The bioaccumulation of tungsten and copper by organisms inhabiting metalliferous areas in North Queensland, Australia: An evaluation of potential health implications

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Abstract

Aspects of the mining history of major metalliferous sites in North Queensland, Australia are described by reference to areas which formerly were important in the production of metals such as tungsten (wolfram) and copper. Bioaccumulation in organisms inhabiting three derelict polluted areas, within this arid open savanna region, is discussed and potential toxicological implications are described. Certain plant species are noted to possess excessively enhanced bioaccumulatory capacities and the cations within these forage plants may affect herbivorous species such as cattle; skeletons of such herbivores are found to exhibit enhanced metal concentrations. Ultimately humans may be recipients of these toxic elements and some health effects are considered.

Key words: Copper, bioaccumulation, environmental health, tungsten /wolfram, toxicology.

Introduction

Bioaccumulation has been described by various workers. Thus Bowell and Ansah (1994), working in Ghana, reported that the distribution of essential nutrients was largely affected by bedrock geology and that the geochemical dispersion of some elements was affected by soil and hydromorphic processes. Iron, manganese and cobalt were recorded as largely fixed in the soil mineral fraction whilst copper and manganese were preferentially concentrated in plants. They found copper uptake to be antagonistic to zinc, iron and molybdenum accumulation in the plants they investigated. In eastern Zimbabwe, Jonnalagadda and Nenzou (1997) studied some spoil tips and reported enhanced concentrations of arsenic in the leaves of Amaranthus hybridus.

Pyatt (1999), Pyatt and Grattan (2001) and Pyatt *et al.* (1997, 1999a/b, 2000) have demonstrated that cations including copper and lead, in areas such as arid parts of Jordan, not only bioaccumulate in organisms and through trophic levels but, additionally, show partitioning in different tissues of the same organism.

The current research programme seeks to explore the bioaccumulation of tungsten (wolfram) and copper derived from the exploitation of these elements within approximately the last 100 years in arid areas of North Queensland, Australia. Little information in this area of toxicological research has previously been published.

The Sites

Plimer (1997) noted "for some time the whole of the Cairns hinterland has been a significant producer of tin (at Irvinebank, Herberton, Mount Garnet, Ravenshoe, for example), tungsten, molybdenum and bismuth (Wolfram Camp, Mount Carbine), gold (Palmer River, Georgetown, Forsayth) and base metals (for example, Herberton, Chillagoe)".

The three sites selected for this research investigation are located within North Queensland, Australia. Mount Carbine lies approximately 140 km, by road, to the north - west of the important coastal resort of Cairns. Chillagoe lies approximately 218 km to the west-south-west of Cairns whilst Mungana is located approximately 16 km. to the west of Chillagoe. The sites, which are considered in more detail below, have an important history in terms of cation extraction; thus Mount Carbine provided tungsten (wolfram), Chillagoe was important for its copper (and lead) smelters whilst Mungana was a major site of copper mining and provided ores for the Chillagoe smelters.

Mount Carbine

Anon (2002) noted that the mine at Mount Carbine was established in the 1880's when wolframite was discovered on the hill. In 1919 the world wolframite market collapsed and production ceased to eventually recommence in 1968 when R. B Mining negotiated option agreements for the purchase of the leases. In recent times however, the mine, as a consequence of low tungsten prices, has not been operational. At its peak however, this was one of the world's major producers of high quality wolframite and generated 1500 tonnes of wolframite (a tungstate of iron and manganese) and scheelite (a tungstate of calcium) concentrate per annum. Both are essential, for example, in the steel industry for the manufacture of wear-and heat-resistant steels as well as in the tungsten carbide industry for manufacturing cutting tools (Anon, 2002). An additional use of tungsten is in the production of filaments for light bulbs.

Two sites were selected; a white tailings area and the sealed off former mining site on the hill; these sites are located approximately 0.8 km. apart. The area is dominated by dry savanna vegetation and is separated from the tropical coast by the Great Dividing Range located to the east. The tailings area is largely devoid of vegetation but there are occasional plants of Eucalyptus melanophloia (silver leaved iron bark), Eucalyptus erythrophloia (blood wood) and Triodia grassland. The tailings area is occasionally grazed by Brahman cattle; the region of earlier deposition of waste is characterized by a low biomass per unit area together with a limited biodiversity. The area (hill) around the former mining extraction activities has a greater biomass per unit area and a greater biodiversity than the tailings area as much of the richer material was formerly removed and deposited in the tailings area.

Chillagoe and Mungana

Plimer (1997) notes that various ores have been located in the area including cuprite, azurite, malachite along with calcite and massive deposits of copper sulphides. The large smelters at Chillagoe were constructed between 1900 - 1901 to service a variety of mines in the area including Mungana, Calciver and Muldiva and operated intermittently until 1943. Ore was transported from the various mines and smelting was employed for the production of copper and lead. Information boards at the abandoned site note that the smelters, and associated plant, were dismantled in the 1950's. Approximately 60% of the ore smelted was extracted from the Girofla and Lady Jane mines at Mungana; the ore contained copper, lead and sulphur as main ingredients. Bolton and Kerr (1998) noted that the Chillagoe Smelters were in pre World War 1 Queensland, major metallurgical developments. "Up to World War 1, 600,000 tons of ore were smelted from the Chillagoe and Etheridge fields for the production of 23,272 tons of copper, 31,758 tons of lead, 4,345,309 ounces of silver and 28,911 ounces of gold".

The Chillagoe and Mungana areas also lie to the west of the Great Dividing Range and are similarly characterised by dry savanna vegetation in which species of Eucalyptus are well represented. The limestone area is dominated by scrubby vegetation containing deciduous tree species which lose their leaves during June and July when the climate is extremely dry. Additional species include bats-wing coral tree (Erythrina vespertilio), and kurrajong (Brachychiton spp). Queensland Government (2000) noted that the following species are also present: native buahinia (Lysiphyllum hookeri), helicopter tree (Gyrocarpus spp), ghost gum (Eucalyptus papuana) together with various species of fig trees.

The Mungana mines are aligned along a zone extending for approximately 3km. from Mungana to the south-east and include the Girofla, Lady Jane, Griffith, Dorothy, and Magazine Face mines (De Keyser and Wolff, 1964). Broadhurst (1953) indicated that total production from these mines was 31,831 tons Pb, 7907 tons Cu and 3,228,000 ounces of Ag from 333,591 tons of ore; massive environmental effects of such activities are conceivable.

The main plant species investigated

Eucalyptus melanophloia F. Muell (silver leaved Iron bark) has been described in detail by Brooker and Kleinig (1994) and by George (1988). Trees grow to 25m and possess a rough bark coloured dark grey to black and is deeply furrowed. Brooker and Kleinig (1994) continue: "Juvenile leaves opposite, ovate to orbicular, often cordate, glaucous, concolous. Adult leaves opposite, ovate to broadly lanceolate, apiculate; lamina 5-9 cm. long, 2-3 cm. wide, glaucous; lateral veins faint, at 40°-55°; intramarginal vein up to 2 mm. from margin; petiole very short or absent. Conflorescence terminal, sometimes axillary, peniculate; umbels 7 - flowered; peduncle terete or quadrangular, 4-16 mm. long; pedicels 1-7 mm. long. Buds fusiform, glaucous; operculum conical, 3-4 mm. long, 3–5 mm. wide; hypanthium obconical, 4-6 mm. long; 3-5 mm. wide. Fruits hemispherical, ovoid or urceolate, 3-8 mm. long and wide, glaucous; disc broad; steeply descending, valves 3 or 4, level or slightly exerted.

Distribution

Occurring widely in Queensland from Brisbane to east of Charleville and northward to north of Chillagoe, occurring as a small mallee south of Mt. Isa; also widely distributed from the western slopes of the northern tablelands of NSW to north of Bourke"

Experimental Procedure

Material was obtained, in the case of the iron bark trees (Eucalyptus melanophloia), from trees of comparable size and health. Samples of wood and leaves were collected at the same height and comparable exposure. Portions adjacent to incisions with the metal scalpel (possibly contaminated by the blade) were eventually discarded and the remaining material was subsequently analysed. All material collected from the three sites was air dried in Cairns and transported to the laboratory in clean polythene bags, (double wrapped and sealed). In the laboratory, samples of Eucalyptus, Triodia, bone (from material of similar size), termites and faeces samples were washed to remove any remnant superficial contaminants using several applications of deionised water, they were then air dried in a new drying cabinet which had been thoroughly washed to be free of metalliferous contaminants. Samples were weighed and digested using nitric acid and were then analysed by ICP-AES. The results are derived from five replicates in each case and are presented in terms of parts per million.

Table 1.0 Tungsten and copper (ppm) in samples of vegetation, animals and soils from metalliferous sites in North Queensland, Australia and control data from Quarantine Bay.

Mount Carbine, North Queensland		**W**	**W^{ct}**	**Cu**	**Cu^{ct}**
Tailings					
Spoil 0 - 5 cm		59.3	N/A	1.3	N/A
			0.1		6.6
Spoil 5 - 15 cm		78.4	N/A	1.4	N/A
			0.1		9.1
Eucalyptus melanophloia	leaves	13.6	0.1	2.4	0.7
E. melanophloia	young stems	2.9	0	1.6	0.3
E. melanophloia	old stems	4.3	0.1	2.1	0.5
Triodia grassland		379.4	6.6	8.7	1.6
Termites		19.8	0.1	1.5	0.2
Cow scapula		34.3	0.2	6.5	0.3
Cow femur		28.6	0.1	6.4	0.2
Cow faeces		37.8	0.1	5.8	N/P
Kangaroo faeces		36.1	N/P	5.8	N/P
Spoil tip area					
Spoil 0 - 5 cm.		24.7	N/A	1.2	6.6
			0.1		
Spoil 5 - 15 cm.		60.0	N/A	1.4	9.1
			0.1		
E. melanophloia	leaves	6.9	0.1	2.4	0.7
E. melanophloia	young stems	1.3	0	1.5	0.3
E. melanophloia	old stems	2.7	0.1	2.0	0.5
Triodia grassland		201.1	0.6	8.6	1.6
Termites (1)		5.3	0.1	1.5	0.2
Cow scapula (1)		9.6	0.2	6.1	0.3
Cow femur (1)		9.2	0.1	6.1	0.2
Cow faeces (1)		12.7	0.1	5.6	0.1

N/A: Not appropriate – data is derived from soil
N/P: Not present
1 Not available on enclosed abandoned site; samples obtained c. 200m from site.
W^{ct} Control samples collected from non-polluted site at Quarantine Bay, North Queensland. Tungsten values.
Cu^{ct} Control samples collected from non-polluted site at Quarantine Bay, North Queensland. Copper values.

Table 2.0 Tungsten and copper (ppm) in samples of vegetation, animals and soils from metalliferous sites in North Queensland, Australia

Chillagoe, North Queensland		**W**	**Cu**
Abandoned copper smelter site			
Spoil 0 - 5 cm		0.6	9005
Spoil 5 - 15 cm		0.9	12604
Eucalyptus melanophloia	leaves	0.1	1335
E. melanophloia	young stems	0.1	987
E. melanophloia	old stems	0.1	1016
Triodia grassland[1]		9.7	7514
Termites[2]		0.6	1374
Cow scapula[3]		1.4	2415
Cow femur[3]		1.3	2111
Cow faeces[3]		1.3	2378

[1] 200 m. from main smelter site
[2] 200 m. from main smelter site
[3] 200 m. from main smelter site

For control values, see Table 1.0

Results and discussion

These results are presented in Tables 1.0, 2.0, and 3.0 and consider material from both autotrophs (e.g., Eucalyptus) and heterotrophs/herbivores (e.g. cattle).

Both soils in the Mount Carbine area and those in the Chillagoe/Mungana area, despite decades of potential weathering processes, still exhibit high quantities of the elements which were formerly mined (Tables 1.0, 2.0 and 3.0). Values are massively enhanced compared with control material obtained from the Quarantine Bay area to the north-north-east of the site.

From Table 1.0, it is apparent that whilst tungsten is well represented in the area and in the organisms selected for study, traces of copper are also present; this area is rich mineralogically. Material of Eucalyptus melanophloia (Table 1.0) contained enhanced concentrations of tungsten especially within the leaves; this pattern is mirrored, but to far lesser extent, by the copper values. However, the Triodia grassland contained massively enhanced values of tungsten (379.4 ppm) and this would be available to herbivores such as the cattle grazing this area. This is indeed reflected by the high values found in the bones of cattle which had grazed the area (cow scapula 34.3 ppm and cow femur 28.6 ppm). Faeces of both cattle and kangaroos contained a high concentration of tungsten (Table 1.0). Cattle and Triodia are acting as important sentinels of tungsten pollution. Furthermore, it should be noted that humans are likely to ultimately be recipients of material, e.g. meat with a high tungsten content and toxicological implications are conceivable. The values in the former mining area, on the hill (Table 1.0), mirror the above findings but the concentrations are markedly diminished.

Termites, which feed especially on wood, contained rather lower concentrations of tungsten than the mammal skeletons. Browning (1961) has indicated that tungsten retention is greater in bone than other tissues; for humans the following results are presented: bone retention (up to 18 mg. per cent), spleen (up to 14 mg. per cent) with much lower values in the kidneys and liver (less than 1 mg. per cent). The values in kangaroo faeces are interesting and reflect those values found in cattle faeces. Thus it may be argued that tungsten is bioaccumulating, and being excreted by, native and domesticated animals.

Material from the Chillagoe smelter also demonstrated the presence of tungsten (Table 2.0). This will have been derived from scheelite (CaW04) which has been listed as present in the excellent text of Plimer (1997). With the exception of the spoil values (Table 2.0) and the animal bone and termite values, the tungsten concentrations are not massively enhanced compared with the control values presented in Table 1.0. The high values within the bones and the termites again reflect marked bioaccumulation through trophic levels. The high value in the Triodia grassland is again worthy of attention in biomonitoring research programmes.

Tungsten is potentially a very important environmental pollutant; Klaassen *et al.* (1996) note that carbides of tungsten emanating from the manufacture of cutting tools can cause pulmonary fibrosis and related effects. De Bruin (1976) indicates that rats exposed to various metals, including tungsten, showed enhanced leucocytary phagocytic potential whilst 'inhibition may be shown in instances of toxic ingestion.' Thus when high concentrations of tungsten are exposed in the environment, the route of dispersion, fate and bioaccumulation through trophic levels, should be given thorough attention.

In this site, copper values are massively enhanced (Table 2.0) as compared with the control values; leaves had higher values than young and old stems whilst again the values in Trioidia grassland were massively enhanced. Additionally, as noted for tungsten, the values in the skeletal samples of herbivores, located in close proximity to the smelter site, are markedly enhanced.

The Mungana data is presented in Table 3.0. Tungsten (wolfram) is still present in all samples with the exception of the young stems of Eucalyptus melanophloia. The values of copper are markedly enhanced compared with those in material collected from the control site. The copper values in organisms from this site, which exhibits recovery in terms of both enhanced biomass per unit area and indeed biodiversity, are high but unsurprisingly much lower than values obtained from the vicinity of the abandoned smelters. Recovery from the former mining activities is well advanced.

Again, high values are found in Triodia grassland and, in the case of E. melanophloia, particularly in the foliage. Cattle bone and termite values reflect the fact that copper is being bioaccumulated by these organisms. The data on the faeces illustrates that, post-grazing, copper is returned via the faeces to the pedosphere where it will eventually continue to be available to other herbivores as a consequence of re-cycling together with bioaccumulation through trophic levels. Kangaroo faeces contained a higher concentration of copper (1785 ppm) than those obtained from domestic cattle (1264 ppm); regrettably kangaroo skeletons were not observed at this time to afford an opportunity to examine bioaccumulation values.

Copper, like tungsten, is potentially a very important environmental pollutant. Whilst it is essential for life, it can become toxic to organisms in high concentrations and this toxicity is enhanced by the presence of other

Table 3.0 Tungsten and copper (ppm) in samples of vegetation, animals and soils from metalliferous sites in North Queensland, Australia

Mungana (Nr. Chillagoe), North Queensland		**W**	**Cu**
Abandoned copper mining area			
Spoil 0 - 5 cm		0.01	964
Spoil 5 - 15 cm		0.01	1408
Eucalyptus melanophloia	leaves	0.02	613
E. melanophloia	young stems	0.0	407
E. melanophloia	old stems	0.01	518
Triodia grassland		3.9	1296
Termites		0.01	17.9
Cow scapula		0.4	1459
Cow femur		0.4	1283
Cow faeces		0.4	1264
Kangaroo faeces		0.3	1785

For control values, see Table 1.0

cations. Effects on humans can include nausea, diarrhoea, convulsions and coma; these are thoroughly reviewed by Scheinberg (1991). Again, in cases where high concentrations of copper, as also noted for tungsten, are available in the environment, careful monitoring of its fate is essential to safeguard plant and animal (including human) health.

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