

The effect of oven drying and grinding on the partitioning of copper and nickel in acid sulfate soil materials

Salirian R Claff, Edward D Burton, Leigh A Sullivan, Richard T Bush

^ASouthern Cross GeoScience, Southern Cross University, Lismore NSW, Australia, Email salirianclaff@gmail.com

Abstract

A sequential extraction procedure was applied to an acid sulfate soil profile to investigate the effect of sample preparation on the partitioning of copper and nickel. The samples were either used as collected (field condition) or subjected to the standard sample preparation, commonly applied to soils to be stored for subsequent analysis (i.e. oven drying and grinding). This effect was investigated both in the oxidised zone and unoxidised zones of the soil profile. Both sets of samples (i.e. oxidised and reduced) showed a substantial loss in the HNO₃-extractable fraction in the dried and ground soil materials, and in the reduced materials there was with a corresponding increase in the copper and nickel recovered in the MgCl₂ and HCl fractions. Based on these findings, it is recommended that when assessing metal partitioning, acid sulfate soil samples be analysed in their field condition.

Key Words

Acid sulfate soils; metals; sample preparation; sequential extraction procedure

Introduction

When analysing soils for metal content, the most common method of sample preparation is to sieve, then air-, oven-, or freeze-dry the soil; the dried material is then sieved and ground (Ahern *et al.* 2004; Klitzke and Lang 2007). Dried, ground soils are homogenous by nature, and the material is relatively stable over extended periods of time (Rao *et al.* 2008). By contrast, the analysis of field condition soils has a number of difficulties, including the inherent heterogeneity of soil materials, variable soil moisture content, as well as the need for a larger soil sample mass. For these reasons, dried, ground soils are often chosen for total metal analysis in preference to field condition soil samples (Furman *et al.* 2007; Rao *et al.* 2008).

The availability (in terms of the toxicity and mobility) of a given metal is linked to its geochemical form. Because of this, total metal concentrations give little indication as to the bioavailability, and hence toxicity of a metal (Gleyzes *et al.* 2002). When analysing a soil for the total metal content, the soil condition is not important – the aim of the procedure is to recover the maximum amount of a given metal present in the soil. When looking at partitioning and the various forms of the metal, sample preparation can have a potentially significant affect on the metal partitioning.

By gaining an understanding of how solid phase metals are stored in the soil some predictions can be made as to the present and future mobility and toxicity, and thus an assessment of potential environmental risk can be made. Sequential extractions can be useful in assessing phase associations of metals and other toxicants of interest. This approach, however, provides results that are only as representative as the samples being analysed. Acid sulfate soils contain a variety of soil redox conditions, from oxidising to reduced. As such, the mineralogy of redox sensitive components such as iron, sulfur and manganese, affect other metals present in the soil profile. The standard soil pretreatment of drying and grinding can potentially have a significant impact on the mineralogy of soils containing reduced minerals, and thus change the portioning of metals and other contaminants within the soil (Bordas and Bourg 1998).

The aim of this study was to assess whether metal partitioning, as measured by a sequential extraction procedure, was affected by the common pretreatment of drying and grinding.

Methods

Sample Collection

The study site is situated near Port Macquarie, NSW (31°25'38"S, 152°51'05" E). A pit was dug to 2.4 meters, and sampled in 13 depth increments, 7 situated in the oxidised zone and 6 in the unoxidised zone. Samples to be analysed as field condition were packed into acid-washed 150ml polypropylene containers, with no headspace, while soils to be dried, sieved and ground (standard treatment) were placed in sealed

plastic bags, with the air extruded, and then transported frozen.

Sample Analysis

All glass- and plastic-ware was soaked in 10% (v/v) nitric acid and rinsed with deionised (Milli-Q) water before use. All reagents were analytical grade and solutions were prepared using Milli-Q water. Both sample pretreatments were subject to the same sequential extraction procedure (Table 1). The supernatant from each extraction step was analysed for copper and nickel by inductively coupled plasma-atomic emission spectrometry (ICP-AES: Perkin-Elmer DV4300) or inductively coupled plasma-mass spectrometry (ICP-MS: Perkin-Elmer Optima 4000/30DV), calibrated using commercially available standards. Samples were first analysed using ICP-AES, and samples containing metal concentrations less than the detection limit were then analysed by ICP-MS.

Table 1. Summary of the six step sequential extraction procedure used to assess metal fractionation.

Fraction	Treatment (extractant, duration of extraction; or method)
1. Exchangeable (MgCl ₂)	1M MgCl ₂ , 1 hour
2. Acid Soluble (HCl)	1M HCl, 4 hours
3. Organic (Pyro)	0.1M Sodium Pyrophosphate, 16 hours
4. Crystalline oxide (CBD)	0.35M Acetic Acid/0.2M sodium citrate buffer with 50g/L sodium dithionite, 4 hours
5. Pyrite Bound (HNO ₃)	Conc. HNO ₃ , 4 hours
6. Residual (Res)	EPA method 3050, (hot acid and peroxide method)

Results and Discussion

Drying and grinding the soil affects the metal partitioning in both the oxidised and the unoxidised soil materials (Figure 1). In most cases, drying and grinding results in a greater percentage of the nickel or copper being extracted in the more environmentally available fractions (that is exchangeable and acid soluble). The exception to this was nickel extracted from the oxidised zone. This is a function of the far greater total amount of nickel extracted following the drying and grinding of the soil materials (average in the dried and ground samples was 24mgkg⁻¹, as opposed to 17mgkg⁻¹ in the field condition samples). Most of this “extra” nickel is recovered in the residual fraction, as a function of the drying and grinding, thus altering the partitioning patterns calculated through the percentage recovery.

In both the oxidised and the unoxidised soils, the field condition soils have a much larger proportion of the total metal in the HNO₃-extractable fraction. In this HNO₃ extraction, metals are recovered through the dissolution of pyrite and other reduced sulfide minerals. Pyrite is stable under reducing conditions, and thus oxidation of the reduced materials can lead to an increase in the amount of a metal in more available fractions (Bordas and Bourg 1998), – this was observed in this study. The decrease in the amount of HNO₃-extractable copper and zinc in the samples is commensurate with the increase in MgCl₂- and HCl-extractable copper and zinc in the oven dried and ground samples.

There was a substantial decrease in pyrophosphate-extractable copper following drying and crushing of the soil materials. This was observed in both the oxidised and reduced soil samples. Copper has a strong affinity for organic matter (McLaren and Crawford 1973), and the oxidation of the organic matter can lead to metal release from more environmentally available phases (Stephens *et al.* 2001). The opposite is observed for nickel, with a slight increase in the proportion of nickel extracted with pyrophosphate in the oven dried sediments. Nickel does not have such a strong association with the organic fraction, and this increase may be due to the oxidation of more recalcitrant organic fractions, made available in pyrophosphate during the drying and grinding process.

The percentage recovery of both copper and nickel was observed to increase in residual fraction following the drying and grinding procedure. This is most likely due to the greater surface area of the soil material,

the exposure of previously protected mineral surfaces, as well as oxidation through the drying process. Sample grinding may also expedite the oxidation of the soil materials.

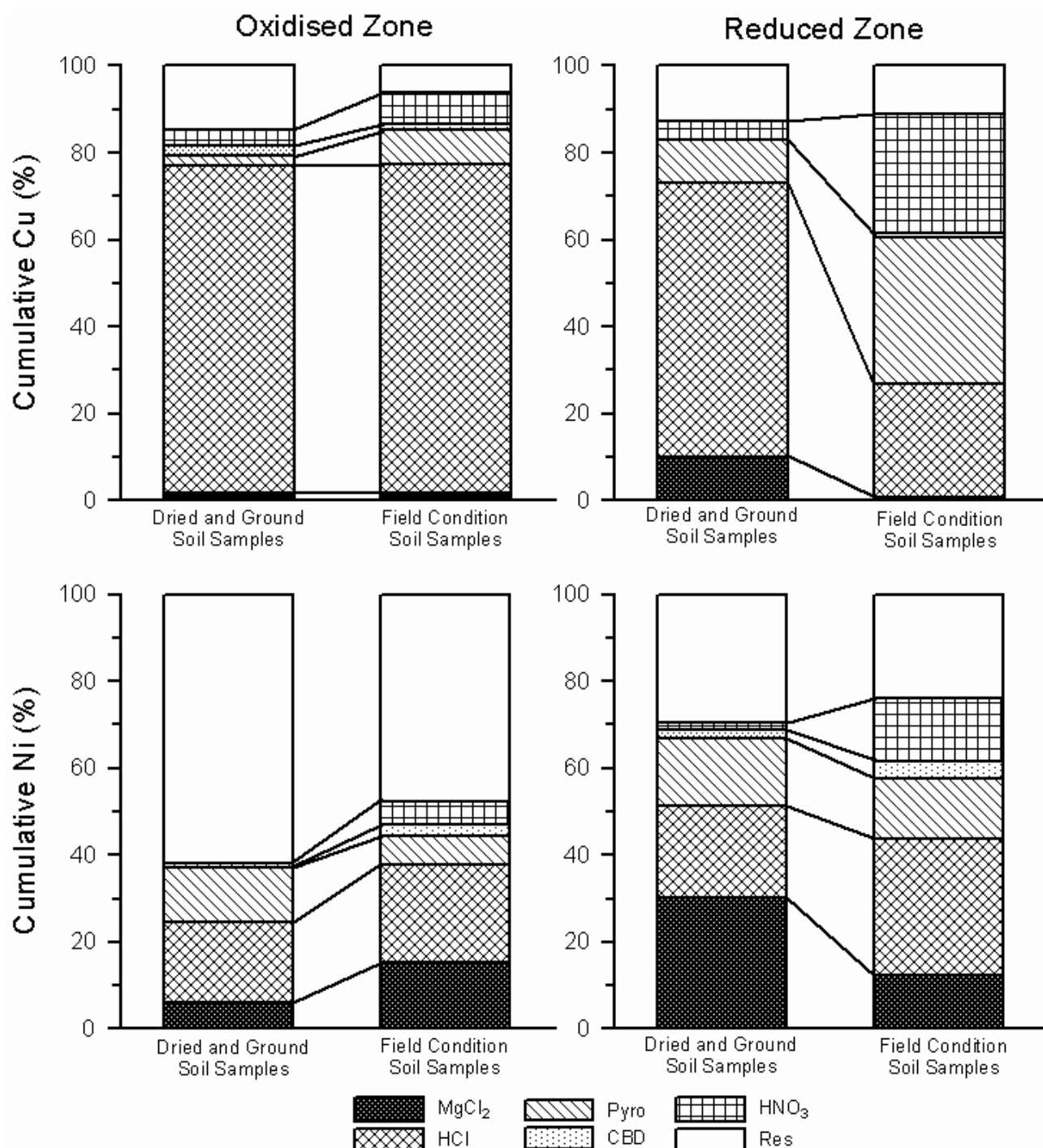


Figure 1. Distribution of copper and nickel in the reduced and oxidised zones of an acid sulfate soil profile. The fractions are presented as a percentage of the total extracted.

Conclusion

Drying and grinding significantly affected the determination of metal partitioning in the examined soil materials. This was especially apparent in the reduced materials, where there was a decrease in the HNO₃ (pyrite) extractable fractions, and a redistribution to the MgCl₂- and HCl-extractable fractions, both more readily available forms. The results indicate that the use of dried and ground soil materials has the potential to overestimate the biological impact of metals in a soil material, and marginalise the effect of metals associated with reduced sulfide phases (i.e. pyrite). Based on these findings, it is recommended that soil samples be used in field condition when assessing the potential impact of metals in acid sulfate soil landscapes.

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