materials	Total C (%)	Total N (%)	C/N ratio	C <sub>org</sub>	H/C <sub>org</sub> ratio <sup>1</sup>	pH	Nitrate (mg kg <sup>-1</sup> )	Ammonium (mg kg <sup>-1</sup> )	Total P (%)	Total K (%)
Chicken manure	16.2	1.2	14	--	--	8.7	612.9	157.3	4.83	1.37
Pig manure	40.7	1.8	23	--	--	7.39	134	1739.1	2.33	1.09
Cow manure	40.5	1.2	34	--	--	8.21	47.3	101.4	0.43	0.6
BC-chicken	11.5	0.6	19	6.84	0.07	10.5	2.27	9.6	2.26	1.34
BC-pig	43.6	1.8	24	42.28	0.32	10.0	2.07	2.9	2.05	2.27
BC-cow	38.0	1.4	27	36.96	0.28	10.7	3.53	5.1	0.39	1.14

<sup>1</sup> Molar H/C<sub>org</sub> ratio.

## 2.5. Incubation Experiments

The assay consisted of incubations of soil mixed with the BC produced at 20 °C [31,32]. An amount of 25 g of soil mixed with BC at a dose of 1% (1g BC per 100 g soil; [33]) was placed into 50-mL Falcon tubes with rubber septum caps by gas sampling (in triplicates). Distilled water was added to the tubes to increase moisture content of the mixture to 60% of water filled pore space (WFPS) for each soil. Simultaneously, an incubation experiment was conducted under the same conditions of temperature and water content, using the same soils but without BC as blanks. Soil samples were pre-incubated for 7–10 days and then rehydrated as needed during 288-days (10 months approximately) in order to maintain soil water content constant. Considering the bulk densities of the different soils, the BC application rates used corresponded to 13, 14.5 and 14.2 t BC ha<sup>-1</sup> for Bulnes, Cauquenes and Collipulli soils, respectively.

## 2.6. Gas Emissions Measurement

The CO<sub>2</sub> emissions were analysed by infra-red spectroscopy using a CO<sub>2</sub> gas analyser (Li-820, LI-COR Bioscience, Shelton, CT, USA) at days 3, 5, 7, 15, 25, 35, 45 and 55 after the start of the incubation and then twice a month until day 288 of incubation. The analyses of CH<sub>4</sub> and N<sub>2</sub>O were performed using gas chromatography; an aliquot of 2–5 mL of gas was extracted from the headspace of each incubation tube and gases were analysed in a gas chromatograph

(Perkin Elmer model Clarus 600, Akron, OH, USA) equipped with FID and ECD detectors.

Data of the gases obtained at each time interval were then analysed by linear interpolation, following the model of  $y = \alpha x + \beta$ , where  $y$  is the day-emission estimated,  $x$  the days,  $\alpha$  the ratio of change between two consecutive periods of time (Equation (1)) and  $\beta$  corresponds at the  $y$ -intercept (Equation (2)); obtaining a fit model; where  $(x_1, y_1)$  and  $(x_2, y_2)$  represent two different time periods. The cumulative gas emission was obtained through the sum of gas emission obtained between two consecutive dates for each time period during the whole incubation.

$$\alpha = \frac{Y_2 - Y_1}{X_2 - X_1} \quad \beta = Y_1 - \alpha X_1$$

To convert the total gas emission obtained at 288-days to CO<sub>2</sub>-eq, the following global warming potentials (GWP) were used: 1, 21 and 310 for CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O, respectively, considering a timeframe of 100 years [34]. The results were extrapolated to 365 days and expressed in kg CO<sub>2</sub>-eq ha<sup>-1</sup> y<sup>-1</sup>.

## 2.7. Soil Organic Carbon Content

Soil organic C content was analysed in the soil samples incubated, considering three incubation phases: early, middle (4 months) and late (10 months). The analysis was made by dry combustion in a CN analyser (Truspec CN, LECO, USA). C stock was converted using the bulk density values of 1.30; 1.45 and 1.42 t m<sup>-3</sup> for Bulnes, Cauquenes and Collipulli, respectively.

## 2.8. Biological Parameters

Microbial biomass was determined using fluorescein diacetate (FDA) hydrolysis [35]; the production of fluoresce in hydrolysed from FDA was evaluated. Absorbance was determined using a UV/VIS spectrophotometer (Thermo Spectronic model Genesys TM 5, Vernon Hills, IL, USA) at 490 nm. In addition, urease activity was determined using a colorimetric method based on the ammonia released [36] after incubating the samples at 37 °C for two hours.  $\beta$ -glucosidase activity was determined according to the colorimetric method

proposed by Eivazi and Tabatabai [37], in which incubation is done at 37 °C for one hour in darkness. Both urease and  $\beta$ -glucosidase activities were determined at 636 nm and 400 nm, respectively, using a UV/VIS spectrophotometer (Thermo Spectronic model Genesys TM 5, USA).

## **2.9. Statistical Analysis**

Data were analysed using one-way analysis of variance for a completely randomized design, consisting of 3 soils x 4 treatments (BCs and controls) with 3 replicates per treatment ( $n = 3$ ). Shapiro Wilks modified [38] was used to verify normality of residuals. Duncan test was used to determine significant differences between treatments at  $p \leq 0.05$ . For the analysis of GHG emissions, only the cumulative emission over the whole experimental period (288 days of incubation) was considered. The data of  $N_2O$  and  $CH_4$  emissions were transformed with normal scores, prior to parametric analysis. Whole data set was used for Pearson correlation coefficient to obtain the correlation between two response variables with a p-value of 0.05. Statistical software Infostat version 2008 was used [39].

## **3. Results and Discussion**

### **3.1. GHG Emissions**

According to the European Biochar Certificate [3] and IBI guidelines [40], different properties allow us classify a product as BC. In this study, the BC-cow and BC-pig have  $C_{org}$  content upper than 30% and a molar  $H/C_{org}$  ratio lesser than 0.7 (Table 3), performing both materials with the classification as BC. BC-chicken has lesser  $C_{org}$  content (6.84%) and it is not considered as BC according to both guidelines; knowing this fact, we will consider this treatment as carbonaceous material and it continues named as BC-chicken for this study to simplify comparisons and discussion between treatments. However, Song and Guo [41] studied the variation in the quality of BC produced from poultry litter under different temperature of pyrolysis, having in all cases higher total C and  $C_{org}$  content that on our study, despite that in this study the temperature pyrolysis used was the same that they recommended (500 °C). Even so, this material (BC-chicken) has a higher ammonium content (9.6 mg  $kg^{-1}$ ; Table 3),



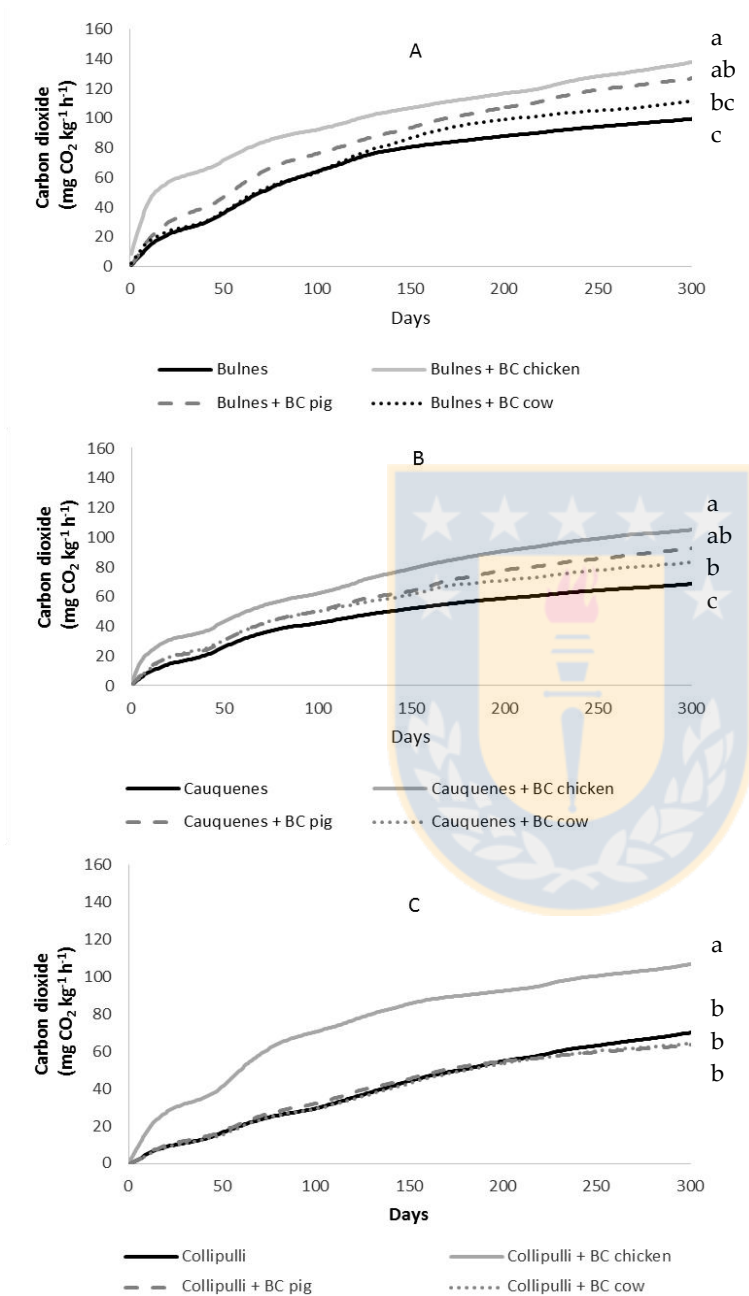
which may account for its higher response in microbial activity, expressed in terms of CO<sub>2</sub> emissions (Figure 1) and lower C/N ratio (C/N =19; Table 3).

The C concentration in BC-cow was higher than the other BCs; the lowest values were obtained with BC-chicken (11.5%; Table 3). The cumulative evolution of CO<sub>2</sub> in soils is shown in Figure 1A–C. After 288-days of incubation, the soils with BC showed an increase of CO<sub>2</sub> emission respect to the control in Bulnes and Cauquenes soils (Figure 1A,B); BC-chicken did not have statistical difference with BC-pig, with an average of cumulative CO<sub>2</sub> emissions of 130 mg CO<sub>2</sub> kg soil<sup>-1</sup> h<sup>-1</sup> for Bulnes soil and 97 mg CO<sub>2</sub> kg soil<sup>-1</sup> h<sup>-1</sup> for Cauquenes soil. However, BC-chicken was statistically higher (25% higher) than BC-cow for both soils. In Collipulli soil (Figure 1C), BC-pig and BC-cow had similar results to the control soil, whereas BC-chicken presented higher cumulative CO<sub>2</sub> emissions (53%) than other treatments. In all soils, the highest CO<sub>2</sub> emissions were produced the first 20 days and then decreased considerably, maintaining a CO<sub>2</sub> flux relatively stable after this period.

Similarly, the application of BC at different soils resulted in an increase in C concentration from early to late incubation (288-days of incubation; Table 4) in treatments of BC-cow and BC-pig but lesser increase in C concentration in soils was obtained with BC-chicken. The persistence of the soil C increase obtained after time of incubation is probably due to the type of C contained in BCs, which are mainly aromatic C-types [42].

The CO<sub>2</sub> emissions monitoring during 288-days of incubation showed a marked effect of type of feedstock used. In general, BC-chicken presented higher CO<sub>2</sub> emissions in the three soils under study, comparing with BC-cow and BC-pig. Similarly, Šlapáková et al. [43] show not effect on soil respiration in soils amended with a BC of digestate from *Zea mays* (80%) and cellulose fibre (20%) in two soils incubated during 1-year. On the other hand, the higher levels of CO<sub>2</sub> emissions obtained from BC-chicken could be produced by the release of carbonates contained in the BC which could be higher in acidic soils according to Sheng and Zhu [44], who reported higher CO<sub>2</sub> emissions from an acidic Ferrasols (pH 5.19) rather than Phaeozems (pH 7.81). It is important to note that this study was done under aerobic conditions (60% WFPS); because of this,

the potential N<sub>2</sub>O and CH<sub>4</sub> emissions are not evaluated since both processes are predominant under anaerobic conditions [45]. However, other studies have described a lesser-known way of non-microbial CH<sub>4</sub> production from aerobic soils [46,47].

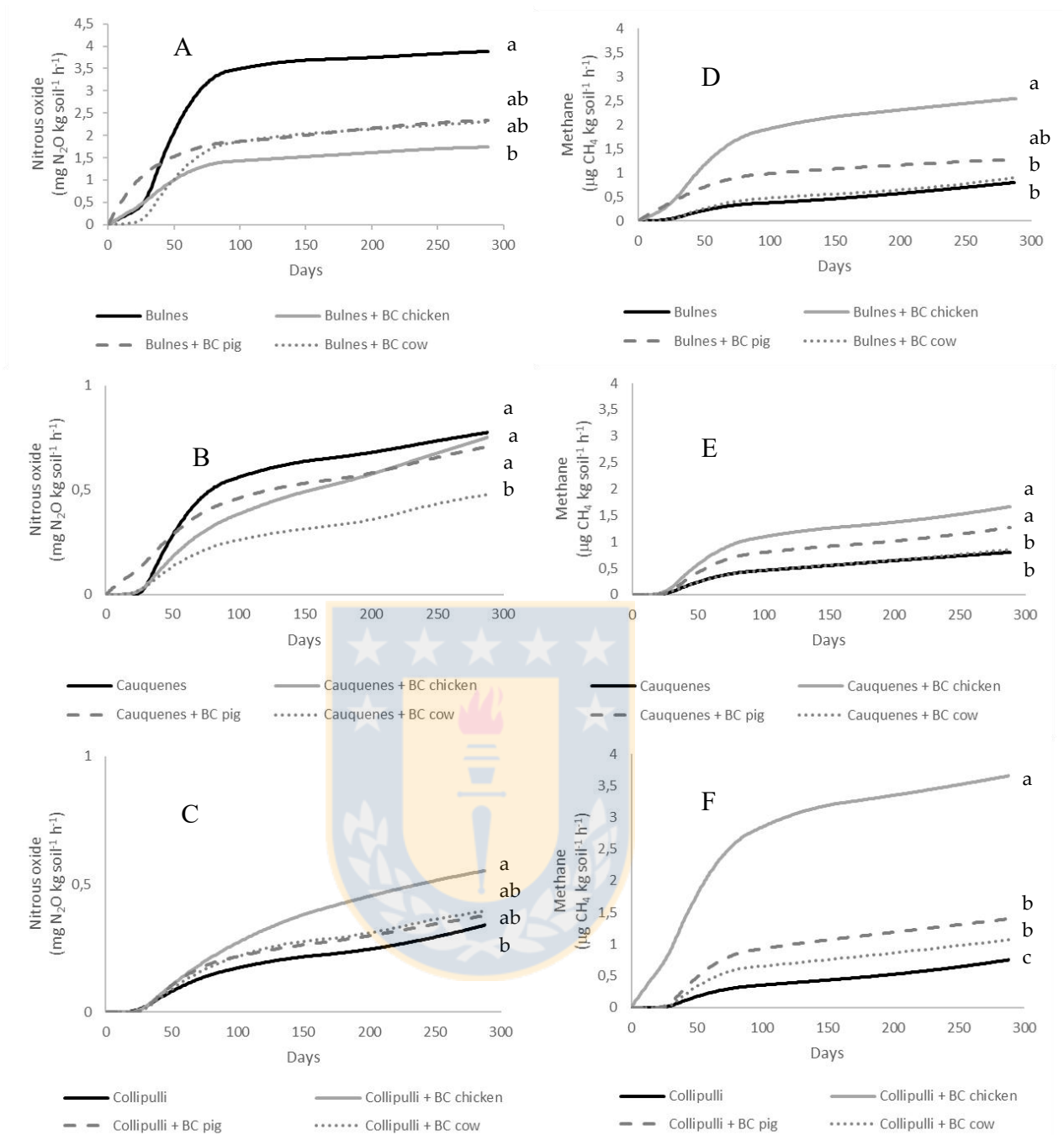


**Figure 1.** Cumulative carbon dioxide fluxes (mg CO<sub>2</sub> kg<sup>-1</sup> h<sup>-1</sup>) in soils with BC application (Different small case letters means statistical difference by Duncan at  $p \leq 0.05$ ). **Source:** Own elaboration

The cumulative N<sub>2</sub>O emissions from soils are showed in Figure 2A–C. The results show that all treatments resulted in decreased N<sub>2</sub>O emissions in Bulnes soil (Figure 2A), showing statistical differences ( $p \leq 0.05$ ) respect to BC-chicken (55% less). In Cauquenes soil (Figure 2B), the emissions obtained from BC-chicken and BC-pig were similar to the control but BC-cow reduced N<sub>2</sub>O emissions by 38%. A different response was obtained in Collipulli soil (Figure 2C), where BC-chicken increased emissions by 62%. It is important to note that Cauquenes and Collipulli soils presented considerably lower N<sub>2</sub>O emissions compared to Bulnes soil (see different scales in Figure 2A–C), with maximum values of 3.9, 0.77 and 0.34 mg N<sub>2</sub>O kg soil<sup>-1</sup> h<sup>-1</sup> in the control soils for Bulnes, Cauquenes and Collipulli, respectively.

Emissions of N<sub>2</sub>O from soils depend on diverse factors such as soil water content, level of oxygen, soil pore space, sulphur and organic matter content, among other factors [48]. In agricultural soils, addition of organic residues [49] and nitrogen fertilization [50,51] produce relevant flush of N<sub>2</sub>O emissions to the atmosphere, mainly in the first days after application of fertilizers [52]. In the case of BCs, it has been acknowledged that thermic decomposition produce the stabilization of C-materials and the volatilization of labile forms of nutrients, for example, nitrogen loss with increased pyrolysis temperature due to the volatilization of organic matter, resulting in a reduction of half of their N at 400 °C [53]. BC-chicken has narrow C/N ratio (Table 3) in comparison to BC-cow (value of 36), which shows that in BC-chicken more labile organic compounds remain in its structure; this was evidenced with the high denitrifying activity at early incubation (see first 35 days of incubation in Figure 2A,B).

Cumulative CH<sub>4</sub> fluxes are shown in Figure 2D–F. Unlike N<sub>2</sub>O emissions, most BC treatments produced higher emissions than the control soils. In BC-chicken in Bulnes soil (Figure 2D), CH<sub>4</sub> emissions were 3-fold greater than the control soil. Similarly, emissions resulting from BC-chicken and BC-pig were 2-fold higher than the control in Cauquenes soil (Figure 2E). A similar response was observed with the application of BC-chicken to Collipulli soil (Figure 2F) and resulted in a 2-fold increase in CH<sub>4</sub> emissions compared to the control soil; in this sense, the results showed that BC-chicken > BC-pig = BC-cow > control.



**Figure 2.** Cumulative nitrous oxide (mg N<sub>2</sub>O kg<sup>-1</sup> h<sup>-1</sup>; A–C) and methane (mg CH<sub>4</sub> kg<sup>-1</sup> h<sup>-1</sup>; D–F) in soils with BC application (Different small case letters means statistical difference by Duncan at  $p \leq 0.05$ ). **Source:** Own elaboration

In the case of cumulative CH<sub>4</sub> emissions, BC-chicken and BC-pig presented higher emissions than the control soils; BC-chicken produced higher emissions in three soils, indicating that methanogen activity increased with the addition of this type of BC. The literature describes variable results respect to the effect of

BC on methanogenic/methanotrophic microorganisms. However, Jeffery et al. [54] conducted a meta-analysis in soils with acid pH and determined that the application of BC increased pH, as well as sink and source processes of CH<sub>4</sub>. However, methanotrophic microorganisms may be more sensible to increases of soil pH and thus the effect of BC on acid soils (pH < 6) tends to mitigate CH<sub>4</sub> emissions. Conversely, emissions tend to increase in soils with pH between 6 and 8. In our study, CH<sub>4</sub> emissions increased with BC (except BC-cow in Bulnes and Cauquenes soils; Figure 2D,E) but cumulative CH<sub>4</sub> emissions were positively correlated to soil pH (Pearson's correlation = 0.50 at p ≤ 0.05); CH<sub>4</sub> fluxes increased in the soils that presented increasing soil pH, particularly with application of BC-chicken; where pH increased from 5.18 to 6.3 in Bulnes soil and from 5.33 to 7.06 in Cauquenes soil. Additionally, He et al. [55] showed the relevance of particle-size BC in response to CH<sub>4</sub> emissions from aerobic composting, indicating that fine material (diameter < 1 cm) increased CH<sub>4</sub> emissions by 58.8%; but materials with higher particle-size (4 mm to 1 cm) reduced the emissions of this gas. This could partly explain our results as the BC used was previously sieved at 250 μm to guarantee a complete incorporation with soil into experimental mesocosm; this particle-size probably had lower pore connectivity and aeration, favoring anaerobic spaces that increase the methanogenic activity. Respect to particle-size of biochar, Genesio et al. [56] indicate that particles smaller than 2.5 μm of black C could cause a positive radiative forcing when is transport to high altitudes (direct) or is deposited over ice or snow (indirect); for that in the production and others forms of manipulation the release of fine particles of BCs should be avoided, in this sense, Maienza et al. [57] studied the impact of pellet and non-pellet formulations.

### **3.2. Soil Carbon Content and CO<sub>2</sub> -eq**

Soil C concentration (Table 4) varied under different BC treatments compared to the control. At early incubation, the incorporation of BC increased the C concentration in all soils, particularly with BC-cow and BC-pig. No statistical differences were found between BC-chicken and the control. At 4 months, fewer differences were found between treatments; however, the soils with BC-pig and BC-cow were higher in most of the cases. At late incubation (288-days), all BC

treatments in Bulnes soil resulted in higher C concentration compared to the control. In Cauquenes and Collipulli soils, BC-pig and BC-cow were statistically higher than the rest of the treatments. By quantifying these differences as C stock (Table 4), BC-pig and cow resulted in increases of 5, 6 and 8 t C per hectare in Bulnes, Cauquenes and Collipulli soils, respectively.

**Table 4.** Variation of total C in treatments during incubation period; C stock in the top 0.10 m of soil and CO<sub>2</sub>-eq after 288-days of incubation. (Source: Own elaboration)

Treatments		Time of incubation (months)			C stock (t ha <sup>-1</sup> )	CO <sub>2</sub> -eq (kg ha <sup>-1</sup> y <sup>-1</sup> )
		0	4	10		
Bulnes	Control	2.84b	2.66c	2.72c	35.36	2144.93a
	+ BC-chicken	2.91b	2.80bc	2.66d	34.52	1110.69a
	+ BC-pig	3.27ab	3.26a	3.16a	41.08	1398.52a
	+ BC-cow	3.41a	3.23ab	3.08b	40.04	1357.63a
Cauquenes	Control	1.45b	1.51b	1.39b	20.16	565.15ab
	+ BC-chicken	1.60ab	1.56b	1.52ab	22.04	618.07a
	+ BC-pig	1.97a	1.83ab	1.81a	26.25	569.97a
	+ BC-cow	1.99a	2.06a	1.81a	26.25	422.49b
Collipulli	Control	2.80b	2.33b	2.57b	36.49	312.87b
	+ BC-chicken	2.91b	2.79ab	2.66b	37.70	497.36a
	+ BC-pig	3.27a	3.25a	3.11a	44.09	323.14b
	+ BC-cow	3.31a	3.23ab	3.15a	44.66	333.92b

Different small case letters mean statistical difference by Duncan at  $p \leq 0.05$ .

CO<sub>2</sub>-eq allowed quantify differences between treatments considering GHG emissions produced. In Bulnes and Cauquenes soils, none of the treatments were different from the control soils, with an average of 1503 and 544 kg CO<sub>2</sub>-eq ha<sup>-1</sup> y<sup>-1</sup>, respectively. For Collipulli soil, BC-chicken resulted in higher emissions of 497 kg CO<sub>2</sub>-eq ha<sup>-1</sup> y<sup>-1</sup>; no statistical differences were found between the other treatments and the control soil.

Our results demonstrate that both BC-pig and BC-cow are an adequate alternative to increase soil C content with a low increase in CO<sub>2</sub> fluxes, which in turn provide promising results to reduce the C footprint for pig and cow farms. Similarly, Gascó et al. [13] evaluated the incorporation of BC-pig with a dose of 8% in a Cambisols with sandy loam texture and reported higher levels of CO<sub>2</sub> emissions than the control treatment (without BC) but lower than those obtained from pig manure in an incubation of 219-days. In addition, Troy et al. [17]

applied BC from pig manure in an Acid Brown Earth (equivalent doses of 18 t ha<sup>-1</sup>), producing lesser CO<sub>2</sub> fluxes respect to feedstock; having less than 1% the C of the BC mineralized during short-term experiment (28-days).

### 3.3. pH

The pH of soils increased with the application of BC in all soils and treatments (Table 5). BC-chicken was the treatment that recorded the highest increases of 1.12, 1.73 and 0.77 units of pH for Bulnes, Cauquenes and Collipulli respectively. In this sense, BC treatments behaved as follows: BC-chicken > BC-pig > BC-cow.

The application of all BCs produced a pH increase that averaged  $0.9 \pm 0.5$  units, which is relevant for acid soils. This increase was variable depending on the type of soil (Table 5); Collipulli soil (an Ultisol) presented a higher increase that reached +1.7 units of pH. Soil pH is a relevant factor that determines soil biological processes, where the biological activity could be increased or decreased depending of soil pH. In terms of denitrification activity, alkaline soil pH resulted in a higher reduction of N<sub>2</sub>O to N<sub>2</sub> and inhibition of this process in acidic soils, increasing N<sub>2</sub>O emissions [33]. In this sense, Van Zwieten et al. [58] indicated that the liming effect of BC in acidic soils decrease N<sub>2</sub>O /N<sub>2</sub> ratio under flooded soil, favouring the dinitrogen formation. However, Wu et al. [8] have indicated that the potential of alkaline BCs to mitigate N<sub>2</sub>O emissions in acidic soils are dependent on soil nitrate content, because higher N<sub>2</sub>O emissions are produced in a time period when soil nitrate was high, decreasing significantly in periods with lower nitrate content soil. In our study, there was an inverse Pearson correlation ( $-0.57$  at  $p \leq 0.05$ ; Table 6) between soil pH and N<sub>2</sub>O emissions, indicating lower N<sub>2</sub>O emissions with increases of soil pH. This fact was particularly observed in Bulnes and Cauquenes soils as N<sub>2</sub>O emissions decreased with the application of BC-chicken and BC-cow, respectively (Figure 2A,B).

**Table 5.** Changes in chemical and biological soil parameters after 288-days of incubation. (**Source:** Own elaboration)

Treatments		pH	Microbial biomass	B-glucosidase	Urease activity
			( $\mu\text{g}$ fluorescein $\text{g}$ dry soil $^{-1}$ )	( $\mu\text{mol}$ PNF $\text{g}$ dry soil $^{-1}$ $\text{h}^{-1}$ )	( $\mu\text{g}$ N-NH $_3$ $\text{g}^{-1}$ $\text{h}^{-1}$ )
Bulnes	Control	5.18d	9.13a	2.11a	47.20a
	+ BC-chicken	6.30a	6.45c	1.44b	43.05b
	+ BC-pig	6.02b	7.12bc	1.57b	30.64c
	+ BC-cow	5.35c	7.95b	1.27c	23.21d
Cauquenes	Control	5.33d	3.70a	2.16a	15.75c
	+ BC-chicken	7.06a	3.16a	1.49bc	19.94b
	+ BC-pig	6.79b	3.11a	1.55b	25.18a
	+ BC-cow	6.33c	3.18a	1.35c	21.40b
Collipulli	Control	5.94c	4.58b	1.15a	6.24c
	+ BC-chicken	6.71a	4.69b	0.75b	6.22c
	+ BC-pig	6.56a	9.33a	1.12a	14.69a
	+ BC-cow	6.37b	8.02a	0.88b	13.24b

Different small case letters means statistical difference by Duncan at  $p \leq 0.05$ .

### 3.4. Microbial Biomass and Enzymatic Activity

No statistical differences were found in the microbial biomass between treatments in Cauquenes soil. However, the other soils had a different behaviour, for example, Bulnes soil (control) presented higher microbial biomass compared to the BCs treatments, reaching values 13% higher than BC-cow and 26% higher than the other BCs. On the contrary, Collipulli soil with BC-cow and BC-pig presented more microbial biomass than the control soil but levels obtained with the BC-chicken were similar.

In the case of  $\beta$ -glucosidase activity, BCs reduced the activity of this enzyme between 24 and 40% in all soils, except for BC-pig in Collipuli soil. Regarding urease activity, BCs reduced the activity in this enzyme in Bulnes soil, particularly with BC-cow (51% decrease). However, there was an increase in the urease activity with the application of BCs in Cauquenes and Collipulli soils. In fact, BC-pig increased the urease activity between 60 and 135%.

Almost all BCs applied produced a decrease in  $\beta$ -glucosidase activity in the three studied soils (Table 5), decreasing until 35-39% respect to the control soils; which probably affected the C-degradation and the low CO $_2$  emissions



obtained in BC-cow and BC-pig (Figure 2). Similarly, Pokharel et al. [19] find that the application of pine sawdust BC in forest soil affect  $\beta$ -glucosidase after 10 days of incubation (26–35%), while the effect was evidenced at 50 days of incubation in a grassland soil. The effect on  $\beta$ -glucosidase activity could be explained by the high capacity of BCs to adsorb substrates, reducing the availability of soluble substrate for enzymes. For instance, Lammirato et al. [59] determined that  $\beta$ -glucosidase activity decreased by 30% probably due to the application of chestnut wood char, hypothesizing that adsorption is produced by non-coulombic forces between uncharged regions of both proteins and char; similarly Teutscherova et al. [60] applied BC from holm oak pruning residues in two contrasting soils, where the  $\beta$ -glucosidase activity not vary in a Calcisol but decreased in an Acrisol with BC application, suggesting that mechanisms of adsorption onto BC surface could affect the response the soils. Therefore, soils amended with charred materials could reduce the organic matter degradation rate, stabilizing nutrients and enhancing soil fertility [59]. On the other hand, changes in soil microbial community have been reported with the application of BCs to soils. Shen and Zhu [44] reported a shift in microbial community composition due to the liming effect produced by BC; higher BC doses led to higher soil pH and bacterial diversity, increasing copiotrophic phylum and decreasing abundance of Acidobacteria after the addition of BC obtained from rice straw.

### **3.5. Relation Between Parameters**

Pearson correlation coefficients are shown in Table 6. GHG emissions are correlated with different soil parameters. CO<sub>2</sub> emissions have a positive Pearson correlation coefficient (r value) with total N (0.59) and urease activity (0.59). N<sub>2</sub>O emissions have a positive correlation with total N (0.72), microbial biomass (0.49),  $\beta$ -glucosidase (0.52) and urease (0.73) but a negative correlation with soil pH (−0.57). In addition, CH<sub>4</sub> emissions present a positive r value with soil pH (0.50) but a negative correlation with  $\beta$ -glucosidase activity (−0.43).

**Table 6.** Pearson coefficient correlation between the parameters studied.  
(Source: Own elaboration)

Parameter	CO <sub>2</sub>	N <sub>2</sub> O	CH <sub>4</sub>	pH	Total C	Total N	MB <sup>1</sup>	β-glu. <sup>2</sup>	Urease <sup>3</sup>
CO <sub>2</sub>	1.00								
N <sub>2</sub> O	0.52*	1.00							
CH <sub>4</sub>	0.43*	-0.10	1.00						
pH	0.01	-0.57*	0.50*	1.00					
Total C	0.16	0.30	0.10	-0.18	1.00				
Total N	0.59*	0.72*	0.10	-0.40*	0.78*	1.00			
MB**	0.04	0.49*	-0.12	-0.38*	0.83*	0.77*	1.00		
β-glu.	0.11	0.52*	-0.43*	-0.54*	-0.44*	0.06	-0.06	1.00	
Urease	0.59*	0.73*	-0.10	-0.33*	0.09	0.65*	0.32*	0.60*	1.00

\* Asterisk indicates statistical significance at  $p \leq 0.05$ . <sup>1</sup> Microbial biomass <sup>2</sup> β-glucosidase activity <sup>3</sup> Urease activity

#### 4. Conclusions

Biochar applied into soils had a strong impact on diverse soil chemical and biological properties and, consequently, on the fluxes of greenhouse gases. The response in greenhouse emissions varied depending on feedstock and soil type. Biochar produced from cow manure decreased emissions of CO<sub>2</sub> and CH<sub>4</sub> fluxes for volcanic and non-volcanic soils, probably due to decreases in β-glucosidase activity. Biochars from cow and pig manures increased soil C content, favouring the persistence of C into the soil after 288-days of incubation. Soil pH increased with the application of biochar into the soils, which is relevant for agricultural areas with problems related to acid soils.

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### CAPÍTULO III

**Title: Biochar impacts on soil chemical properties, greenhouse gas emissions and forage productivity: A field experiment** (publicado en Science of the Total Environment , 25/09/2021)

#### **Abstract**

Biochar is a promising alternative to agricultural productivity and climate change mitigation. However, quantitative data are needed to better understand the productivity and greenhouse gas (GHG) emissions from agricultural fields amended with biochar. To assess the impacts of the four biochars on soil properties, forage productivity, and GHG emissions, a 1-year field experiment was conducted in a Humic Haploxerands (Andisol). Three manure-derived biochars and one wood residue biochar (all pyrolyzed at 550°C) were applied at rates of 1% (equivalent to 11 t ha<sup>-1</sup>) in two parallel and independent experiments. The changes in (i) soil chemical properties and yield of *Sorghum sudangrass* (*S. bicolor* × *S. bicolor* var. Sudanese) and (ii) soil CO<sub>2</sub> and N<sub>2</sub>O emissions were monitored. Two controls, with and without NPK, were included. The added amendments produced from residues of poultry and pig systems increased soil pH by 0.73 and 0.19 units, respectively. Increased sorghum yield were associated with fertilizer and the liming potential of the added biochar. Soil total carbon (TC) increased with the addition of different biochars, especially during the wood biochar treatment. Biochar application, regardless of the feedstock, had no significant impact on the cumulative soil CO<sub>2</sub> emitted after a year. Soil N<sub>2</sub>O fluxes decreased (23%–50%) in treatments containing biochars with low mineral N contents and high C stability (i.e., low H:OC and Cox:TC ratios). NPK treatment resulted in the highest N<sub>2</sub>O emissions. Wood residue–derived biochar has a great potential in mitigating climate change, reducing soil N<sub>2</sub>O emissions, and promoting soil C storage. Manure-derived biochars could be instrumental in circular economy livestock systems, where pyrolyzed animal manure can satisfy the demand for nutrients and/or liming of Andisols under sustainable forage models.

## **1. Introduction**

The use of biochar as a soil amendment has been a subject of research in the last two decades (Jeffery et al., 2015; Lehmann et al., 2015). Biochar is a material produced by the pyrolysis of different feedstocks, including forest or animal wastes, which are applied to soils to improve their properties (e.g., pH, nutrient content, water holding capacity, and C sequestration)(Lehmann et al., 2015; Paustian et al., 2016). Multiple environmental co-benefits of biochar application onto soils include mitigation of greenhouse gas (GHG) emissions (Cayuela et al., 2014; Grutzmacher et al., 2018; Abagandura et al., 2019), and enhanced crop yields (Zhang et al., 2019; Wei et al., 2020; Ye et al., 2020).

Biochar properties mainly depend on the feedstock type and processing conditions (Calvelo Pereira et al., 2011; Hassan et al., 2020; Stylianou et al., 2020). Some biochars are rich in non-crystalline (amorphous) and mineral constituents, which originate from certain feedstock and/or materials mixed within the feedstock (Singh et al., 2010). These constituents significantly improve biochar alkalinity (Vassilev et al., 2013); therefore, under acidic soil conditions, biochar can be used as a liming agent, depending on its  $\text{CaCO}_3$  equivalent proportion ( $\text{CaCO}_3\text{-eq}$ ) (Camps-Arbestain et al., 2015; Singh et al., 2017a). Nonetheless, the pH response also depends on the soil buffering capacity (Camps-Arbestain et al., 2015; Garbuz et al., 2020).

Manure-derived biochars typically have a high liming potential and fertilizer value, and can provide nutrients such as P, K, Ca, and Mg to soil and plants (Wang et al., 2012a; Subedi et al., 2016; Camps-Arbestain et al., 2017). In contrast, mineral constituents are reportedly low in woody material-derived biochars, which contain a higher carbon content than the manure-derived biochars (Hassan et al., 2020).

The organic C content in soils is governed by the balance between C inputs and  $\text{CO}_2$  fluxes emitted during decomposition processes (Powlson et al., 2013; Lal, 2018). Although biochar can have a long residence time in the soil, it is not an inert material (Powlson et al., 2013; Lehmann et al., 2015) and its labile C fraction can be rapidly mineralized (Bruun et al., 2012). The increase in  $\text{CO}_2$  released after soil biochar addition can be influenced by the presence of



inorganic carbon (Maestrini et al., 2015), the relative stability of C in the pyrolyzed material (i.e., labile or oxidizable C vs. stable or non-oxidizable C) (Calvelo - Pereira et al., 2011; Cely et al., 2014), and by the C:N ratio of the added biochar. Grutzmacher et al. (2018) reported that chicken manure biochar (C:N <10) produced higher CO<sub>2</sub> emissions than eucalyptus wood biochar (C:N >100). The highest emission from chicken manure biochar-amended soil has also been associated with its carbonate content (Muñoz et al., 2019), and the CO<sub>2</sub> released from the carbonates is higher in acidic soils (Sheng and Zhu, 2018).

The addition of biochar to soils impacts the dynamics of soil organic matter (SOM). Herath et al. (2015) observed a negative priming effect (lower SOM mineralization) in an Alfisol amended with biochar; however, Andisol remained unaffected. This phenomenon is attributed to differences in the type of SOM, soil aggregation, and microbial communities.

The soils derived from volcanic materials account for approximately 0.84% of the world's land surface (approximately 124 million hectares) (Shoji et al., 1993), and over 60% of soils in Chile with agronomic potential have this origin (Besoain M, 1985). Andisols are characterized by highly-reactive soil mineral phase and low rates of respiration, promoting long-term C storage (Doetterl et al., 2015). However, chemical variations (such as increases in P availability and/or pH) can negatively affect the C stored in these soils (Shen et al., 2018b). Several studies have investigated the effect of biochar on volcanic soils (Herath et al., 2015; Koga et al., 2017; Muñoz et al., 2019; Yamamoto et al., 2019; Stylianou et al., 2020); however, to date, data on the effect of nutrient-rich biochars on soil C concentrations and crop productivity are limited.

The use of biochar as a soil amendment is a practical strategy for mitigating N<sub>2</sub>O emissions from agricultural soils (Cayuela et al., 2014; Van Zwieten et al., 2015). On average, a N<sub>2</sub>O emission reduction of 28 ± 16% has been reported in biochar-amended soils under field conditions (Cayuela et al., 2015). The effect of biochar on cumulative N<sub>2</sub>O emissions is highly variable and depends on (i) biochar production (feedstock and pyrolysis conditions); (ii) biochar inherent properties (C:N, H:OC ratios, liming effect, N content); and (iii) the pedo-climatic

environment that is exposed to the biochar (soil C and N content, pH, bulk density). Recently, Li et al. (2019) found via a meta-analysis that biochars with high mineral N contents (such as manure-derived biochars) can increase soil N<sub>2</sub>O emissions.

Biochar application to cropping systems can improve yield by improving soil pH, enhancing nutrient availability, and/or improving the water-holding capacity of the soil (Liu et al., 2013; Jeffery et al., 2011, 2017; Abbruzzini et al., 2019). Several meta-analyses have calculated the average increase in crop yield associated with biochar amendments, which ranged from 9% to 17% (Liu et al., 2013; Jeffery et al., 2011, 2015, 2017), particularly when nutrient-rich biochars are added to acidic soils that limit crop productivity (Jeffery et al., 2011; Ye et al., 2020). Garbuz et al. (2020) reported that even low-nutrient biochars have positive effects on plant productivity in volcanic soils, which is linked to changes in soil biological communities.

In summary, biochar has numerous potential positive effects (Gascó et al., 2016; Abagandura et al., 2019; Abbruzzini et al., 2019) but in several cases, it is impossible for all benefits to appear concurrently, which may also lead to trade-offs associated with different uses of biochar (Jeffery et al., 2015; Li et al., 2019; Zhang et al., 2019). Recently, in a lab-scale study, a biochar rate of 1% notably altered key soil properties, mitigating GHG emissions in volcanic and non-volcanic soils (Muñoz et al., 2019). However, a quantitative field data set that explains the contribution of manure-derived biochars and woody biochars towards climate change mitigation and productivity in Andisols is still lacking. Here, we hypothesized that *(a) soil CO<sub>2</sub> and N<sub>2</sub>O emissions in an Andisol vary according to the biochar characteristics (i.e., Cox: TC, C: N ratio, mineral N), with greater mitigation potential by adding wood-derived biochar, while manure-derived biochars are more efficient in increasing soil quality and productivity. Nonetheless, (b) certain biochar(s) at a rate of 1% can positively affect both dimensions (productivity and climate change mitigation).* Therefore, the aim of this study was to evaluate the effects of four different biochars on productivity, soil quality, and CO<sub>2</sub> and N<sub>2</sub>O emissions. We also determined if a 1% rate of certain biochar under field conditions can positively affect both dimensions

(productivity and climate change mitigation) in an Andisol. The quantitative data from this study can be useful to better understand the effects of biochar in Andisols on a field-scale.

## **2. Material and Methods**

### **2.1. Experimental site and soil description**

Two independent field experiments were established from October 2018 to October 2019 in the experimental station at the University of Concepción, located in Quinquihua, Ñuble Region, Chile (36°32.46'S and 71°52.44'W). This region is known for its pasture and forage production, and livestock farming. Furthermore, Humic Haploxerands (Andisol) (Soil Survey Staff, 1999) is predominantly present in the area, which is developed from modern volcanic ashes deposited on a fluvio-glacial substrate (gravel and sand) (Stolpe, 2006). The main properties of the topsoil (0–10 cm) are listed in Table 1. The experimental station, under a Mediterranean climate, receives approximately 700 mm of annual precipitation, primarily during the winter season (580 mm from May to September). The annual average air temperature is 14.4 °C, which during the coldest month (July) reduces to 8.3 °C.

### **2.2. Biochars and carbonaceous material**

Farm wastes (poultry, pig, and dairy) and eucalyptus wood residues were used as feedstock, which were obtained from local farms and the forest industry of Biobío and Ñuble regions of Chile. The animal wastes were air-dried at ambient temperature for 2 weeks, homogenized, and sieved through a 5 mm mesh sieve. The particle size of the wood residues was heterogeneous (< 1 cm).

Biochars were produced by slow pyrolysis (maximum temperature of 500–550 °C) in a locally manufactured oven, with a residence time of 2 h. The gases produced during the pyrolysis process, which were condensed and recovered as a liquid fraction, were not considered in this study. According to the feedstock, three biochars and one carbonaceous material were produced: eucalyptus wood residue biochar (EWBC), dairy manure biochar (DMBC), pig manure biochar (PMBC), and poultry litter carbonaceous material (PLCM). The material produced from poultry litter had a low organic carbon (OC) content

(5.64%), and was rejected as a biochar according to the European Biochar Certificate (EBC, 2012) and IBI guidelines (IBI- International Biochar Initiative, 2013). In this study, we considered this amendment to be a carbonaceous material. The amendments were homogenized, sieved (<250  $\mu\text{m}$  mesh), and stored in desiccators until use. Their characteristics are presented in Table 1.

**Table 1.** Properties of the biochars and initial soil characteristics. (**Source:** Own elaboration)

Properties	Units	PLCM	DMBC	PMBC	EWBC	Soil (0-10cm)
pH	-	10.24	10.16	8.2	5.73	5.86
TN	$\text{g kg}^{-1}$	8.4	16.7	33.9	2.8	4.1
TC	$\text{g kg}^{-1}$	116.1	472.2	418.8	841.5	69.1
C:N	-	13.8	28.2	12.4	300.5	16.9
$\text{NO}_3^- \text{N}$	$\text{mg kg}^{-1}$	9.4	0.3	7.86	0.38	10.3
$\text{NH}_4^+ \text{N}$	$\text{mg kg}^{-1}$	5.79	1.02	9.58	0.55	7.6
Av. K	$\text{g kg}^{-1}$	14.78	8.88	16.15	0.32	0.27
Av. P	$\text{g kg}^{-1}$	22.19	4.35	13.17	1.58	0.015
Av. Mg	$\text{g kg}^{-1}$	12.32	3.75	12.85	0.06	0.15
Av. Ca	$\text{g kg}^{-1}$	223.8	10.76	30.57	0.71	1.14
H	$\text{g kg}^{-1}$	0.7	5.3	19.4	25.8	-
S	$\text{g kg}^{-1}$	2.3	0.1	2.6	>d.l <sup>b</sup>	-
IC	$\text{g kg}^{-1}$	59.7	2.6	4.7	0.8	-
H:OC <sup>a</sup>	-	0.14	0.13	0.56	0.30	-
$\text{CaCO}_3\text{-eq}$	%	12.69	1.69	2.45	0.39	-
Cox	$\text{g kg}^{-1}$	45	287.8	294.4	81.3	-
Cox : TC	$\text{g kg}^{-1}$	387.6	609.7	703.9	96.6	-
Sand	%					47.9
Silt	%					31
Clay	%					21.1
Bulk density	$\text{Mg m}^{-3}$					1.1

<sup>a</sup> Atomic ratio

<sup>b</sup> under detection limit

### **2.3. Experiment 1. Forage establishment and measurements**

To evaluate the forage yield and the changes in key soil chemical properties, we established 1 m<sup>2</sup> plots with buffer zones 1 m wide between plots (Fig. S1). Treatments included (i) unamended soil as control, soil; (ii) “business-as-usual” fertilizer, NPK; (iii) PLCM; (iv) PMBC; (v) DMBC; and (vi) EWBC. The rate used for each amendment was 11 t·ha<sup>-1</sup>. This rate was calculated by fixing a biochar/soil ratio of 1:100 (w/w) (Muñoz et al., 2019), using the soil bulk density (1.1 g cm<sup>-3</sup>) at a depth of 10 cm. Each amendment was uniformly spread over the soil surface and then combined manually up to a soil depth of 10 cm, immediately before seeding. The same soil disturbance was simulated in plots without any amendments (NPK and soil control). In the NPK treatment, 68.7 kg P<sub>2</sub>O<sub>5</sub> ha<sup>-1</sup> was added at the start of the experiment as triple superphosphate (TSP), 36.15 kg ha<sup>-1</sup> K<sub>2</sub>O as muriate of K, and 50 kg N ha<sup>-1</sup> as urea; finally, after the first forage cut, 50 kg N ha<sup>-1</sup> as urea was added.

*Sorghum sudangrass* (*S. bicolor* × *S. bicolor* var. Sudanese) was cultivated and irrigated for 24 weeks (October 2018–March 2019), and harvested after 14 and 24 weeks by cutting the forage at a height of 5 cm above the soil. Cut forage was oven-dried (70 °C), and the dried biomass was used to calculate the yield (first and second harvest); productivity was presented as herbage dry matter (DM) per hectare. After the second harvest, the plots were subjected to a fallow period up to one year, which is commonly practiced in the area. Soil samples were obtained at a depth of 0–10 cm to analyze the effect of treatments on soil chemical properties after the second harvest and fallow period.

### **2.4. Experiment 2. Sampling and analysis of greenhouse gases**

The same aforementioned treatments were set up in parallel to evaluate the GHG emissions in plots without forage cropping. The field design is shown in Fig. S1. Soil CO<sub>2</sub> and N<sub>2</sub>O fluxes were monitored regularly from October 2018 to October 2019, at 5, 10, 15, 30, 45, 105, 165, 225, 285, and 365 days after the treatment application. Static chambers (Ø 250 mm, 100 mm depth) with a two-piece system were used to collect air samples and the base of the static chambers was permanently installed on the treatments. In each sampling, the chambers were closed with a hermetic lid to concentrate gas emissions. Gas

samples were collected using 60 mL syringes equipped with a stopcock at three evenly spaced time intervals (0, 30, and 60 min). The samples were stored in vacuumed vials (Exetainer, Labco Ltd., UK) and maintained under pressure until analysis. To avoid variations due to solar exposure, gas samples were withdrawn between 8:00 and 10:00 in the morning. The soil temperature and humidity were measured after each sampling. Soil water content was determined gravimetrically after oven drying at 105°C for 48 h and expressed as water-filled pore space (WFPS), and the % WFPS was calculated from the initial soil bulk density (Table 1) using a particle density of 2.65 g cm<sup>-3</sup> (Blake, 2008).

The concentrations of CO<sub>2</sub> and N<sub>2</sub>O were determined using a gas chromatograph (Perkin Elmer model Clarus 600, Akron, OH, USA) equipped with an electron capture detector (ECD) and flame ionization detector (FID), respectively. CO<sub>2</sub> and N<sub>2</sub>O daily fluxes were calculated according to the ideal gas law and the linear change ( $r^2 > 0.9$ ) of the gas concentration in the chamber over 60 min. Cumulative CO<sub>2</sub> and N<sub>2</sub>O emissions were estimated by linear interpolation of the daily fluxes (Muñoz et al., 2019).

## **2.5. Chemical characterization of amendments and soil samples**

Elemental analyses of biochar (total C, N, H, and S) were determined by dry combustion using an elemental analyzer (Elementar Analysen systeme GmbH, Hanau, Germany). Inorganic C (IC) was measured using the titrimetric method (Calvelo Pereira et al., 2017). Organic C (OC) was obtained from the difference between total C and IC. Other key chemical properties of biochars and carbonaceous materials were determined using analytical methods developed for biochar characterization (Singh et al., 2017a). Electrical conductivity (EC) and pH were measured in a sample/deionized water ratio of 1:10 (w/v) (Singh et al., 2017b). The liming potential (% CaCO<sub>3-eq</sub>) was determined in a biochar suspension with 1M HCl by titrating against 0.5M NaOH, using CaCO<sub>3</sub> as a reference sample (Singh et al., 2017b). Mineral N was extracted with 2M KCl, and the KCl-NH<sub>4</sub><sup>+</sup> and KCl-NO<sub>3</sub><sup>-</sup> were measured using an auto-analyzer (Technicon AA-II, USA) (Camps-Arbestain et al., 2017). Available phosphorus was extracted with 2% formic acid, and determined using a spectrophotometer

(Thermo Spectronic model Genesys TM 5, Vernon Hills, IL, USA) (Wang et al., 2012a). Available bases were extracted following the method of Camps-Arbestain et al. (2017) and were determined using a microwave plasma atomic emission spectrophotometer (Agilent Technologies 4200 MP-AES, USA).

Soil samples from Experiment 1 were characterized as described by Sadzawka et al. (2006). TC and TN were analyzed by dry combustion using a C, N analyzer (Truspec CN, LECO, USA). Soil pH was determined in 1:2.5 (w/v) ratio of soil-water extracts. Mineral N was measured by titrating with standardized H<sub>2</sub>SO<sub>4</sub>. Olsen P was extracted with 0.5 M NaHCO<sub>3</sub> (pH 8.5) and measured colorimetrically using a spectrophotometer (Thermo Spectronic model Genesys TM 5, Vernon Hills, IL, USA). Soil bases were determined using an atomic absorption spectrophotometer (Unicam, Solaar 9000). Initial soil bulk density was measured following the volumetric ring method. Sand, silt, and clay contents were determined by the pipette Method, using the USDA system (Soil Survey Staff, 2009)

Subsamples of both (i) the amendments and (ii) the soils from Experiment 1 were additionally treated with potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) following the method described by Herath et al. (2014) and Calvelo Pereira et al. (2011) to determine the oxidizable organic C (C<sub>ox</sub>). The non-oxidizable C (C<sub>nox</sub>), that is, the difference in total C – C<sub>ox</sub>, was also calculated for the same samples. C<sub>nox</sub> corresponds to the sum of alkyl and pyrogenic C that is not oxidized after mixing with a concentrated dichromate solution, which is the resistant or more stable C (Knicker et al., 2007; Calvelo Pereira et al., 2011; Suárez-Abelenda et al., 2014).

## **2.6. Statistical analyses**

Statistical analysis was performed using R software (version 4.0.3). Randomized block designs for experiments, (1) crop yield and (2) GHG emissions were analyzed independently; the six treatments in both assays had three replicates, totaling 18 plots for each assay. The field design is shown in Fig. S1. The independent variables were blocks (three levels) and treatments (six levels: four different biochars, added at the same doses 11 t ha<sup>-1</sup>, equivalent to 1% biochar with soil, and two controls: unamended soil and NPK treatment as “business-as-usual” fertilizer in sorghum cropping). The dependent variables

for the crop yield assay were yield and soil properties, while cumulative CO<sub>2</sub> and N<sub>2</sub>O emissions were used for the GHG emissions assay. Normality of data was verified using the Shapiro-Wilk test. Analysis of variance (ANOVA) with LSD Fisher tests ( $p=0.05$ ) was performed to determine significant differences between treatments. Pearson's  $r$  correlation coefficient was used: (i) to obtain correlations between forage yield and soil chemical properties (0–10cm depth), and (ii) to investigate the effect of biochar properties on soil N<sub>2</sub>O emissions.

### **3. Results**

#### **3.1. Experiment 1.**

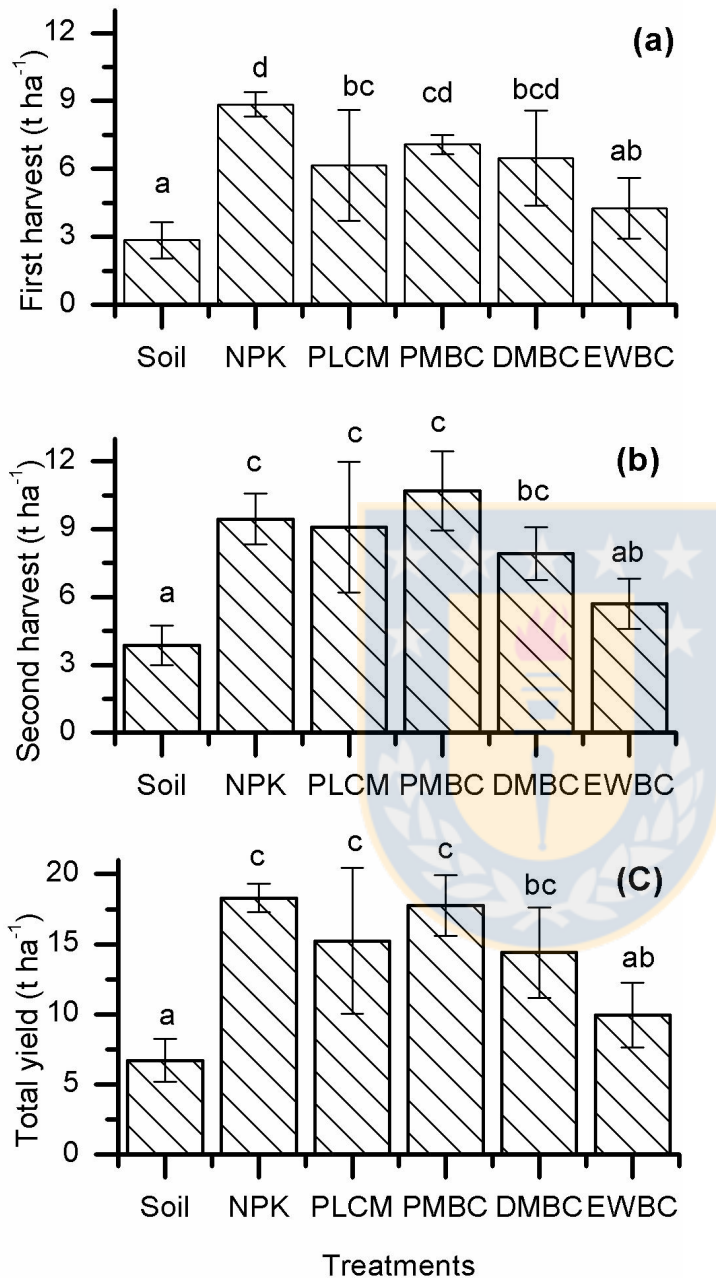
After the crop season, the soil chemical properties (Table 2) varied according to the added biochar. The addition of different amendments modified the soil pH (Table 2). In particular, PLCM and PMBC significantly ( $p \leq 0.05$ ) increased soil pH from 6.07 to 6.80 and 6.26, respectively. As expected, soil available P was significantly higher with P-rich amendments (PLCM and PMBC). The largest increase in available P was observed in treatments with the highest soil pH. Plots with PMBC and DMBC had larger exchangeable potassium contents (on average 0.80 cmol<sub>c</sub> kg<sup>-1</sup>) than the control soil (0.45 cmol<sub>c</sub> kg<sup>-1</sup>); this result is significant at  $p \leq 0.05$ . The mineral N (NO<sub>3</sub><sup>-</sup>-N and NH<sub>4</sub><sup>+</sup>-N) did not differ statistically from that of the control soil (Table 2).

Soil TC concentration measured after the fallow period (Table 2), exhibited significant differences between unamended soil and plots amended with EWBC, DMBC, and PMBC (Table 2). The impact on soil C<sub>nox</sub> was less evident, and was only significant with DMBC and EWBC treatments.

Forage productivity is shown in Figure 1. After two cuts, the sorghum yield increased significantly with the addition of manure-derived biochars and mineral fertilization, ranging from 14.40 to 18.30 t ha<sup>-1</sup> (Fig. 1C). EWBC treatment had a low forage yield (9.96 t ha<sup>-1</sup>), which was not significantly different from unamended soil ( $p \leq 0.05$ ). For the first sorghum harvest, manure-derived biochars increased productivity with respect to the control soil (Fig. 1A). In the second forage cut, all amendments had a similar response to productivity



compared to mineral fertilization, except for EWBC, whose yield values were 40% less than the NPK treatment (Fig. 1B).



**Figure 1.** *Sorghum Sudangrass* dry matter (A) First harvest (B) Second harvest, and (C) Total forage yield, (n = 3) ± standard deviation (S.D.). Different letters indicate significant differences between treatments at  $p \leq 0.05$  using LSD test.

**Source:** Own elaboration

**Table 2.** Soil properties after forage and fallow season. (**Source:** Own elaboration)

Treatment	pH	After forage season (5.5 months)				After forage and fallow season (1 year)			
		Available P mg kg <sup>-1</sup>	Exch. K cmol <sub>c</sub> kg <sup>-1</sup>	NO <sub>3</sub> <sup>-</sup> -N mg kg <sup>-1</sup>	NH <sub>4</sub> <sup>+</sup> -N mg kg <sup>-1</sup>	TN g kg <sup>1</sup>	TC g kg <sup>1</sup>	Cox g kg <sup>1</sup>	Cnox g kg <sup>1</sup>
Soil	6.07 ± 0.18ab	13.9 ± 1.7a	0.5 ± 0.1a	3.0 ± 1.7a	9.7 ± 6.8a	6.9 ± 0.3a	66.3 ± 0.6a	59.8 ± 0.6a	6.4 ± 0.4a
NPK	5.92 ± 0.08a	20.5 ± 1.5b	0.5 ± 0.1a	2.3 ± 0.8a	8.6 ± 3.7a	6.7 ± 0.2a	65.9 ± 0.6a	59.3 ± 0.9a	6.6 ± 1.2a
PLCM	6.80 ± 0.01d	44.3 ± 6.7c	0.7 ± 0.3ab	2.8 ± 1.4a	14.2 ± 7.2a	6.7 ± 0.2a	68.8 ± 1.8a	63.6 ± 1.4b	5.2 ± 2.1a
PMBC	6.26 ± 0.06c	41.5 ± 3.0c	0.8 ± 0.1b	5.5 ± 2.5a	11.7 ± 2.8a	7.6 ± 0.9b	83.6 ± 0.5b	76.3 ± 0.8cd	7.3 ± 1.0a
DMBC	6.12 ± 0.06bc	16.9 ± 1.6ab	0.7 ± 0.3b	4.0 ± 0.7a	9.5 ± 4.8a	6.9 ± 0.3a	85.4 ± 1.6b	75.1 ± 0.4c	10.3 ± 1.5b
EWBC	5.91 ± 0.12a	13.3 ± 2.9a	0.5 ± 0.1a	4.8 ± 3.0a	10.8 ± 7.4a	6.6 ± 0.3a	97.3 ± 3.2c	77.8 ± 1.5d	19.5 ± 2.1c

Pearson correlation coefficients (*r* values) between soil properties and their effects on forage yield are shown in Table 3. Forage yield was positively correlated with available P ( $r = 0.49, p < 0.040$ ). In contrast, soil pH and available P were positively correlated ( $r = 0.77, p < 0.000$ ), demonstrating the association between these variables. In addition, positive correlations were found between soil TC and Cox ( $r = 0.95, p < 0.000$ ), and between soil TC and Cnox ( $r = 0.86, p < 0.000$ ), whereas Cnox was negatively correlated with soil pH ( $r = -0.47, p < 0.050$ ) and soil available P ( $r = -0.48, p < 0.040$ ).

**Table 3.** Pearson's *r* correlation coefficient between total forage yield and soil properties. (**Source:** Own elaboration)

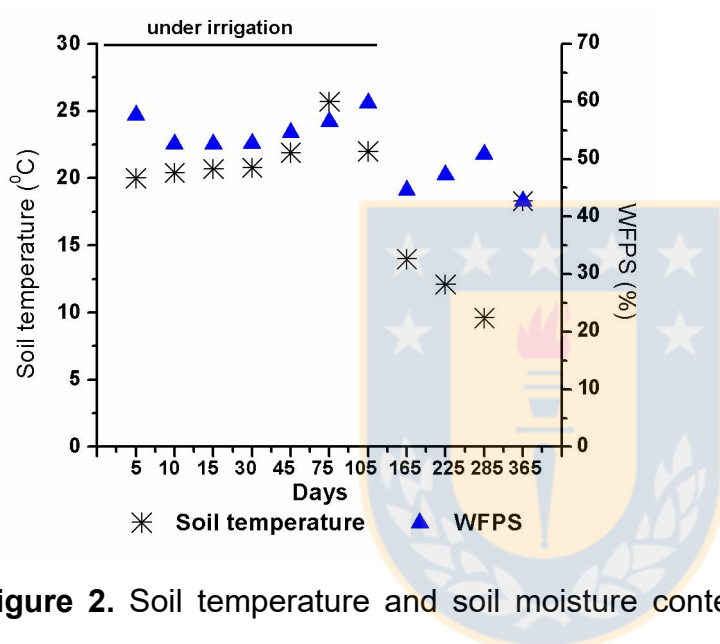
	Yield	Exch.K	Av. P	Av. N	pH	Cnox	Cox	TC
Av. K	0.14 (0.57)	-						
Av. P	0.49 (0.04)	0.52 (0.03)	-					
Av. N	-0.28 (0.26)	0.59 (0.01)	0.33 (0.18)	-				
pH	0.20 (0.43)	0.34 (0.17)	0.77 (0.00)	0.16 (0.53)	-			
Cnox	-0.23 (0.35)	-0.22 (0.39)	-0.48 (0.04)	-0.02 (0.94)	-0.47 (0.05)	-		
Cox	0.03 (0.90)	0.36 (0.14)	-0.01 (0.97)	0.21 (0.40)	-0.12 (0.64)	0.65 (0.00)	-	
TC	-0.08 (0.76)	0.15 (0.55)	-0.20 (0.43)	0.13 (0.59)	-0.28 (0.26)	0.86 (0.00)	0.95 (0.00)	-
TN	0.06 (0.82)	0.45 (0.06)	0.26 (0.29)	0.25 (0.31)	-0.05 (0.83)	-0.20 (0.42)	0.26 (0.30)	-0.09 (0.73)

Exch. K exchangeable K; Av.P Available P; Av.N Available N ( $\text{NO}_3^-$ -N plus  $\text{NH}_4^+$ -N); Cox oxidizable.  
Cnox difference between TC and Cox.

### 3.2. Experiment 2.

#### CO<sub>2</sub> emissions

Figure 3 shows the flux and cumulative CO<sub>2</sub> emitted from the soil across the treatments. The CO<sub>2</sub> flux was initially high after incorporating the amendments, but was mainly influenced by soil temperature and moisture (Fig. 2). In this study, the soil temperature ranged from 9.6 °C to 25.7 °C, and the WFPS ranged from 42.7 to 59.7% (Fig. 2). These conditions are favorable for aerobic biological processes, where CO<sub>2</sub> is the final product.



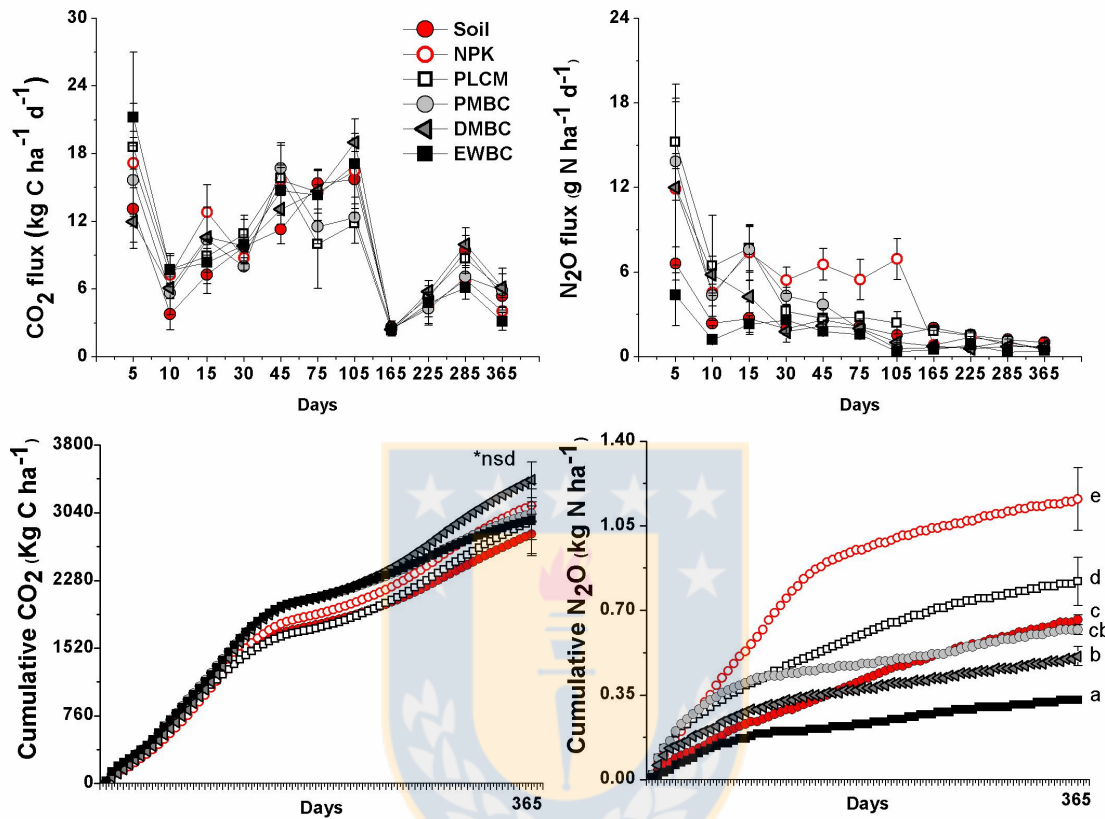
**Figure 2.** Soil temperature and soil moisture content at a depth of 0–10 cm during each sampling throughout the study period. WFPS: Water-Filled Pore Space. Points represent mean (n = 3). **Source:** Own elaboration.

Overall, in the first 45 days, the PLCM and EWBC treatments increased CO<sub>2</sub> fluxes compared to the unamended soil (Fig. 3), but after this initial evolution, the CO<sub>2</sub> flux tended to decrease. At the end of the experiment, there were no significant differences ( $p \leq 0.05$ ) in the cumulative CO<sub>2</sub> emissions among the treatments (Fig. 3).

#### N<sub>2</sub>O emissions

Nitrous oxide cumulative emissions (Fig. 3) were affected by season and treatments; and ranged from 0.22 to 0.93 kg N ha<sup>-1</sup> after the first 165 days, and from 0.32 to 1.15 kg N ha<sup>-1</sup> after the fallow season in the EWBC and NPK

treatments, respectively. The highest N<sub>2</sub>O fluxes were registered in all treatments related to seasons with higher soil temperatures and larger WFPS values (Fig. 2).



**Figure 3.** CO<sub>2</sub> and N<sub>2</sub>O emissions during 365 days (fluxes and cumulative emissions, (n = 3) ± standard deviation (S.D.). Different letters indicate significant differences between treatments in cumulative emissions at  $p \leq 0.05$  using LSD test. \*nsd, no significant differences. **Source:** Own elaboration.

Regardless of the amendment, all treatments registered lower cumulative N<sub>2</sub>O emissions than the NPK treatment. The cumulative N<sub>2</sub>O emission at 365 days in the NPK treatment was 2-times higher than that in the control soil. The addition of EWBC reduced total N<sub>2</sub>O emissions from the beginning compared to the soil control. In contrast, during the experimental period, the PLCM treatment had significantly higher cumulative N<sub>2</sub>O emissions than the unamended soil, representing a 24% increase (Fig. 3). At the end of our study, the biochar N<sub>2</sub>O mitigation potential was 23% and 50% for DMBC and EWBC treatments, respectively. The N<sub>2</sub>O fluxes after incorporating PMBC were initially high, which

gradually decreased without any significant differences with the control soil at 365 days.

Table 4 shows Pearson's correlation between N<sub>2</sub>O -N emissions and chemical properties of materials added, which were significantly positively correlated ( $p < 0.05$ ) with Cox:TC ratio, mineral N, pH, and liming potential of the amendments, and negatively correlated ( $p < 0.05$ ) with OC content and C:N ratio.

**Table 4.** Pearson's r correlation coefficient between amendment properties and N<sub>2</sub>O-N emissions. (**Source:** Own elaboration)

	N <sub>2</sub> O-N
Cox:TC	0.89 (0.0001)
OC	-0.96 (0.0000)
C : N	-0.78 (0.0030)
TN	0.25 (0.4400)
NH <sub>4</sub> <sup>+</sup>	0.65 (0.0200)
NO <sub>3</sub> <sup>-</sup>	0.80 (0.0002)
pH	0.73 (0.0100)
Liming potential	0.86 (0.0003)

## 4. Discussion

### 4.1. Effect of amendments on crop productivity and soil properties

The influence of manure-derived biochars on soil fertility and crop yield was evident in this experiment, which contributed significantly to forage productivity in the PLCM, PMBC, and DMBC treatments, as compared to the unamended soil (Fig.1). The improvement in forage yield was directly correlated with the increase in soil available P. Phosphorus-rich biochars (such as PLCM and PMBC) are potentially available P sources with high agronomic performance (Wang et al., 2012a, 2014). However, soil pH also plays an important role in the crop yield response and P availability, especially in acidic soils where plant-

phosphorous accessibility is affected by processes such as P fixation with Fe or Al (Johnson and Loeppert, 2006; Subedi et al., 2016). The optimum P availability occurs at a soil pH near 6.5 (Plante, 2007); thus, alkaline biochars could improve P availability in acidic soils (Cui et al., 2011; Nelson et al., 2011). Here, PLCM and PMBC mixed at a depth of 0–10 cm significantly increased the soil pH to approximately 6.5, which also increased the soil available P (Table 2).

The above mentioned soil pH improvement may be attributed to the liming potentials of PMBC and PLCM (liming classes: PLMC = 2, PMBC = 1, following the methodology of Camps-Arbestain et al. (2015)). Previous results on a lab scale experiment published by Muñoz et al. (2019) showed that biochars produced from pig and chicken manure efficiently increased the pH of diverse soil types after a similar time frame. Volcanic soils have a high pH-buffering capacity; therefore, their response to the added alkaline materials (such as biochar) can be limited (Koga et al., 2017; Yamamoto et al., 2019; Garbuz et al., 2020). However, similar to our results, other studies have reported the liming effect of manure-derived biochars, with considerable results in acidic soils (Van Zwieten et al., 2010; Singh et al., 2017b; Jeffery et al., 2017; Sheng and Zhu, 2018; Muñoz et al., 2019).

One unanticipated finding was the pH of the EWBC at 5.73 (Table 1), which is lower than the common pH reported in the literature (Camps-Arbestain et al. (2015); Singh et al., 2017b). This low pH is possibly associated with the acidity of the feedstock, which has not been determined in this study. Although the EWBC slightly acidified the soil compared with the control and was not statistically significant, the effects of EWBC on soil pH must be interpreted with caution, especially for volcanic soils. In this study, no significant differences in forage yield were observed between the EWBC plots and unamended soil. Since the EWBC had a low nutrient content (fertilizer class =0), no direct effect on forage productivity was expected.

Overall, no significant differences in forage yield were observed between the NPK and manure-derived biochar treatments. Nutrient-rich biochars can positively affect crop yield (Slavich et al., 2013; Jeffery et al., 2017; Ye et al., 2020), mainly in acidic soils (Jeffery et al., 2011). The manure-derived biochars

in this study were classified according to Camps-Arbestain et al. (2015) as having a fertilizer class of 3, completing the sorghum crop's hypothetical demand for at least three nutrients (P, K, and Mg). However, a limitation of this study was that the N content of the amendments was lower than the NPK treatment. In addition to the input of available nutrients, other indirect effects of biochar on crop productivity, such as changes in soil biological activity (Garbuz et al., 2020), higher soil water retention (Haider et al., 2017), and substantial plant nutrient uptake (Mandal et al., 2019) have been suggested. This study shows that animal manure-derived biochars, which are considerable nutrient source that increase forage yields, can offer a potential option for a circular economy. This result can be strategic to areas possessing a sizeable pig, poultry, or dairy farming industry. The use of biochar as a soil amendment is a viable alternative to current waste management practices (Gascó et al., 2016; Stylianou et al., 2020).

#### **4.2. Evaluation of amendments on greenhouse gas emissions from soil and soil C concentration**

Typically, biochars decompose gradually; therefore, they can be useful in C sequestration and increasing soil C storage (Paustian et al., 2016; Zhang et al., 2019b). After 12 months under field conditions, the incorporation of pyrolyzed offsite feedstocks increased the C concentration in the soil, following the order of the OC content present in the amendments added (Table 2). The biochars used in this study contained more than 41.4% OC and a low H:OC ratio, which is associated with high aromaticity, potentially increasing the resistance to microbial attack (Wang et al., 2013; Camps-Arbestain et al., 2015). The increase in soil TC was consistent with our previous laboratory incubations using volcanic and non-volcanic soils (Muñoz et al., 2019). However, in this experiment, the improvement in soil TC observed in manure-derived biochar treatments may also be attributed to the enhanced forage root growth associated with the increase in yield. This C is plant-derived (more oxidizable), which remains after a fallow season. The amount of soil Cox in the PLCM treatment (material with low OC content, 5.5%) also notably increased, perhaps due to the return of C into the soil via crop roots.



The results also showed that the soil stable C ( $C_{nox}$ ) only increased significantly in the DMBC and EWBC treatments, mainly with EWBC addition. Previously, low-cost analytical techniques (i.e., wet oxidation with  $K_2Cr_2O_7$ ) were used to assess the degree of carbonization of the biochar (Calvelo Pereira et al., 2011). According to this method, DMBC and EWBC added 2.03 and 8.36 t ha<sup>-1</sup> of  $C_{nox}$  to soil, respectively.  $C_{nox}$  is related to highly resistant materials, such as pyrogenic C and aliphatic structures (Suárez-Abelenda et al., 2014); thus, as expected, the amount added was completely recovered after a year. However, PLCM and PMBC with lower TC and higher "oxidability" added a few tons of  $C_{nox}$  (less than 1.3 t ha<sup>-1</sup>), which was practically undetectable after a year.

This study did not observe a significant variation in the cumulative CO<sub>2</sub> emissions (Fig.3) despite differences in TC content, H:OC ratio, and Cox:TC fraction of the amendments. After the initial CO<sub>2</sub> evolution, the C flux decreased in all soil amendments, especially in the PLCM and EWBC treatments. The effects of biochar on soil pH and nutrient availability are indirect mechanisms by which biochar may increase soil C mineralization by stimulating microbial and enzymatic activities (Whitman et al., 2015). Here, the soil CO<sub>2</sub> emissions during the first 45 days are probably associated with the fast Cox mineralization, which was added with the amendments. However, this effect on CO<sub>2</sub> fluxes is short-term, and emissions gradually decrease (Fidel et al., 2017a, 2017b, 2019). In contrast, the early emissions from the PLCM treatment are seemingly related to its high CaCO<sub>3-eq</sub> content. Muñoz et al. (2019) suggested that chicken manure biochar can increase the cumulative CO<sub>2</sub> emissions due to the release of carbonates; this phenomenon tends to be higher in acidic soils (Sheng and Zhu, 2018).

#### **4.3. Mitigation of N<sub>2</sub>O emissions**

In this study, N<sub>2</sub>O emissions were lower in all amendment treatments than in the NPK treatment (Fig 4). Soil N<sub>2</sub>O emissions notably increase with inorganic fertilizer addition, and mineral N provides sufficient substrate for nitrification and/or denitrification, leading to increased fluxes (Cai et al., 2013, 2016; Wei et al., 2020). Agricultural soils are the main source of anthropogenic N<sub>2</sub>O emissions (IPCC, 2019), and considering the large N<sub>2</sub>O global warming

potential ( $\text{GWP}_{\text{N}_2\text{O}} = 265 \text{ CO}_2 \text{ equivalent}$  in a 100-year time horizon) (Myhre et al., 2013; IPCC, 2019), small reductions in these emissions could contribute to mitigating climate change. Here, NPK treatment had a  $\text{GWP}_{\text{N}_2\text{O}}$  of  $482 \text{ kg CO}_2 \text{ equivalent ha}^{-1}$ , while PLCM, PMBC, DMBC, and EWBC produced 314, 259, 212, and  $137 \text{ kg CO}_2 \text{ equivalent ha}^{-1}$ , respectively. The  $\text{N}_2\text{O}$  mitigation potential of the amendments compared with the NPK treatment obtained in this study is consistent with other studies conducted in paddy soils (Inceptisol) (Zhang et al., 2010), tropical soil (Oxisol) (Grutzmacher et al., 2018), and semi-arid soils (Cambisol) (Wei et al., 2020).

Several studies have indicated that biochar can mitigate  $\text{N}_2\text{O}$  emissions, when compared to unfertilized soils (Cayuela et al., 2015; Fidel et al., 2019; Huang et al., 2019). In our case, the high reduction in the cumulative  $\text{N}_2\text{O}$  observed at the end of the experiment in the EWBC and DMBC treatments may be attributed to the immobilization of N due to the high C content added to the soil (Cayuela et al., 2014). According to Cayuela et al. (2013), biochar can also act as an “electron shuttle,” promoting the reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$  in soils amended with biochar. This mechanism is favored in biochars with low molar H:OC ratios (such as EWBC and DMBC) (Cayuela et al., 2015). In general, lower H:OC ratios imply high aromaticity and redox activity (Klöpffel et al., 2014), which facilitates the electron exchange between soil denitrifying microorganisms and the biochar surface, favoring the last step of denitrification (Cayuela et al., 2015).

Manure-derived biochar can also act as a source of mineral N (Schouten et al., 2012) and its available C can be an additional energy source for soil heterotrophic denitrifiers (Fidel et al., 2017b), increasing  $\text{N}_2\text{O}$  emissions (Cayuela et al., 2013; Grutzmacher et al., 2018). This might explain the positive correlation observed in this study between  $\text{N}_2\text{O}$  emissions and the Cox:TC ratio of the amendments (Table 4). Moreover, PMBC and PLCM achieved high “fertilizer” potential (promoting nutrient content); the trade-off was that their “aromatic C” was lower. As discussed above, the TC content and aromaticity of biochar are directly linked to its potential to mitigate soil  $\text{N}_2\text{O}$  emissions (Wang et al., 2012b; Cayuela et al., 2015; Grutzmacher et al., 2018). Therefore, evidently, the synergistic effect between low aromaticity and a considerable

fraction of labile C and mineral N did not favor N<sub>2</sub>O mitigation mechanisms in these treatments.

Changes in soil pH can modify the microenvironment conditions, with relevant alterations in biological responses and N<sub>2</sub>O emission patterns. In this regard, Cayuela et al. (2013) proposed that biochar liming potential is another factor that facilitates the last step of denitrification, decreasing soil N<sub>2</sub>O emissions. However, Yamamoto et al. (2019) found that biochar did not affect the cumulative N<sub>2</sub>O emission over two years under field conditions; this result was attributed to the high pH-buffering capacity of volcanic soil. Here, PLCM had the highest effect on soil pH. Nevertheless, it increased N<sub>2</sub>O emissions. This material has a poor OC fraction but a large CaCO<sub>3-eq</sub> content (> 12%). The autotrophic nitrifier community obtains its C from CO<sub>2</sub> or carbonates, rather than from organic matter (Robertson and Groffman, 2007), and the nitrification process can result in the production of N<sub>2</sub>O. Therefore, the increase in nitrifiers due to C obtained from carbonates might explain the higher N<sub>2</sub>O emissions in the PLCM treatment, at least at the beginning of the experiment. The N<sub>2</sub>O mitigation potential of the alkaline biochars also depends on soil NO<sub>3</sub><sup>-</sup> (Wu et al., 2018). Hence, the available N added with the PLCM could also play an important role in the emission of N<sub>2</sub>O from the soil. Consistent with this result, Grutzmacher et al. (2018) found that an alkaline biochar produced from poultry manure increased soil N<sub>2</sub>O emissions without N fertilizer, which was associated with the high available N of the biochar added.

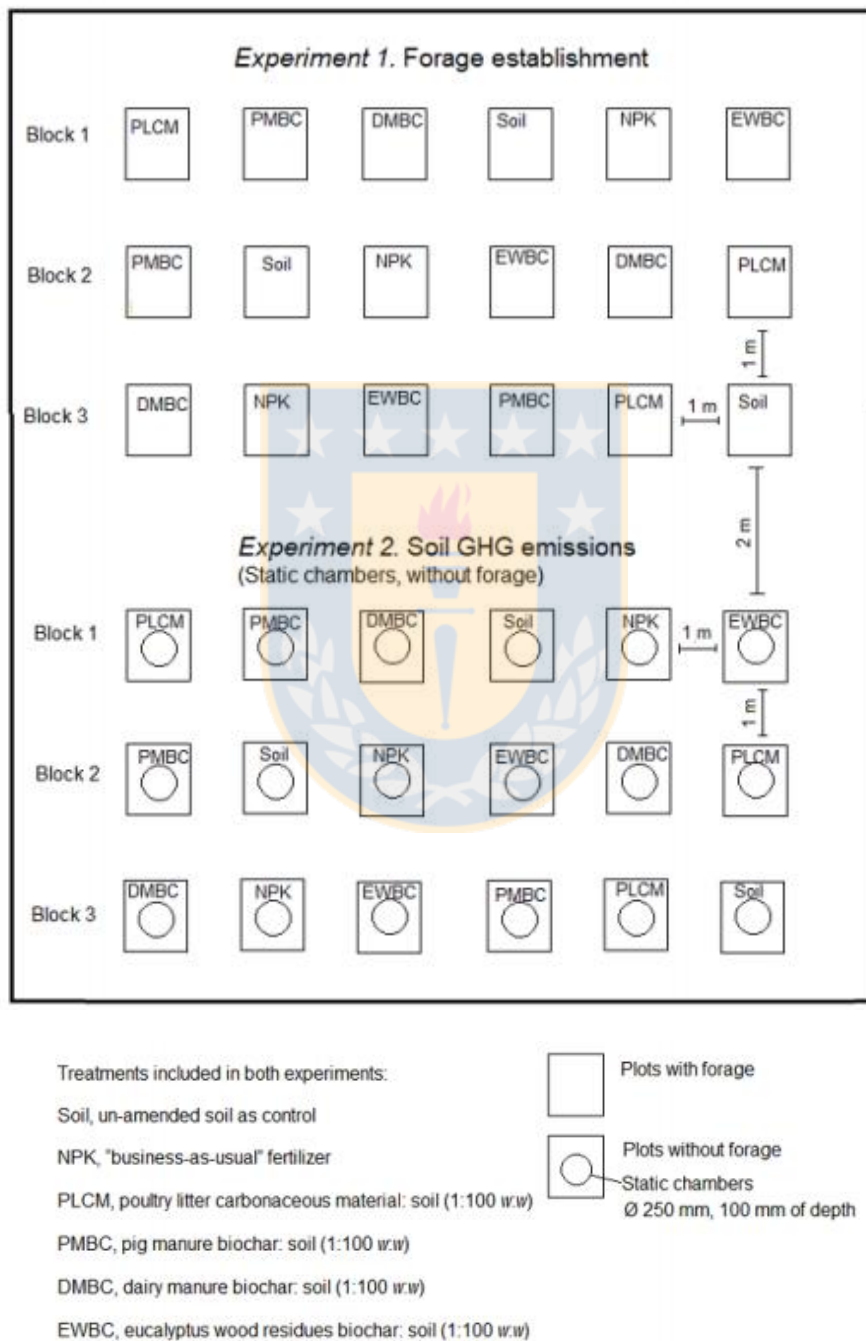
## **5. Conclusions**

Our field study demonstrated that PMBC and PLCM, applied at a rate of 1%, could be useful in forage systems, ameliorating critical soil properties such as pH and available P in Andisols. The benefits of EWBC are associated with mitigating climate change, increasing recalcitrant C, and decreasing 50% of soil N<sub>2</sub>O emissions, without affecting forage yield. In case of soil GHG emissions, biochar did not affect CO<sub>2</sub> fluxes, whereas only PLCM increased N<sub>2</sub>O emissions. Overall, 11 t ha<sup>-1</sup> of manure-derived biochars increased yields and produced less soil N<sub>2</sub>O emissions than “business-as-usual” fertilizer used in sorghum cropping. In particular, DMBC had a triple positive impact on (i) forage yield, (ii)

soil C storage, and (iii) preventing soil N<sub>2</sub>O emissions. Such potential could be explored for designing a win-win strategy for livestock systems, producing biochars that promote productivity and mitigate climate change.

**Supplementary material**

(Source: Own elaboration)



**Fig. S1. Experimental (field) design**

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## CAPÍTULO IV

### Title: **Pyrolyzed or unpyrolyzed manure? Implications to C stability and soil N<sub>2</sub>O emissions** (artículo pendiente de enviar)

#### **Abstract**

Pyrolysis is a useful alternative to current waste management practices. Manure biochars could be used as C-rich soil amendments, reducing the risk of greenhouse gases (GHG) emissions derived from the decomposition of unpyrolyzed manures. Here, two manures biochars and their feedstock were used as soil amendments to evaluate the impact of pyrolysis on CO<sub>2</sub> and N<sub>2</sub>O emissions, C stability, and the global warming potential (GWP) during a year under field conditions. The experiment included five treatments: unamended soil (control), pig manure (PM), pig manure biochar (PMB), dairy manure (DM), and dairy manure biochar (DMB). The amendments were applied at rates of 1% w/w, adding 0.5 kg C m<sup>-2</sup> approximately. All amendments increased soil CO<sub>2</sub> emissions, but C mineralization was lower using pyrolyzed manures than their corresponding feedstocks. CO<sub>2</sub>-C emissions were 8.35% and 63% of the C added with biochars and feedstocks, respectively. Biochars reduced soil N<sub>2</sub>O emissions, while the N<sub>2</sub>O emission factor (N<sub>2</sub>O Ef) of the manures treatments was 0.27%. The variations in soil C stock avoided 16.4 and 6.58 t CO<sub>2</sub>-eq ha<sup>-1</sup> in biochars and manures treatments, respectively. However, the mitigation potential of unpyrolyzed manures was affected by the high CO<sub>2</sub> and N<sub>2</sub>O fluxes, while the biochar treatments reduced of GWP due to the changes in soil C stock with low impact on soil emissions. Overall, manures were more stable after pyrolysis, which favors the manure biochars as soil amendments for environmental purposes. Such potential could reduce the C footprint for pig and dairy farms, promoting the enhancement of soil C stocks.

#### **1. Introduction**

The increase of animal manure as a result of livestock production leads to large quantities of waste, becoming an environmental concern (Guo et al., 2020; Shakoor et al., 2021; Zhou et al., 2017). According to the IPCC, agriculture and livestock activities have a mitigation potential between 2.3 and 9.6 Gt CO<sub>2</sub> eq yr



<sup>-1</sup>, playing a key role in global warming reduction by 2050 (IPCC, 2019). Manure application onto agricultural soils is a common practice for transfer C and N, improving soil quality (Maillard and Angers, 2014). The use of manure as an organic fertilizer improves soil physical, chemical, and biological properties (Lupwayi et al., 2014; Mangalassery et al., 2019), increases crop yields (Zahra et al., 2021), and enhances soil organic C stocks (Maillard and Angers, 2014; Qin et al., 2021). However, animal manures can be mineralized rapidly to CO<sub>2</sub> due to the decomposition process (Grutzmacher et al., 2018; Zhang et al., 2021), and the effects on soil greenhouse gases (GHG) could offset the C net gains (Zhou et al., 2017).

Usually, manures have a high content of mineral N (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) and they are a source of energy (i.e., C) for soil nitrifiers and denitrifiers, providing the essential substrates required for nitrification and denitrification processes (Meyer et al., 2021; Zhou et al., 2016, 2014). Nowadays, it is estimated that livestock in South America excretes about five times more N than the amount excreted in the 1860s, drastically increasing anthropogenic emissions of N<sub>2</sub>O (Zhang et al., 2017). The N<sub>2</sub>O emission factors (Efs, %) indicate the N<sub>2</sub>O-N loss following the application of different N sources (organic or inorganic) (Shakoor et al., 2021b). Manure Efs can range from < 0.1 to 3%, depending on soil type and application process (method, manure type, rate, climatic conditions) (Chadwick et al., 2011). According to Zhou et al., 2017, the application of manures to soil can stimulate N<sub>2</sub>O emissions even more than inorganic fertilizers, with Efs greater than 1%, which is the IPCC default value (IPCC, 2019).

The N<sub>2</sub>O global warming potential is 265 times greater than CO<sub>2</sub> (based on a 100-year time horizon), being one of the most important greenhouse gases (IPCC, 2019; Myhre et al., 2013). N<sub>2</sub>O released by soils following the addition of manures can drastically contribute to the atmospheric GHG concentration. However, these emissions also occur from livestock bedding and solid manure stores (Chadwick et al., 2011). Therefore, better methods are needed to convert animal wastes into more C and N stable sources (Zhang et al., 2017, 2021).

The pyrolysis process permits the conversion of biowastes into new value-added products in those situations where high biomass quantity is available with difficult final disposal (Lehmann and Joseph, 2015). Animal manures are more stable after pyrolysis achieving high polymerization, aromatization, and carbonization (Gascó et al., 2016; Grutzmacher et al., 2018; Stylianou et al., 2020). Therefore, manure biochars could be used for environmental purposes (e.g., increase soil C stocks or sorbent materials) (Stylianou et al., 2020; Subedi et al., 2016). Biochars also improve crops yield in agricultural soils (Jeffery et al., 2017; Ye et al., 2019). Typically they have a significant liming potential (Muñoz et al., 2019; Singh et al., 2017; Vassilev et al., 2013), supplies nutrients (Camps-Arbestain et al., 2017; Hassan et al., 2020; Wang et al., 2012b, 2012a), and have positive effects on soil biological quality (Brassard et al., 2018; Garbuz et al., 2020).

Recently, the biochar addition to soil has been included as a useful mitigation option in the special report on climate change (IPCC, 2019) because biochars have a high potential to increase soil TC (Bruun et al., 2012; Budai et al., 2016) and mitigate soil N<sub>2</sub>O emissions (Cayuela et al., 2015, 2014, 2013; Shi et al., 2019). Although the woody biochars have better properties for these targets (e.g., high TC and C:N, low H:C, O:C and volatile mater) (Brassard et al., 2018; Calvelo Pereira et al., 2011; Cely et al., 2014; Ghodake et al., 2021; Grutzmacher et al., 2018; Wang et al., 2013), the manure biochars have the additional potential to stabilize wastes, avoiding CO<sub>2</sub> and N<sub>2</sub>O emissions (Gascó et al., 2016; Grutzmacher et al., 2018; Lehmann and Joseph, 2015). Nonetheless, the pyrolysis process can be expensive (El-Naggar et al., 2019); thus, the mitigation potential of manure biochar should be demonstrated in contrast to low-cost conventional practices such as the direct application of manure to the soil.

Based on the above, we hypothesized that: In order to enhance waste reuse in agriculture, slow pyrolysis process increase the manure potential for climate change mitigation in agricultural soils because (i) manure biochars as soil amendments have lower C mineralization than its feedstock and remain longer increasing the soil C stock, (ii) the soil N<sub>2</sub>O emissions are mitigated by manure biochars, while unpyrolyzed manures increase them. To test this hypothesis a

field experiment with pig and dairy manures (pyrolyzed and unpyrolyzed) was conducted, where we evaluate: (i) the C persistence of pyrolyzed and unpyrolyzed manures, regarding their mineralization as CO<sub>2</sub> and C- retention coefficient in the soil after a year (ii) the N<sub>2</sub>O Ef of pyrolyzed and unpyrolyzed manures (iii) the GWP induced by additions of pyrolyzed and unpyrolyzed manures.

## 2. Material and Methods

### 2.1. Manure sampling and pyrolysis

Dairy and pig manure samples were collected from local farms of the Biobío and Ñuble regions, Chile. Original samples had more than 60% of humidity; therefore, they were air-dried in an outdoor covered area, during two weeks, the final humidity was less than 20%. Finally, manures were homogenized, sieved at 5 mm, and stored in an indoor room until use as biochar's feedstock or soil amendment.

The dried-feedstock samples were pyrolyzed under nitrogen atmosphere (flux 1L/min) at a heating rate of 20 °C min<sup>-1</sup> up to the target temperature (550 °C), using a pilot kiln at a laboratory scale placed in the University of Concepción, Chile. The gas produced through the pyrolysis process was collected as bio-oil using a condenser and an electrostatic precipitator. The biochars were sieved (250 µm) and kept at ambient temperature in desiccators until further use. The main characteristics of pyrolyzed and unpyrolyzed manure are shown in Table 1.

**Table 1.** Main chemical characteristics of pyrolyzed and unpyrolyzed manures. (Source: Own elaboration)

Parameters	Pig manure		Dairy manure	
	Feedstock	Biochar	Feedstock	Biochar
Yield %	-	42	-	41
Ash%	-	52.50	-	50.8
pH	7.39	8.20	8.21	10.16
TC %	40.70	41.90	40.50	47.2
TN %	3.6	3.39	2.50	1.67
C: N ratio	11.31	12.30	16.2	27.80
Nitrate (mg kg <sup>-1</sup> )	134.00	7.86	47.30	0.30
Ammonium (mg kg <sup>-1</sup> )	1739.10	9.58	101.40	1.02
H/OC	-	0.56	n.d	0.13

## 2.2. Experimental treatments and soil GHG emissions

The study was carried out under field conditions in the experimental station of the University of Concepción, located in Ñuble Region, Chile (36°32.46'S and 71°52.44'W). The experimental station receives approximately 700 mm of annual precipitation, primarily during the winter season (580 mm from May to September). To avoid soil dryness, the trial was irrigated once a week from October to April (dry months), maintaining soil moisture above 50% throughout the year. According to Soil Survey Staff (1999) and Stolpe (2006), Humic Haploxerands is the predominant soil in the area. Relevant properties of the topsoil (0–10 cm) were as follows: pH, 5.86; bulk density, 1.1 Mg m<sup>-3</sup>; TC, 6.91%; TN 4.1%; and Olsen P, 15.4 mg kg<sup>-1</sup>, with sand, silt and clay contents of 47.9%, 31 and 21.1%, respectively.

To evaluate the effect of pyrolyzed and unpyrolyzed manures on soil CO<sub>2</sub> and N<sub>2</sub>O emissions 15 plots of the 1 m<sup>2</sup> were established. The plots included five treatments by triplicate: dairy manure (DM); dairy manure biochar (DMB); pig manure (PM); pig manure biochar (PMB); un-amended soil (Control). The amendments were incorporated up to 10 cm soil depth, at a rate of 1% (w/w). According to the TC and TN of the amendments, each plot received around 0.5 kg C m<sup>-2</sup> and between 18.37 to 39.6 g N m<sup>-2</sup>. After amendments addition, static chambers (Ø 250 mm, 100 mm depth) were installed on the treatments, and gas samples were collected from the chambers on days 5, 10, 15, 30, 45, 105, 165, 225, 285, and 365. In each sampling, three gas samples were collected from each chamber, using a 60 mL syringe at three evenly spaced time intervals (0, 30, and 60 min). Gas samples were stored and transferred from the field to the laboratory in vacuumed vials (Exetainer, Labco Ltd., UK), where CO<sub>2</sub> and N<sub>2</sub>O content were analyzed by gas chromatography (Perkin Elmer model Clarus 600, Akron, OH, USA).

The gas fluxes were calculated based on linear change of the gas concentration, during 60 minutes and they were adjusted for volume and area chamber. All temporal fluxes were corrected by the air temperature and reported as mg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup> or mg CO<sub>2</sub>-C m<sup>-2</sup> h<sup>-1</sup>, following the method described by Van Zwieten et al. (2010). CO<sub>2</sub> and N<sub>2</sub>O daily fluxes were estimated by linear interpolation of

two adjacent measurements (Equation 1). The cumulative fluxes were calculated by adding successive daily fluxes, during 365 days (equation 2):

$$\text{Daily flux} = (\alpha t + \beta) \times 24 \quad (1)$$

$$\text{Cumulative fluxes} = \sum_{t=1}^{365} \text{Daily flux} \quad (2)$$

$\alpha$  and  $\beta$  are the slope and intercept of the emissions obtain from two adjacent measurements ( $\text{mg m}^{-2} \text{h}^{-1}$ ), 24 is the conversion from hours to days,  $t$  is the day of the emission (from 1 to 365). Cumulative fluxes are the total emissions during 365 days in  $\text{kg} [\text{CO}_2\text{-C or N}_2\text{O-N}] \text{ha}^{-1}$ .

Finally, the difference between GHGs emissions of the amendment-soil treatments and the control soil was defined as gas emissions induced or avoided by the amendments.

### 2.3. C and N stability

To estimate the C and N lost after 365 under field conditions, the C decomposition rate ( $\text{CD}_{\text{rate}}$ ) and  $\text{N}_2\text{O Ef}$  were calculated and expressed in percentage of N or C applied with the amendments as follows:

$$\text{CD}_{\text{rate}} (\%) = [\text{CO}_2 (t) - \text{CO}_2 (c)] / \text{applied C} * 100 \quad (3)$$

$$\text{N}_2\text{O Ef} (\%) = [(\text{N}_2\text{O} (t) - \text{N}_2\text{O} (c))] / \text{applied N} * 100 \quad (4)$$

$\text{CO}_2 (t)$  and  $\text{N}_2\text{O} (t)$  are the cumulative  $\text{CO}_2$  and  $\text{N}_2\text{O}$  emissions ( $\text{kg CO}_2\text{-C ha}^{-1}$ ,  $\text{kg N}_2\text{O-N ha}^{-1}$ ) from each treatment.  $\text{CO}_2 (c)$  and  $\text{N}_2\text{O} (c)$  are the cumulative  $\text{CO}_2$  and  $\text{N}_2\text{O}$  emissions from the control. Applied C and N are the total amounts applied via unpyrolyzed or pyrolyzed manures ( $\text{kg C ha}^{-1}$  or  $\text{kg N ha}^{-1}$ ).

Additionally, after one year of application of treatments, topsoil samples (0-10cm) from each chamber were analyzed by dry combustion using a C, N analyzer (Truspec CN, LECO, USA).

The  $\text{GWP}_{(\text{net})}$  was estimated in  $\text{CO}_2$ -equivalents, ( $\text{t CO}_2 \text{eq ha}^{-1}$ ), following equations 5 and 6:

$$\text{GWP}_{(\Delta \text{C stock})} = - [\text{C stock}_{(\text{treatment})} - \text{C stock}_{(\text{control})}] * \text{molar ratio CO}_2/\text{C} \quad (5)$$

$$\text{GWP}_{(\text{net})} = \text{cumulative CO}_2 + \text{cumulative N}_2\text{O} * 265 + \text{GWP}_{(\Delta\text{C stock})} \quad (6)$$

$\Delta\text{C}$  stocks were measured in the topsoil (0-10 cm), using the bulk density (1.1 t m<sup>-3</sup>). The  $\text{GWP}_{(\Delta\text{C stocks})}$  were used as CO<sub>2</sub> eq avoided. Cumulative CO<sub>2</sub> and N<sub>2</sub>O were the total emissions emitted during one year; the value 265 is the default GWP of N<sub>2</sub>O in a 100-year time horizon (IPCC, 2019; Myhre et al., 2013). Due to the aerobic conditions of the field during the study, soil CH<sub>4</sub> emissions were not measured, therefore, this gas is not included in the  $\text{GWP}_{(\text{net})}$  estimation.

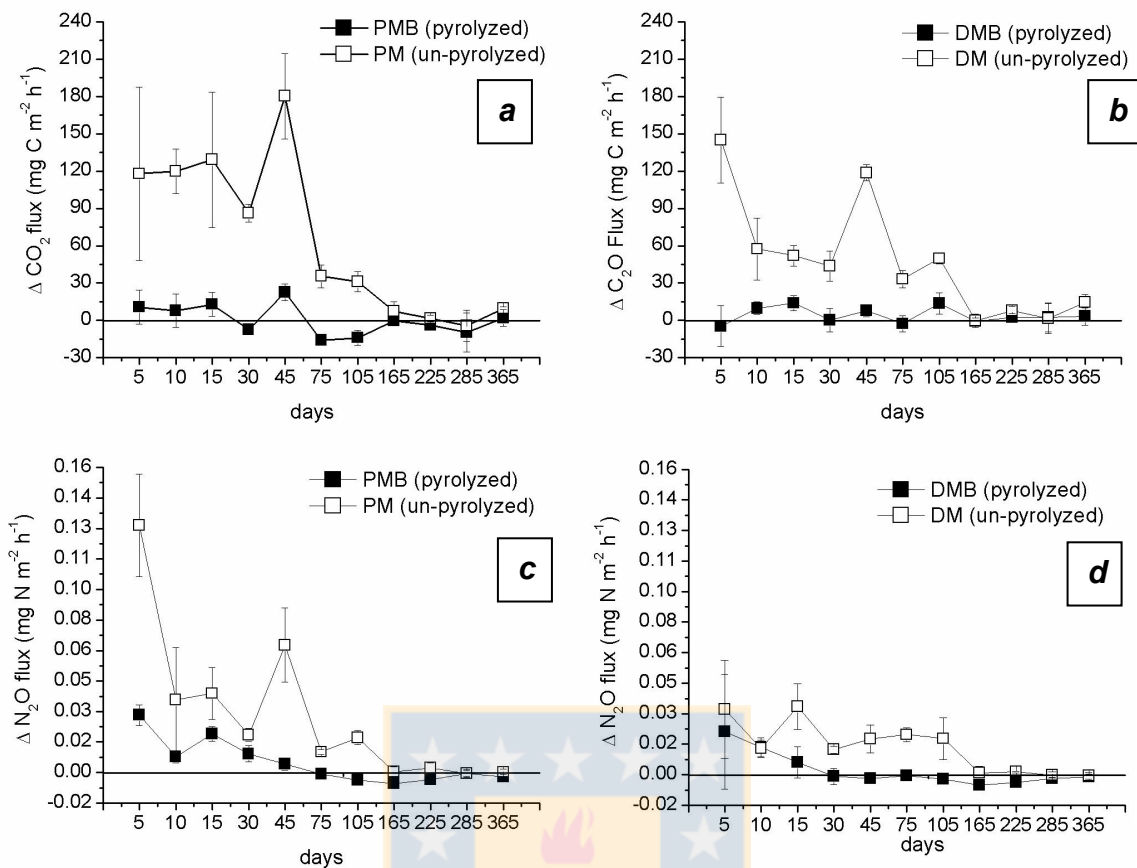
#### 2.4. Statistical analyses

The statistical analyses (calculation of means and standard deviations, differences of means, regression analysis) were performed using R software (version 4.0.3). Normality of data was verified using the Shapiro-Wilk test. Differences of means were tested using an analysis of variance (ANOVA). In the case of significant effects ( $p \leq 0.05$ ), mean comparisons were performed by Tukey test ( $p \leq 0.05$ ). The experiment was laid out in a randomized complete block design ( $n=3$ ), considering blocks (three levels) and treatments (five levels: DM, DMB, PM, PMB, control) as the independent variables, while the dependent variables were cumulative emissions, Ef, CDrate, TC, TN, and GWPs. Moreover, a linear regression ( $p \leq 0.05$ ) was performed between the C mineralized as CO<sub>2</sub> from unpyrolyzed and pyrolyzed manures.

### 3. Results

#### 3.1. GHG emissions and C permanency

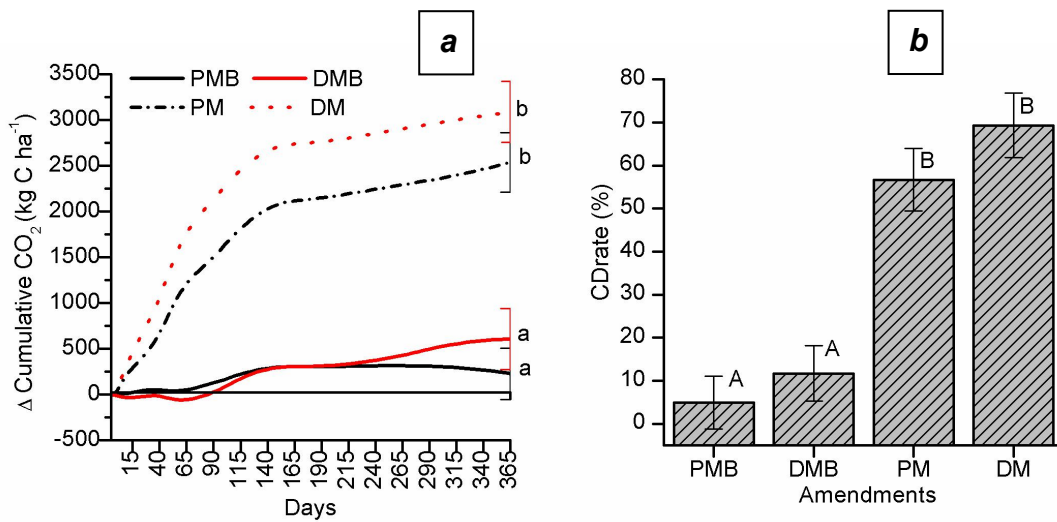
The highest induced peaks of CO<sub>2</sub> (Fig. 1 a, b) were observed after 5 and 45 days of manure addition (ranging from 117.8 to 180.2 mg CO<sub>2</sub>-C m<sup>-2</sup> h<sup>-1</sup>) and after 15 and 45 days of biochar addition (ranging from 7.6 to 22.6 mg CO<sub>2</sub>-C m<sup>-2</sup> h<sup>-1</sup>). CO<sub>2</sub> fluxes of manure and biochar treatments declined after 165 days (Fig. 1 a, b). After the first 30 to 75 days, treatments with DMB and PMB produced neutral or avoided N<sub>2</sub>O emissions in relation to soil control (ranging from -0.005 to 0 mg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup>, Fig. 1 c, d), while unpyrolyzed manures induced N<sub>2</sub>O emissions during 105 day (ranging from 0.01 to 0.13 mg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup>, Fig. 1 c, d).



**Fig. 1.** Changes in soil emissions induced by the pyrolyzed and unpyrolyzed manure CO<sub>2</sub> (**a**, **b**) and N<sub>2</sub>O (**c**, **d**). Values over the black line mean induced emissions, and values under the black line avoided emissions, (points are mean,  $n = 3 \pm \text{S.D.}$ ). **Source:** Own elaboration.

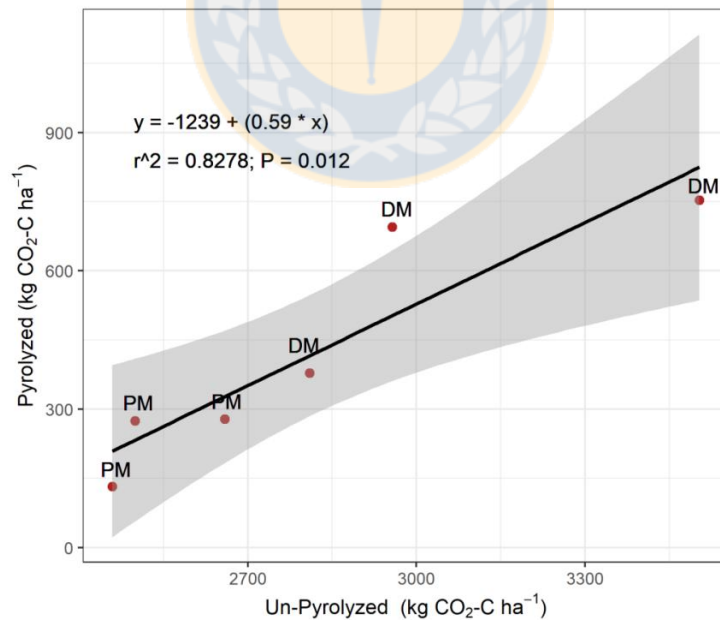
\*In order to evaluate feedstock and biochar mineralization, unamended soil N<sub>2</sub>O and CO<sub>2</sub> emissions were subtracted of all treatments (considering the block design).

Figure 2a show that the cumulative CO<sub>2</sub>-C emissions were over the black line, indicating induced CO<sub>2</sub> emission by all treatments respect to soil control, with significant greater emissions in unpyrolyzed manures (average: 2815 kg CO<sub>2</sub>-C ha<sup>-1</sup>) than in biochar treatments (average: 420 kg CO<sub>2</sub>-C ha<sup>-1</sup>). Regardless of the manure type, the CD<sub>rate</sub> was lower in biochars treatments (average: 8.35 %) than in manures treatments (average: 63.04 %) (Fig. 2b). Finally, the regression suggests a linear reduction of the C emitted as CO<sub>2</sub> from pyrolyzed manures in relation to their respective feedstocks (Fig. 3).



**Fig. 2 a.** Cumulative soil CO<sub>2</sub>-C emissions induced by amendments addition, (unamended soil value was subtracted of all treatments). **b.** Amendments C decomposition rate (CD<sub>rate</sub>, %) after 365 under field conditions. **Source:** Own elaboration.

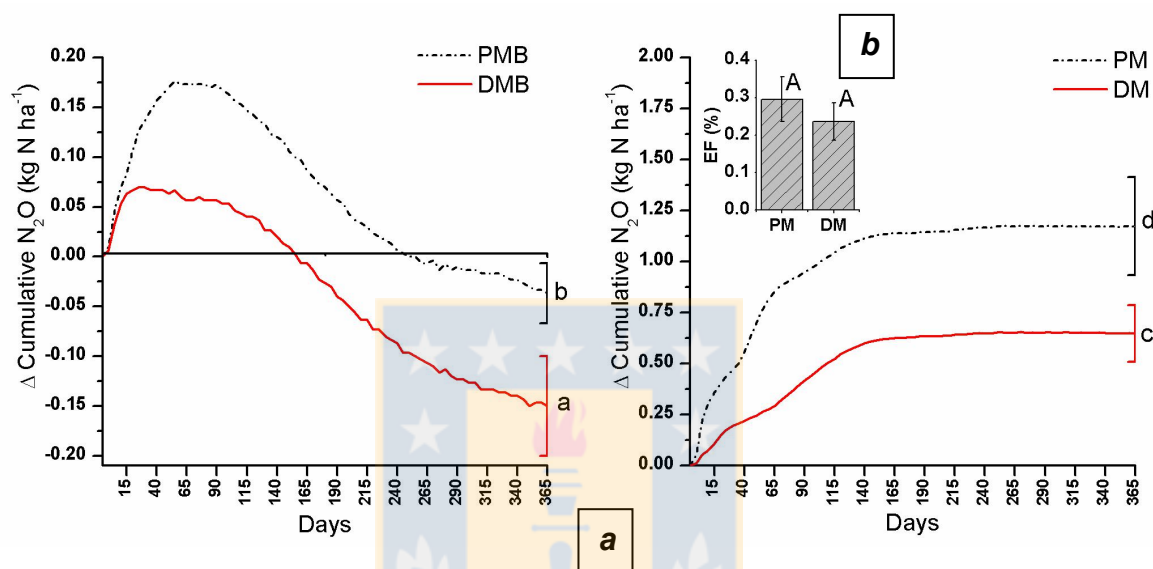
Different lowercase letters between lines indicate significant differences and same capital letters between bars do not differ in Tukey test ( $p \leq 0.05$ ). Lines and bars are mean,  $n = 3 \pm S.D.$



**Fig. 3** Relationship between C mineralized of unpyrolyzed and pyrolyzed manures. ( $n = 6$ ). Grey shaded areas around regressions lines represent 95% confidence intervals. Points: DM, dairy manure, PM, pig manure. **Source:** Own elaboration.



Cumulative N<sub>2</sub>O emissions (induced or avoided; Fig. 4a) after one year by amendments followed the sequence PM > DM > PMB > DMB, ranging from  $-0.15 \pm 0.02$  to  $1.17 \pm 0.24$  kg N<sub>2</sub>O-N ha<sup>-1</sup>. Although pig manure induced higher N<sub>2</sub>O emissions than dairy manure, there was no significant difference in N<sub>2</sub>O Ef between the two manures (on average 0.27%, Fig. 4b). The biochars N<sub>2</sub>O Efs were not calculated because avoided emissions were produced in these treatments after one year (average:  $-0.09$  kg N<sub>2</sub>O-N ha<sup>-1</sup>, Fig 4a).



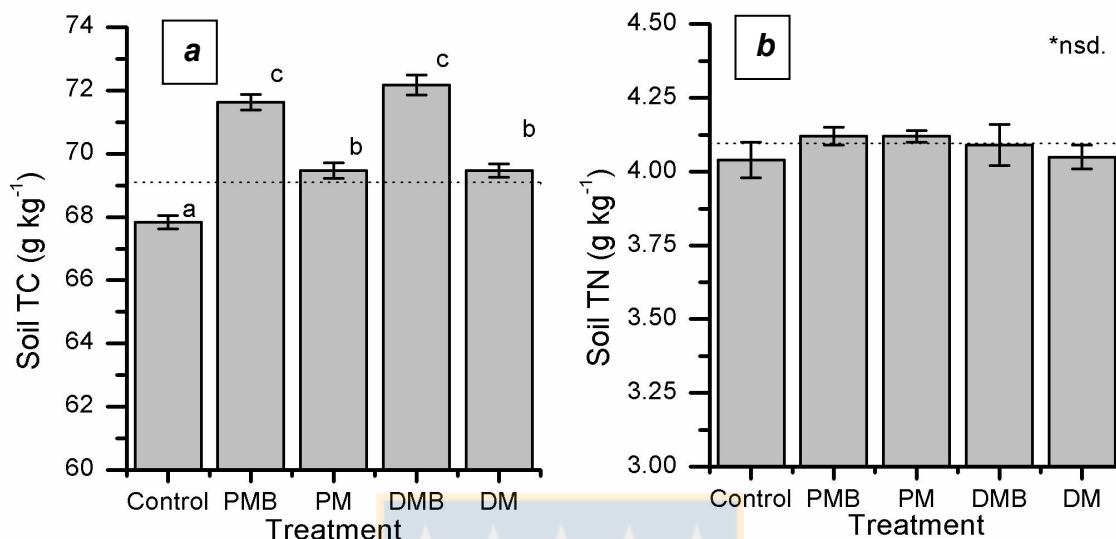
**Fig. 4 a** Cumulative soil N<sub>2</sub>O-N emissions induced (or avoided) by amendments addition, (unamended soil value was subtracted of all treatment). **b** TN emission factor of the manures, Ef (%) after 365 days under field conditions. **Source:** Own elaboration.

\*The cumulative N<sub>2</sub>O emissions of all treatments were analyzed in the same statistical analysis. Manure and biochar were plotted separately considering the difference in scales. Different lowercase letters between lines indicate significant differences and same capital letters between bars do not differ in Tukey test ( $p \leq 0.05$ ). Lines and bars are mean,  $n = 3 \pm$  S.D.

\*Values over the black line in cumulative N<sub>2</sub>O emissions mean induced emissions, and values under the black line avoided emissions.

Soil TC and TN contents in topsoil (0–10 cm) after one year of amendments incorporation are shown in Figure 5 (a, b). Soil TC contents increased significantly in all treatments compared to control ( $p \leq 0.05$ ). As expected, soil

TC was lower in the treatments with unpyrolyzed manures (average: 69.4 g kg<sup>-1</sup>) compared to treatments with biochar (average: 71.9 g kg<sup>-1</sup>). Pyrolyzed or unpyrolyzed manures did not significantly influence soil TN. ( $p \leq 0.05$ ).



**Fig. 5** Soil TC (**a**) and TN (**b**) contents in soil surface (0–10 cm) after one year of amendments incorporation ( $n = 3 \pm \text{S.D.}$ ). Different letters between treatments indicate significant differences in Tukey test ( $p \leq 0.05$ ). **Source:** Own elaboration.

\*nsd. Not significant differences.

\*Dot line represents the initial soil TC or TN.

### 3.2. Global warming potential

The annual GWP<sub>(net)</sub> is shown in Table 2. The negative values obtained in both biochar treatments indicate the mitigation potential of pyrolyzed manures (-4.4 t CO<sub>2</sub>-eq ha<sup>-1</sup>, on average) compared with their feedstocks (14.63 t CO<sub>2</sub>-eq ha<sup>-1</sup>, on average). The changes in soil C stock produced a negative GWP<sub>(Δ C stock)</sub> for all treatments; however, this effect was 59.8% major using biochars than unpyrolyzed manures. On the other hand, there was no significant difference in GWP between biochar treatments and the control by avoided emissions (CO<sub>2</sub> or N<sub>2</sub>O). However, pig and dairy manures increased twice the GWP<sub>(N<sub>2</sub>O emitted)</sub> and GWP<sub>(CO<sub>2</sub> emitted)</sub> compared with the control.

**Table 2.** Effect of pyrolyzed and unpyrolyzed manures on GWP due to changes in soil C stocks and CO<sub>2</sub> and N<sub>2</sub>O emission after one year. (**Source:** Own elaboration)

Treatment	GWP ( $\Delta$ C stock)	GWP (CO <sub>2</sub> emitted)	GWP (N <sub>2</sub> O emitted)	GWP (net)
	t CO <sub>2</sub> -eq ha <sup>-1</sup>	t CO <sub>2</sub> -eq ha <sup>-1</sup>	t CO <sub>2</sub> -eq ha <sup>-1</sup>	t CO <sub>2</sub> -eq ha <sup>-1</sup>
Control	-	10.25 ± 0.81 a	0.27 ± 0.01 a	10.53 ± 0.81 b
PMB	- 15.30 ± 1.84 a	11.09 ± 0.31 a	0.26 ± 0.01 a	-3.95 ± 2.14 a
PM	- 6.58 ± 1.82 b	21.18 ± 1.84 b	0.76 ± 0.10 c	15.36 ± 1.94 c
DMB	- 17.45 ± 1.01 a	12.48 ± 0.74 a	0.21 ± 0.02 a	-4.76 ± 0.71 a
DM	- 6.58 ± 0.84 b	19.92 ± 0.65 b	0.54 ± 0.06 b	13.89 ± 0.22 bc

Mean ± SD (n = 3). Values in the same column followed by the same letters do not differ in Tukey test ( $p \leq 0.05$ ).

#### 4. Discussion

Slow pyrolysis was an effective tool for the management of pig and dairy manures. The lower  $CD_{rate}$  in pyrolyzed manures than in those unpyrolyzed (Fig. 2b) led to a higher C retention in soil-biochar mixtures after one year under field conditions (Fig. 5a). CO<sub>2</sub> fluxes are mostly emitted from agricultural soil as a result of the soil microbial respiration (Ray et al., 2020) being an indicator of amendments stability (Brassard et., 2018). While the pyrolysis of manure generates a detachment of functional groups that contain O and H, producing materials with higher aromaticity, polymerization, and carbonization (Stylianou et al., 2020), usually, unpyrolyzed manures have a high content of volatile matter and they can improve dehydrogenase activity, increasing soil CO<sub>2</sub> fluxes (Gasco et al., 2016). Therefore, unpyrolyzed feedstocks have a short half-life in the soil environment due to the larger labile C pool (Budai et al., 2016).

Although biochars usually have low mineralizable C (Grutzmacher et al., 2018) and high fixed carbon index (Gascó et al., 2016; Cely et al., 2014), here, we observed that both biochars induced CO<sub>2</sub> fluxes at the start of the experiment (Fig. 1a,b). This result indicates that the pyrolyzed manures are not totally inert to biological decay and biochar labile fraction is rapidly oxidized (Bruun et al., 2012). However, CO<sub>2</sub>-C emitted from biochar treatments represent a small proportion of biochar-C and does not compromise its potential to enhance soil C

stocks (Brassard et al., 2018). Zhu et al. (2014) found a  $CD_{rate}$  of 7.62% in soil treated with pyrolyzed manure, while 25% of the applied C was emitted as  $CO_2$  from manure-treated soils. We found greater  $CD_{rate}$  values in manure treatments (Fig. 2b) than those authors, but our experimental period three times as long could explain the higher C mineralization. The release of  $CO_2$  after biochar or manure addition to soil may also result from priming native soil C pools (Gasco et al., 2016; Cely et al., 2014). In this study, it was impossible to confirm whether biochar or manure caused a priming effect on soil C mineralization because the C was not labeled.

Generally, the increases in soil C stock by amendments addition are due to (i) direct C input by the amendment, and (ii) indirect C input (e.g., net primary production). Here, to avoid the effect of indirect C input all plots were maintained without plants, therefore, the soil TC changes can be mainly attributed to C input by the amendments. Soil C stock increased significantly in plots receiving pyrolyzed or unpyrolyzed manures compared with the control (Fig. 5a). The relationship between the C input and the soil TC stock difference (TC treatment – TC control) is considered an approximation of the C retention coefficient, which represents the proportion of C remaining in soil (Maillard and Angers, 2014). According to the soil TC values obtained after a year (Fig. 5), the manure and biochar C retention coefficients were 45 and 92.8% (on average), respectively. These manure-C retention coefficients are higher than the value of 12% +/- 4 reported by Maillard and Angers (2014) in a meta-analysis including studies with an average of 18 years. One limitation of our study is the short time evaluated, where we included only the initial decomposition (one year) and a single application; consequently, the retention coefficient could be overestimated. However, our results clearly show that manure biochar represents a tool for "C protection" since, in relation to the unpyrolyzed manures, a larger amount of the added C is stored on soil through time.

The effect of manure or biochar with climatic purposes can be attenuated or increased according to their  $N_2O$  mitigation potential (Qin et al., 2021). Here, pyrolysis avoided  $N_2O$  emissions because both manure biochars slightly decreased the soil cumulative  $N_2O$  emissions, while their unpyrolyzed feedstock

drastically increased those emissions. Several biotic and abiotic mechanisms affect soil N<sub>2</sub>O emissions; however, microbial denitrification and nitrification are considered the main processes regulating N<sub>2</sub>O fluxes from agricultural soils (Shakoor et al., 2016). Denitrification, such as soil respiration, is a C-consuming process (Gao et al., 2015; Lanza et al., 2016). Therefore, the easy decomposition of animal manure can stimulate denitrification communities, generating high soil N<sub>2</sub>O and CO<sub>2</sub> fluxes (Meyer et al., 2021; Zhou et al., 2017). In fact, Zhou et al. (2017) found that manure application can increase soil N<sub>2</sub>O emissions even more than synthetic N fertilizers because the manures provide labile organic C as energy for denitrification activity. Instead, biochar has high C content, but this C is not easily available to soil microbes (Cely et al., 2014). Another relevant factor mediating soil N<sub>2</sub>O fluxes is the N content of the amendment (Chadwick et al., 2011). On average, Shakoor et al. (2021b) found that animal manure increases N<sub>2</sub>O emissions by 17.7% while biochar application mitigates N<sub>2</sub>O emissions by 19.7%. One of the main drivers influencing this result is the C:N ratio of the amendment; the low C:N ratio provides a favorable environment for denitrification, while higher C:N ratios limit the inputs that promote soil N<sub>2</sub>O emissions (Shakoor et al., 2021b). In our case, the C:N ratio of biochars are higher than those of unpyrolysed manures, but they remain low (<30); however, the NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> contents decreased considerably after pyrolysis (Table 1). Mineral N influences the soil microbial community (Dambreville et al., 2006), affecting the rates of nitrification, denitrification, and respiration (Meyer et al., 2021; Shah et al., 2016; Xu et al., 2017). In this context, Cayuela et al. (2010) analyzing several organic residues found high soil N<sub>2</sub>O emissions mainly linked to amendments with high contents of NH<sub>4</sub><sup>+</sup>.

In this study, pig manure induced higher cumulative N<sub>2</sub>O emissions than dairy manure (Fig. 4a); nevertheless, the N<sub>2</sub>O emitted from N sources in agronomic soils should be expressed per unit of N applied (i.e., N<sub>2</sub>O Ef) (Zhou et al., 2017; Grutmacher et al., 2018). We don't found significant differences between N<sub>2</sub>O Ef from both manures treatments (average, 0.27%), while this factor in both biochar treatments was less than zero. Shakoor et al. (2021) also reported negative N<sub>2</sub>O Ef values after biochar application. This is probably because biochars are not an N-rich source and they can decrease soil N<sub>2</sub>O fluxes,

facilitating electron transfer to denitrifiers and enhance the reduction of N<sub>2</sub>O to N<sub>2</sub> (Cayuela et al., 2015, 2014). On the other hand, high uncertainty is found in the scientific literature about N<sub>2</sub>O Efs after manure additions; the default IPCC value is 1%, but two recent global analyses estimated 0.56% and 0.46% (Zhang et al., 2020; Shakoor et al., 2021), while a mean of 1.87% was reported by Zhou et al. (2017). Unfortunately, none of these meta-analyses included studies developed in Chile, and only three studies from South America were included by Shakoor et al. 2021. Recently, an international project, called DATAMAN, was created to refine the international N<sub>2</sub>O Efs where only one study was reported from Chile (Beltran et al., 2021), indicating a value of 0.41% from an Andisol amended with dairy manure (Alfaro et al., 2018). According to our knowledge, few studies are focusing on this topic in our region. Therefore, our results provide values at the field scale, which reduces this knowledge gap and could be useful for future national GHG inventories.

Overall, the annual GWP<sub>(net)</sub> was largely influenced by the changes in topsoil C stock. However, the CO<sub>2</sub> and N<sub>2</sub>O emissions from the unpyrolyzed manure treatments offset the effect of C retained in the soil. Recently, the special report on climate change indicated that anthropogenic N<sub>2</sub>O emissions are rising primarily due to N application, including manure deposition (IPCC, 2019). In this sense, pyrolysis is an alternative to reduce GWP due to the biochar impact on soil C sequestration via exogenous C inputs (Paustian et al., 2016) and its N<sub>2</sub>O mitigation potential (Cayuela et al., 2014). Our finding confirmed under field conditions that the soil biochar application is a promising option for climate change mitigation (IPCC, 2019), increasing C stock with low impact on the CO<sub>2</sub>-eq produced by soil CO<sub>2</sub> or N<sub>2</sub>O emissions. Previously, in a lab study, Muñoz et al. 2019 found an increase in the C content of different soils with low GHGs emissions after pig or dairy manure biochars application; nevertheless, they separated the CO<sub>2</sub>-eq due to GHG emissions and the changes in soil C contents. Here, we use the changes in soil C stock as CO<sub>2</sub>-eq avoided, obtaining negative GWP<sub>(net)</sub> in biochar treatments. These results suggest the importance of include soil C contents in the GWP analyses, showing the total mitigation potential of different amendments.

## 5. Conclusions

This study demonstrates that slow pyrolysis increases the pig and dairy manure potential for climate change mitigation since, in relation to the unpyrolyzed manures, biochars had a lower GWP<sub>(net)</sub> as soil amendment. Although pyrolyzed and unpyrolyzed manures increase the soil C stock, C stability is higher after pyrolysis, leading to a longer permanence of the added C into the soil. However, further life cycle analyses that consider C losses during the pyrolysis process may be necessary for more accurate C balances. Regarding GHG emissions, the high CO<sub>2</sub> and N<sub>2</sub>O fluxes after unpyrolyzed manure addition offset the positive effect of C addition, while the addition of manure biochars are a promising alternative to reduce the C footprint for pig and dairy farms, promoting the increase of soil C stocks and reducing the soil N<sub>2</sub>O emissions. The success of manure biochar as a soil amendment also indicates that manure pyrolysis could mitigate the pressures associated with sourcing biochar feedstock.

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## CONCLUSIONES GENERALES

La pirólisis de desechos orgánicos surge como una posibilidad de re-utilización de los residuos generados por la agricultura y ganadería hacia el mismo sistema productivo, potenciando la economía circular y evitando la contaminación que generan los materiales en fresco. Sin embargo, diversos aspectos de su factibilidad agronómica y efectos en el ambiente no habían sido evaluados en suelos de origen volcánico. En esta investigación, se determinó que la aplicación de biocarbón como material enmendante en suelos de origen volcánico y no volcánico tuvo efectos relevantes sobre el incremento de C en el suelo, modificó propiedades químicas y biológicas de los suelos y disminuyó emisiones de GEI; contribuyendo a mitigar el impacto sobre el potencial de calentamiento global del sistema agropecuario estudiado.

En aspectos agronómicos, se demostró el potencial del uso de biocarbón generado a partir de diferentes tipos de estiércol (guano de ave, estiércoles de cerdos y de ganado lechero) como enmendante de suelos volcánicos. Una única aplicación de los biocarbones al establecimiento del cultivo de sorgo forrajero incrementó el rendimiento, con menor impacto sobre el calentamiento global que la adición de estiércoles sin pirolizar o la fertilización mineral del cultivo. El incremento del rendimiento se asoció a la modificación de propiedades claves de los Andisoles como son su pH y contenido de P disponible. El potencial de encalado y contenido de nutrientes disponibles en 11 t ha<sup>-1</sup> de biocarbón fue suficiente para obtener rendimientos similares a la fertilización mineral usada en el cultivo, incrementando además el P y K disponibles residuales después de la cosecha.

Respecto a las implicancias ambientales de los biocarbones, se determinó que los biocarbones de estiércoles de cerdos y de ganado lechero incrementaron el contenido de C en el suelo, lo que se demostró en condiciones de laboratorio y de campo, durante aproximadamente un año de ensayo. En condiciones de campo, el biocarbón proveniente de desechos de la industria forestal (aserrín de Eucalipto) resultó ser más efectivo en el incremento de C estable en el suelo, incrementando el contenido de C recalcitrante y disminuyendo las emisiones de N<sub>2</sub>O; mientras, los biocarbones de estiércol aumentaron los contenidos de C

oxidable posiblemente asociado al aumento del rendimiento y por tanto a la transferencia de C al suelo vía las raíces.

Se demostró que la pirólisis es una herramienta efectiva para aumentar la estabilidad del C del estiércol, consiguiéndose menores tasas de descomposición (C emitido como CO<sub>2</sub>) con estiércoles pirolizados que sin pirolizar. Sin embargo, para balances más precisos de C se recomienda el desarrollo de estudios de análisis de ciclo de vida donde se consideren las pérdidas de C asociadas a puntos críticos del proceso (transporte, almacenaje, proceso de pirólisis y aplicación al suelo).

El efecto del biocarbón sobre las emisiones de GEI varió de acuerdo al tipo de suelo y materia prima añadida, sin embargo, solamente el material carbonoso de cama de ave, que posee los más altos contenidos de N disponible, incrementó las emisiones de N<sub>2</sub>O del suelo, tanto en condiciones de laboratorio como de campo. En general, el uso de biocarbón de estiércol de cerdo y de ganado lechero emite menos N<sub>2</sub>O que la fertilización habitual del sorgo forrajero y que dosis equivalentes de sus materias primas (estiércoles sin pirolizar).

Las emisiones de CO<sub>2</sub> y CH<sub>4</sub> del suelo a escala de laboratorio disminuyeron con la aplicación de biocarbón aparentemente asociadas a la modificación de la actividad bioquímica del suelo (disminución de la actividad de β-glucosidasa). Sin embargo, ningún efecto significativo fue encontrado sobre las emisiones acumuladas de CO<sub>2</sub> durante un año a escala de campo, donde la emisión de CH<sub>4</sub> no fue evaluada debido a las condiciones aeróbicas predominantes del suelo.

A modo general, se concluye que la pirólisis del estiércol produce enmendantes de suelo con alto potencial para su uso en cultivos forrajeros en Andisoles, evitando la descomposición natural del estiércol y favoreciendo el reciclaje de nutrientes, a la vez que se incrementa el almacenaje de C en el suelo. Por lo que se sugiere su producción y aplicación como una práctica agronómica y ambientalmente factible, que además brinda una alternativa al manejo de residuos generados desde sistemas ganaderos.