



Hydrogen Pyrolysis as a new tool to assess the abundance and isotopic composition of Pyrogenic Carbon

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Hydrogen pyrolysis (HyPy) can be used to quantify the production, fate and stable isotope composition of the pyrogenic carbon (PC) produced by vegetation burning. HyPy is pyrolysis (up to $\sim 600^{\circ}\text{C}$) combined by high hydrogen pressures ($> 10 \text{ MPa}$) in the presence of a catalyst. Application of HyPy to sediments, soils or organic samples results in the reductive removal of all labile organic matter. Therefore, this technique offers great potential to effectively isolate and quantify pyrogenic carbon (commonly referred also as black carbon) in a rapid and cost effective manner. The carbon isotope composition of PC can provide information as to the type of vegetation burnt, but this study also takes into account some of the potential complications in its interpretation. The present study aims quantify a 'savanna isotope disequilibrium effect', inferred from the imbalance shown by models of terrestrial ^{13}C discrimination that indicate that about one quarter of the gross primary productivity (GPP - total carbon fixed as biomass by plants) by the terrestrial biosphere is attributable to tropical savanna/grassland plants that use the C_4 photosynthetic pathway, while field observations suggest that the fraction of C_4 -derived biomass in soil organic carbon in savanna systems is much lower than GPP estimates imply. Quantifying this effect has significant implications for correctly interpreting soil and palaeosol carbon isotope data, and modelling studies that use variations in the atmospheric $\text{CO}_2 \delta^{13}\text{C}$ record to apportion sources and sinks of CO_2 .

Here, we present preliminary results showing the significance of HyPy in carbon cycle studies that are being carried out in tropical savannas in North Queensland (Australia). In the study, controlled savanna burning experiments are being conducted to capture organic and PC particulates to enable a full isotope mass balance for carbon during savanna burning. In addition, sediment is being collected over a series of micro-catchments covering the broadest possible range of C_3 and C_4 environments, in order to enable robust interpretation of the sedimentary record of the abundance and isotopic composition of PC.

The results indicate that the $\delta^{13}\text{C}$ value of PC in the sediments is decoupled from the $\delta^{13}\text{C}$ value of total organic carbon (TOC), suggesting that hyPy does effectively isolate a component that is distinct in isotopic composition. The $\delta^{13}\text{C}$ value of PC is up to 6\textperthousand higher than the $\delta^{13}\text{C}$ value of TOC, with the difference being largest when the $\delta^{13}\text{C}$ of TOC abundances in the sediments is low. This suggests a significant component of C_4 -derived PC is present in the sediments, even when the proportion of C_4 biomass in the catchment is relatively low. This in turn, provides evidence for the preferential combustion and transport of C_4 -derived PC in tropical savannas. Savanna fires preferentially burn the grass understorey rather than large trees, leading to a bias toward the finer C_4 -derived PC being exported from a fire and accumulated in the sedimentary record while large particles of C_3 -derived PC are more likely to remain at the site of burning.

The preliminary data suggests that application of HyPy in environmental studies enables accurate quantification of an essential component of the terrestrial C cycle, and more so now that the topic is gaining momentum given the potential of PC to become a powerful tool for soil carbon sequestration. Moreover, the use of HyPy also enables the reliable determination of the stable composition of PC, which will enable deeper understanding of the dynamic role of biomass burning in the global carbon cycle.