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Bio-availability of tungsten in the vicinity of an abandoned mine in the English Lake District and some potential health implications

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Abstract

This research addresses the occurrence, detection and possible fate of tungsten in the vicinity of an abandoned mine in the English Lake District. Aqua regia extraction and subsequent analysis of spoil and vegetation confirmed the presence of tungsten and other heavy metals. Spoil samples examined were last worked almost 100 years ago and the concentrations of copper, zinc, tungsten and arsenic detected demonstrate the environmental persistence of these metals in an area of relatively high rainfall. The bioaccumulation of tungsten by two species of plants is indicated and partitioning within different tissues of *Calluna vulgaris* is demonstrated. Mechanisms relating to mobility and speciation of the metals present were explored using sequential and single stage extraction systems. Tungsten appears to be relatively immobile when subjected to sequential extraction but increased bioavailability is indicated when single stage extraction using EDTA is employed.

Keywords: Bioaccumulation; Mobility; Partitioning; Environmental persistence; Tungsten

1. Introduction

Tungsten has been extensively employed since its discovery in the last quarter of the 18th century, due to its high melting point and hardness especially when used in alloys. Johnson et al. (1996) highlighted the ability of tungsten as a co-factor in particular enzymes where it replaces molybdenum in certain oxidases found in thermophilic organisms and aids the functioning of the enzymes at higher temperatures. Until recently it was not considered important in an environmental and health context; however, Legget (1997) proposed a model for the retention of tungsten in the human body and highlighted the need for a more systematic study of the metal. Koutospyros et al. (2005) postulated that increased demand for tungsten would produce a greater number of possible entry points into the natural and human environment. They further stated that the existing knowledge base does not provide clear information about the behaviour of tungsten based products in the environment or possible effects on living organisms and exposure pathways. Evidence of lung disease in guinea pigs caused by inhalation of hard metal dusts containing tungsten has been demonstrated (Fedan and Cutler, 2001). Kraus et al. in 2001 established that tungsten and some of its compounds, despite their low solubility, were bioavailable to humans working in tungsten processing industries leading to possible adverse health effects. Childhood leukaemia clusters in Fallon, Nevada, Sierra Vista, Arizona and Elk Grove, California, were reported

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associated with mining and or military operations in close proximity. High tungsten concentrations were additionally reported in trees from each of these communities (Sheppard and Witten, 2003).

Metalliferous pollution as a result of old mining operations and subsequent bioaccumulation of heavy metals by vegetation growing in British Columbia, Canada and Anglesey, UK continued to occur in various plant tissues long after mining operations cease (Wilson et al., 2005a; Wilson and Pyatt, in press). Plants growing around old tungsten mine workings in Australia demonstrated significant bioaccumulation of tungsten (379 mg kg^{-1}) and other organisms in the locality exhibited evidence of tungsten accumulation (Pyatt and Pyatt, 2004). The mines examined in Australia produced ore containing wolframite ($FeMnWO_4$) and scheelite ($CaWO_4$). Kraus et al. (2001) concluded that tungstate was the most bioavailable of the three tungsten compounds which they examined. This communication reports a reconnaissance examination of an old tungsten mine originally producing these ores.

Carrock Fell Mine, Cumbria, UK (Grid Reference NY325328) is situated in the valley between Carrock Fell and Combe Height, approximately 11 km NNE of Keswick and at an altitude of 340 m above sea level (Fig. 1). The mine and associated workings have been exploited periodically since 1854 and the mine was last worked in 1981 (Blundell, 2000). The area has higher than average rainfall, 2000 mm per annum (Lake District National Park Authority, 2003), although being situated close to the northwest coast of England, has not suffered from significant acid rainfall. The mine was operated for the extraction of tungsten and the predominant ore types are wolframite and scheelite (Ball et al., 1985). Other heavy metals noted by the authors in the current work occurring in spoil from the mine include copper, zinc, lead and arsenic. The predominant vegetation in the area is *Calluna vulgaris*, *Agrostis* spp. and *Sphagnum* spp. and the area in general is grazed by sheep during spring, summer and autumn.

The determination of total metal content in spoils collected from the site can be related to the amount accumulated by plants; however the mobility and mechanisms relating to bioaccumulation, especially in the case of tungsten are not documented. In an endeavour to clarify the position it was decided to carry out a further investigate relative mobility of tungsten in spoil samples collected from the old processing area around Carrock Fell Mine which was worked until the early part of the 20th century (Tyler, 2003).

The development of procedures to address the question of mobility of heavy metals in soils and sediments has been examined by many workers over the years, however Tessier et al. in 1979 produced a sequential extraction scheme (SES) to determine (a) exchangeable, (b) bound to

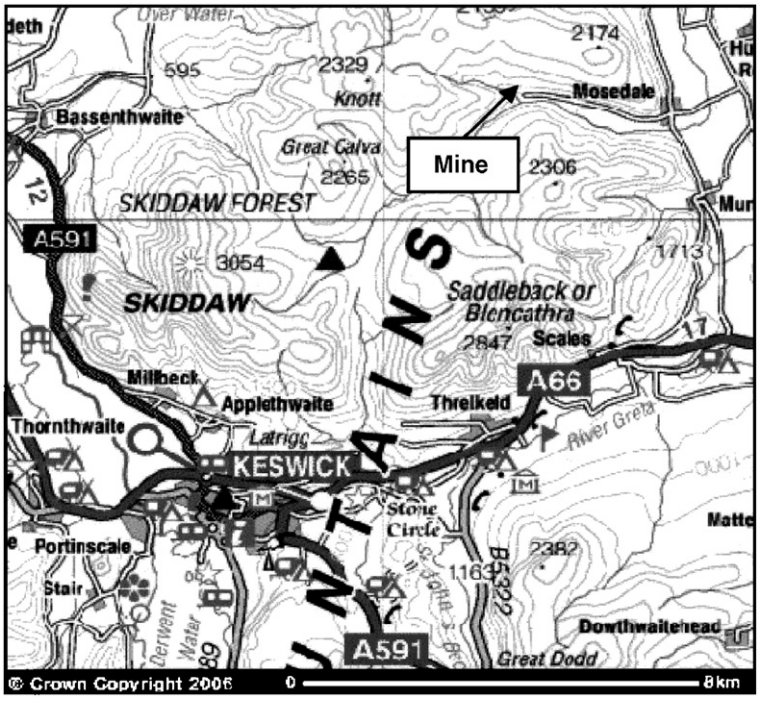

Fig. 1. Location of Carrock Fell Mine.