

# Changing Metal Lability, Fractionation and Toxicity in an Oxidising Sediment

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## INTRODUCTION

The dredging of anoxic sediments exposes them to an oxidising atmosphere which may alter metal speciation and availability. Sediment that was contaminated with heavy metals and mineral oil and had a high loss on ignition (26%) and low carbonate content (0.06%) was dredged from the site of a phytoremediation field trial and was oxidised over a period of 48 days. The changing labilities of Cd, Cu, Ni and Zn (totals: 20, 598, 61 and 2415 mg/kg, respectively) were investigated using isotopic dilution techniques (E values), which take into account both solution concentrations and exchangeable metals on the sediment solid phases. Changing fractionation was quantified by the use of an anoxic sequential extraction scheme, modified from Clark et al. (2000). Changing toxicity of the sediment was tested through a root elongation study.

## METHODS

Sediment was dredged from the canal bottom and stored, covered with a layer of native water, in polyethylene barrels, until needed.

### Isotopic Dilution Techniques

This technique was used to quantify metal lability changes during oxidation. Sediment was oxidised in a layer 1 cm deep for up to 48 days. The method used was from Lombi et al. (2003) although samples were spiked with <sup>63</sup>Ni as well as <sup>109</sup>Cd, <sup>65</sup>Zn and <sup>64</sup>Cu. The Ni spike contained 1886 kBq/mL <sup>63</sup>Ni. A 1:10 sediment-to-deionised water suspension was shaken in a N<sub>2</sub> atmosphere for 4 days to allow equilibration. The radioactive spike was added, the tube was purged with N<sub>2</sub> and the samples were shaken for a further 3 days to equilibrate (1 day in the case of Cu). After centrifugation at 3000 g for 30 mins, the supernatant was filtered through a 0.2 µm filter. Gamma and beta radiation were counted as appropriate. A resin step was added as per Lombi et al. (2003). Metals were analysed by ICP-OES, ICP-MS or GF-AAS where necessary.

### Sequential Extractions

Sediment was oxidised in air for up to 48 days. The anoxic fractionation scheme used was modified from Clark et al. (2000). Metals fractions are defined as “exchangeable” (H<sub>2</sub>O and 0.1 M NH<sub>4</sub>Cl extractable), “carbonate bound/adsorbed” (1 M NaOAc buffered to pH 5 extractable), “Fe/Mn oxides” (dithionite/citrate extractable) and “sulphides and organics” (HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> microwave digested). Metals were analysed by ICP-AES.

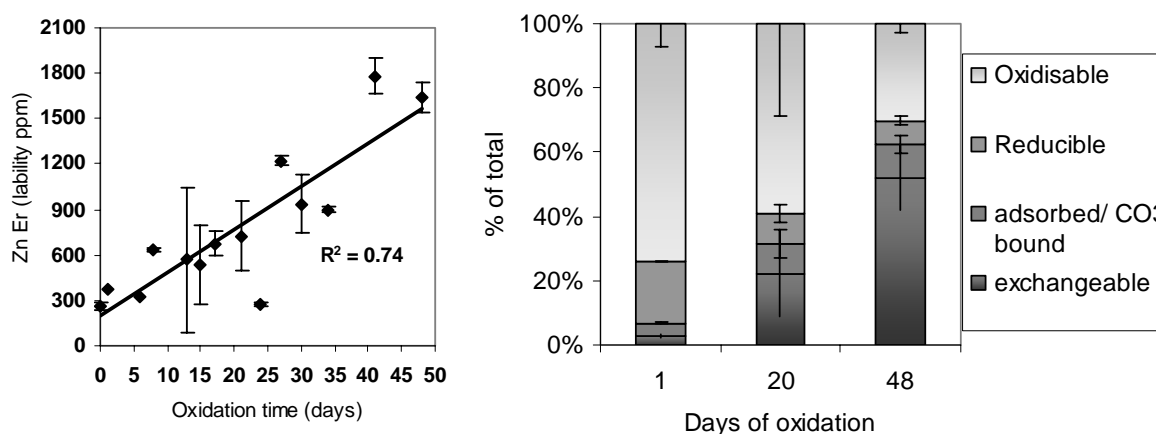
### Root Elongation

Sediment was oxidised over 47 days and root elongation of pre-germinated canola (*Brassica napus L*) seedlings over 72 hours were recorded as a measure of the toxicity of the sediment. Seedlings were kept in the dark at 20°C.

## RESULTS AND DISCUSSION

A natural drop in pH from ~6 to ~3 occurred over the 48-day oxidation period due to oxidation of sediment sulphides to sulphates. The lability of all metals increased with increasing oxidation. Zinc (Fig. 1) and Ni labilities increased from <10% to approximately 70% and 40% of total, respectively. Lability of Cu increased from ~4% to ~30% and lability of Cd increased from below detection limits, to ~60% of total.

The sequential extraction showed increased movement of Zn to more available pools during oxidation (Fig. 1). The Zn data also showed the highest variability. Almost 80% of Cu remained in the organic/sulphide phase while the Fe/Mn oxide bound Cu decreased and exchangeable and adsorbed Cu started to appear after 1 week of oxidation. Nickel in the exchangeable and adsorbed fractions increased from 20% to 30% whilst Fe/Mn oxide bound Ni decreased from 20% to ~10%.



**Fig. 1. Changing lability of Zn with time and changing Zn fractionation over the same time period whilst sediment was oxidising in air. Bars represent standard errors (n=4).**

## CONCLUSIONS

Metal lability increased during oxidation. Zinc and Ni fractionation showed large increases in the more available phases, although the Cu fractionation change was small compared to the lability change. A fractionation study may therefore underestimate the change in lability for this metal. Oxidation leads to a highly acidic sediment with high metal availability and may therefore pose an environmental hazard, if exposed to oxidising conditions. The sediment toxicity may lead to phytotoxicity at the field site.

## REFERENCES

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