## Coffee-waste biochar and nano-biochar applications to reduce nitrous oxide and carbon dioxide emissions from agricultural soils

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Denitrification is one of important pathways responsible for nitrous oxide ( $N_2O$ ) emissions from soil. Biochar can decrease  $N_2O$  emissions because it acts as an electron shuttle that would enhance the denitrification processes. It also provides favorable conditions for denitrifers by increasing soil pH and water retention capacity. However, research on effects of biochar with different particle sizes on  $N_2O$  emissions is currently limited. The objective of the study was to determine effects of biochar and nano-biochar applications on  $N_2O$  and  $CO_2$  emissions in the denitrification processes with reference to surface structures of the biochar materials, soil pH, electrical conductivity (EC), mineral nitrogen, and soil type.

Topsoil soil samples, collected from a paddy field in Ushimado, Okayama (TC 14.7 g kg<sup>-1</sup>, CN ratio 10.2) and a greenhouse at Kochi University (TC 62.6 g kg<sup>-1</sup>, CN ratio 16.0), Japan, were air-dried and 2-mm sieved for the following experiment. Soil NO<sub>3</sub><sup>--</sup>N contents were 3.5 and 373 mg N kg<sup>-1</sup> for Ushimado (U) and Kochi (K) soils, respectively and it increased in subsamples of U soil to 400 mg N kg<sup>-1</sup> (U400) to eliminate the effect of initial NO<sub>3</sub><sup>--</sup>N content. Coffee grounds waste was pyrolyzed for biochar at 600°C for 1 hour and that mixed with Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O for nano-biochar at 900°C for 1 hour. Values of pH and EC (1:10) were 10.0 and 0.4 dS m<sup>-1</sup> for biochar and 10.1 and 2.8 dS m<sup>-1</sup> for nano-biochar. Five grams of air-dried soil amended with or without 5% biochar materials were adjusted to 100% water holding capacity and anaerobically incubated at 25°C for 4 days in 125-mL glass bottles in triplicate. Concentrations of N<sub>2</sub>O and CO<sub>2</sub> in the headspace of bottles were analyzed with gas chromatograph (GC-8A, Shimazu, Japan) equipped with an electron capture detector (ECD) and a thermal conductivity detector (TCD), respectively.

Fluxes of N<sub>2</sub>O were generally the largest from K soil, followed by U400 and U soils. The lowest N<sub>2</sub>O emissions in U soil occurred due to much lower initial NO<sub>3</sub><sup>-</sup>-N content. Cumulative N<sub>2</sub>O emissions decreased in K and U400 soils amended with biochar and nano-biochar. These are probably due to the electron shuttle effect and pH increase by application of these biochar materials. Moreover, nano-biochar reduced more cumulative N<sub>2</sub>O emissions than biochar, which can be explained by Fe added in nano-biochar production and a larger specific surface area of nano-biochar (325 m<sup>2</sup> g<sup>-1</sup>) than that of biochar (1.7 m<sup>2</sup> g<sup>-1</sup>). Trends of NO<sub>3</sub>-N content decreases in each soil were similar among treatments with and without biochar materials, indicating the last reduction process of N<sub>2</sub>O to N<sub>2</sub> in denitrification was more enhanced by application of nano-biochar. Emissions of CO<sub>2</sub> decreased in K and U400 soils amended with nano-biochar than with biochar. Nano-biochar with a larger specific surface area would have absorbed more CO<sub>2</sub> than biochar. Nitrogen mineralization in soils amended with nano-biochar was lower than with biochar, which is indicated by more increases in NH<sub>4</sub><sup>+</sup>-N content in nano-biochar amended soils.

Applications of biochar and nano-biochar reduced  $N_2O$  and  $CO_2$  emissions from different two agricultural soils when  $NO_3$ -N contents were as high as 400 mg kg<sup>-1</sup>. Nano-biochar reduced  $N_2O$  emissions more than biochar did. This is because nano-biochar had a larger specific surface area and increased more soil pH than biochar. Further research is needed to investigate effects of biochar and nano-biochar on soils with

different microbial and chemical properties before applying them to a real field condition.

Keywords: biochar, nitrous oxide, carbon dioxide