

## NATURALLY OCCURRING CHARCOAL: A TRACE ELEMENT SINK?

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Charcoal (burnt plant remains) forms a significant proportion of the organic carbon content of Australian soils and is relatively widespread given the high frequency of forest fires in Australia (Skjemstad *et al.* 1998). The strong ability of charcoal to adsorb organic compounds and metal ions has been exploited in water treatment processes for the removal of organic wastes and micro-pollutants as well as in the recovery of metals from various industrial processes (Gustafsson *et al.* 2003). The strongly adsorptive nature of activated or artificial charcoal stems from its large surface area as well as its high porosity and reactive chemical structure (Skjemstad *et al.* 1998). Given that up to 50% of the soil carbon store (dependent on soil type) consists of charcoal (Skjemstad *et al.* 1998), it is possible that the immobilisation of metals through their interaction with natural charcoal may be a significant sink that has yet to be accounted for in the biogeochemical cycling of trace elements in terrestrial ecosystems. Testing this hypothesis becomes problematic considering the typically small size (< 53 µm; Skjemstad *et al.* 1998) of charcoal particles that occur naturally in Australian soils. Manually isolating such charcoal particles has proven difficult and exhaustive in the past. Hence, in this study, we test the robustness of a typical sequential extraction technique by applying it to naturally occurring charcoal that had been spiked with five different concentrations of metals (Al, Cr, Cu, Ni, Zn, Cd, Ag, Pb). The method was then applied to soils that were mixed with this spiked charcoal. Briefly, our sequential extraction scheme was based on that of Hall *et al.* (1996) and consisted of the following five extractions in the order: 1) Sodium acetate (targeting the acid-exchangeable-carbonate fraction); 2) sodium pyrophosphate (organic fraction); 3) ammonium oxalate (amorphous iron/manganese-oxides); 4) hydroxylamine hydrochloride (crystalline iron/manganese oxides); and, 5) residual (*aqua regia* digest).

Surprisingly, the majority of metals added to the charcoal were extracted in the fractions targeting both the amorphous and crystalline iron and manganese oxides, at low added metal concentrations. At higher concentrations of metals added to the charcoal, the metals were mostly extracted from the adsorbed-exchangeable-carbonate fraction (e.g., Cu in Figure 1). When the spiked charcoal was added to soils, a similar trend was observed in the sequential extraction of these soils (Figure 2). Higher concentrations of metals (compared with the control) were extracted, for the charcoal-amended soils, in the same extraction fractions as the charcoal-only extractions (compare Figures 1 and 2). It could be inferred that a large pool of trace elements could potentially be misrepresented when the sequential extraction technique is applied, particularly for soils in which there is a large concentration of charcoal. Our results demonstrate that a selective sequential extraction is inadequate for quantifying the significance of the charcoal trace element pool. Hence, there is still a large gap in knowledge with regard to the significance of charcoal in “real” soils. This is especially true with respect to the development of appropriate methodology that will allow us to selectively examine charcoal as a trace element pool.

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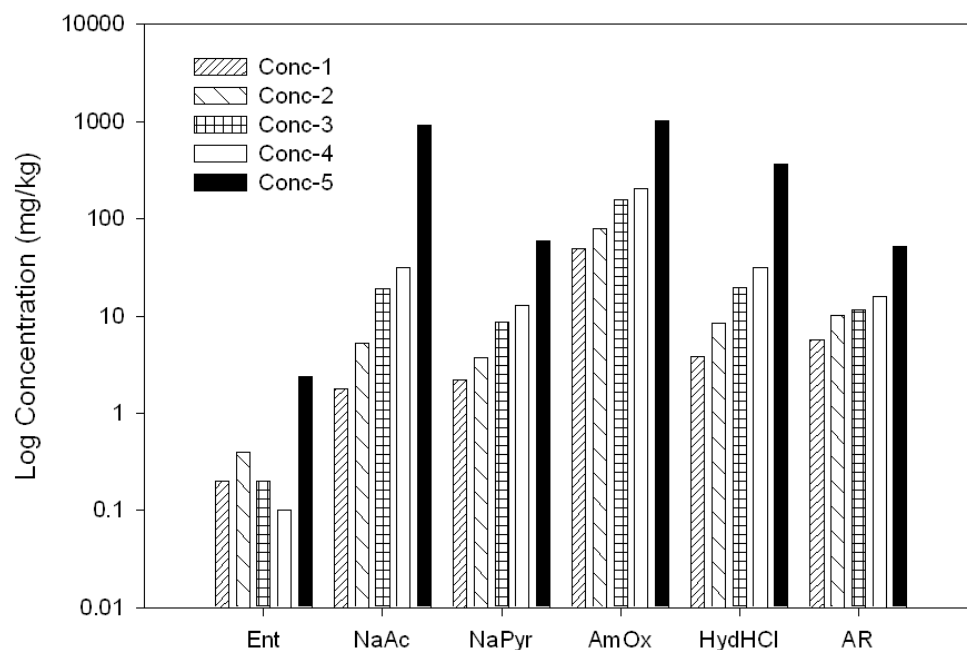


Figure 1. Concentration of copper extracted in each fraction of a sequential extraction scheme on charcoal loaded with five different concentrations of metals, grading from lowest concentration added (Conc-1) to highest (Conc-5). Ent- entrained fraction; NaAc- sodium acetate extractable; NaPyr- sodium pyrophosphate extractable; AmOx- ammonium oxalate extractable; HydHCl- hydroxylamine hydrochloride extractable and AR- aqua regia extractable.

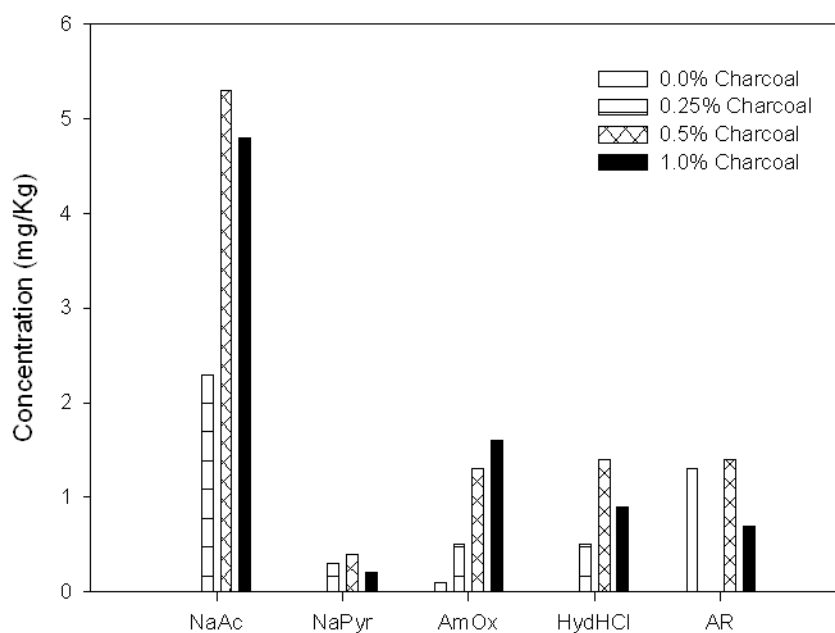


Figure 2. Sequential extraction results for copper in a sandy soil amended with metal-loaded charcoal. The graph shows an increasing concentration of metals extracted at increasing charcoal concentrations in the same fractions corresponding to the charcoal-only sequential extraction for copper. NaAc- Sodium acetate extractable; NaPyr- sodium pyrophosphate extractable; AmOx- ammonium oxalate extractable; HydHCl- hydroxylamine hydrochloride extractable and AR- aqua regia extractable.