

Carbon in Manganese Oxides

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We present experimental data showing how manganese oxides trap dissolved organic carbon (DOC) at 3%w/wC transforming it into two isotopically distinct fractions, one of which is highly thermally stable. We examine in detail the physiochemical relationships between the trapped organic carbon and manganese oxide, which is present as birnessite coatings on sand grains in a water treatment works filter bed (Mosswood WTW, Northumberland, UK, Co. Durham, UK, 54°51'N - 53°59'W). The birnessite coating is analysed using thermogravimetric analysis (TGA) combined with differential scanning calorimetry (DSC) and mass spectroscopy. Carbon dioxide (m/z 44) is detected in the 200-375°C and the 550-750°C range and the DSC curve detects exothermic reactions at 270°C and 600°C, that could be associated with labile and refractory carbon [1] and a small endothermic reaction at 712°C, which could be associated with inorganic carbon (calcium carbonate present at 0.5%w/w). The trapped organic carbon has been isotopically fractionated and the labile fraction has an enriched $\delta^{13}\text{C}$ signature (-24.9‰) compared to the original DOC (-27‰). Our data supports a previously unknown mechanism for carbon fractionation and stabilisation within manganese oxides, which has significant implications for our understanding of the carbon cycle.

[1] Lopez-Capel *et al* (2005) *Soil Sci. Soc. Am. J.* **69**, 136-140