Partitioning the heavy metals in soils contaminated by past mining and smelting activities

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Soils from two historical mining and smelting regions in England have been sequentially extracted by the widely used technique of Tessier *et al.* into five operationally-defined fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic /sulphide and residual. The extracted solutions at each step were analysed by ICP-AES for some 20 elements. Results for Pb, Zn and Cd are discussed.

The extraction data showed that the largest amount of Pb, expressed as per cent of the total, were found in the carbonate and FeMn oxide fractions (50-70%) of the soils contaminated by old Pb mine workings. The highest total Pb concentration in soil exceeded 50,000 mg kg^{-1}, but less than 1% Pb was in the exchangeable form. Most Zn was in the Fe-Mn oxide and carbonate phases at high Zn sites, while the residual fraction was the dominant phase in low Zn soils. A significant amount of Cd was present in the exchangeable fraction (7-25%) in soils from the old mining areas. At the historical Pb smelting sites, Pb was very closely associated with the carbonate and Fe-Mn oxide fractions. However, the percentage of Pb in exchangeable form (average 14%) was much higher than that of the mining sites. The residual Zn was the most abundant fraction at the smelting sites, while the exchangeable form accounted for 2-15% of the total Zn. Significant amounts of Cd were in the exchangeable phase (12-35%), which was higher at the smelting sites than in the mining area. Uptake of these metals by grass was generally related to the distribution of the various fractions of these elements in soils.

The chemistry of iron oxide/hydroxide precipitates associated with acid drainage abandoned metal mines in Wales

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Drainage from several of the many abandoned metal mines of Wales is characterised by the precipitation of red-brown coloured ochre. These ochres result from the oxidative weathering of and biological action on the iron sulphides pyrite and marcasite. The mineralogy of these ochres is complex and thought to vary in response to pH, but basically they have been described as iron oxide/hydroxides.

The precipitating ochres can absorb ions from solution and their chemistry is very variable. Of the major components, Al varies from 1.4% to 0.043%, Pb from 8.0% to 0.013% and Zn from 2.5% to 0.25%. Trace elements also show considerable variation with highest values as follows: As 2,170 mg kg^{-1}, Cu 3,060 mg kg^{-1}, Mo 240 mg kg^{-1}, Bi 275 mg kg^{-1}, Sn 462 mg kg^{-1}, Sb 110 mg kg^{-1}, W 42 mg kg^{-1} and elevated levels of rare earth elements such as Ce 50 mg $kg^{-1}$and Nd 26 mg kg^{-1}. While much of the variation reflects the chemistry of mineralisation and the host rock, the pH of the drainage water has a marked effect on the composition of the ochre. This pH-dependent variation in the chemical composition of the precipitates probably reflects the effect of the hydrogen on cation absorption by the ochres but could also be due to the role of varying mineralogy of the ochres which has been shown to vary with pH conditions.