Application note 028

The impact on CO_2 emissions from soil of photooxidation of pyrogenic organic matter

Pyrogenic organic matter (PyOM) produced during forest fires is an important component of soil C cycling in many forest systems influencing both the rate of stable C input to soils and the microbial interaction with soil organic carbon (SOC) pools. We have an incomplete understanding of how the environmental transformation of PyOM, such and photochemical and microbial weathering, influences its decomposition in soil and subsequent SOC dynamics. PyOM is also an important source or sink of atmospheric CO_2, adding to or subtracting from the CO_2 from mankind's combustion of fossil fuels. Hence the rate and mechanism of oxidation of carbon in soils is important not only for the health of soils, but also for models of the earth system, in order to accurately predict future climate scenarios.

The Sercon cryoprep – IRMS system was used to study rates of CO_2 emissions from a natural soil, and a soil mixed with charred Ponderosa pine wood (mimicking debris from biomass burning), (a) with the PyOM exposed to UV light to imitate natural weathering, and (b) with the PyOM unexposed. Because the Ponderosa pine sapling was grown in an atmosphere enriched in $^{13}CO_2$, the rates of oxidation of the PyOM and the soil in the mix can be measured separately by analysing the $\delta^{13}C$ of the CO_2 released.

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The soil studied was taken from a biological station in Michigan USA, in an area last burned 32 years earlier. Although dried, and sieved to remove plant litter > 2mm, the soil was not sterilised, in order to maintain its bacterial composition. The $\delta^{13}C$ value of the soil was -27.5 ‰. The ponderosa pine saplings were charred by heating to 450˚C under N_2 for 5 hours to simulate the incomplete combustion of biomass burning products. The resultant $\delta^{13}C$ value of PyOM was 848 ‰. Some PyOM was exposed to short wavelength UV light (254 nm) for a month, approximately simulating 11 day's mid-latitude exposure at about 3000m altitude.

During this study, the soil was incubated for 5 days after re-wetting. Subsequent incubations were then carried out for a further 30 days on samples of soil, of soil mixed to 10% with unexposed PyOM, and of soil mixed to 10% with exposed PyOM. This second incubation was in the dark at 25˚C, rates of production of O_2 and CO_2 were measured daily, and samples were re-wetted at day 24. Throughout, $\delta^{13}C$ in the CO_2 was measured with a Sercon 2022 IRMS and Cryoprep trace gas pre-concentrator. At the end of the incubation, enzymes produced by microbe activity were measured, as were the decomposition products lignin and substituted fatty acids.

Results showed:

1. UV-exposed PyOM itself produced 10% less CO_2 than the unexposed PyOM over the full 30 days. However the rate was 98% less on the first day (when the unexposed PyOM produced over 0.6 mg/g) - weathering of biomass-burning products mixed with soil greatly reduces their short-term oxidation rate.
2. On average, adding PyOM to the soil halved the soil's rate of production of CO2, with a slightly smaller average production from adding UV-exposed PyOM than from adding unexposed PyOM.
3. After re-wetting the samples at day 24, the soil mixed with PyOM produced only 1/5 the CO_2 of the unmixed soil – a very significant difference.

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In conclusion, the use of biogenic samples raised in enriched $^{13}CO_2$, together with the analysis of $^{13}CO_2$ emitted from soils in experiments where the soils and the biogenic samples are mixed, is a powerful tool for distinguishing emissions from the biogenic samples themselves from emissions from the soils. In this experiment, CO_2 emission from the soil was halved by the addition of 10% charred wood. There was little difference in soil emission between addition of weathered wood and unweathered wood, but emission from the wood itself was reduced by weathering, especially in the short term.

Sercon are grateful to the Filley group at Purdue University for contributions to this applications note. Further information and data from the study can be found in **R. Wang, C.D. Gibson, et al., "Photooxidation of pyrogenic organic matter reduces its reactive, labile C pool and the apparent soil oxidative microbial enzyme response",** *Geoderma* **293**, 10–18 (2017).