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Metal and solute transportation through a wetland at a Lead Zinc Mine, Northern Territory, Australia

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ABSTRACT

This paper presents an evaluation of historical data for metal and solute transport from underground dewatering through a wetland at the Woodcutters lead-zinc mine in the Northern Territory, Australia. Groundwater aquifers drain into the underground workings that were then pumped into an ephemeral stream, which was developed as an extended wetland system, dominated by *Typha* sp. The tropical monsoonal climate comprising an extended wet season from December to April gave flow to the creek system. Only dewatering contributed flow during the dry season. The significant metal contaminants were antimony, cadmium, copper, lead and zinc and the major components of solutes magnesium and calcium sulfates. Retardation ratios for each metal relative to sulfate showed attenuation of all metals by the wetland system except for some copper under high creek flow conditions. Measurement of electrical conductivity by continuous logger at the inlet and the outlet of the wetland showed that solutes were higher at the outlet compared to the wetland inlet. This anomaly was attributed to the addition of solutes from tailings seepage to the wetland system. Comparison of the loads of solutes revealed a higher load at the inlet indicating that some loss of salts occurred within the wetland. The characteristics of carbon in water were investigated and revealed that inorganic carbon was derived essentially from dewatering and seepage whereas organic carbon was added to the water column from the wetland vegetation. Generally there was a reduction in metal load for wetland inlet compared to that downstream. The efficiency of the wetland system was considered to be high and presents a model system for treating mine wastewater containing such metal impurities. © 2003 SDU. All rights reserved.

Keywords: Wetlands; Mine wastewater; Heavy metals; Tropical; Organic carbon

1. INTRODUCTION

1.1. Woodcutters mine location and study outline

The Woodcutters mine (Figure 1) is located about 80km south of Darwin and was a major producer of lead, zinc and silver concentrates for export. Operations began in 1985 and ceased production in May 2000.

The major silver-lead-zinc deposits were discovered in 1964. The project comprised an open-pit, which was subsequently further developed into an underground operation in 1987. A $65 (€59.4) million expansion project commenced in 1991, with major works being upgrades to the mine, the mill, the concentrator, the heavy media plant and the construction of a mine shaft and a tailings dam (ERAES, 1992).

The principal ore minerals are galena (PbS) and sphalerite (ZnS), associated with pyrite (FeS$_2$), with minor lead antimony/arsenic sulfosalts, accessory sulfide species including arsenopyrite

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(FeAsS; a total of 18 sulfide minerals have been identified), in a mainly quartz and dolomite gangue (Taube, 1984). Additional metals present in significant (although not necessarily economic) quantities are silver, nickel, cobalt, cadmium, tin, gold, and indium. The ore is hosted in the Whites Formation, a dolomitic, calcareous, carbonaceous, pyritic shale, interlayered with dolostone (denoted dololutite because of its fine grained nature). The Whites formation is underlain by the Coomalie Dolomite; the uranium and base metal deposits of the Rum Jungle area 11 kilometres to the west also occur near this geological contact (Taube, 1984). Because of the sulfide rich ore and (in part) waste rock, acidification from the oxidation of sulfide with a possible resulting increase in the leaching rates and concentrations of trace elements and sulfate in drainage waters from the site was recognised from the initiation of the project. The acid-forming potential of overburden was briefly investigated on three samples by Bell (1983), reported by Lancaster (1983). The tests indicated that oxidation would occur, but that generally there was sufficient dolomite present to neutralise the acid formed. The possibility of exhaustion of this neutralising capacity was mentioned, but careful planning of rock placement on the dump was envisaged to keep acid drainage within acceptable limits.

Ore was crushed to less than 14mm to liberate the sulfide minerals from the non-sulfidic gangue. The crushed ore was screened, gravity separated and lead and zinc concentrated via flotation. The concentrate then required dewatering. The resultant tailings composition is 0.54% boulangerite, 1.55% galena, 3.4% sphalerite, 5.7% arsenopyrite, 58.3% pyrite and 30.51% non-sulfides (dolomitic and carbonaceous gangues) (ERAES, 1992). These tailings have the potential to produce acid if allowed to oxidise, but acid has not as yet been detected up to the time of completion of mining.

Groundwater aquifers drain into the underground workings. This water drained though sumps to a pumping station and two main pump wells that were then pumped to the sedimentation dam at the surface. The water from this dam then flowed to a wetland system for polishing of constituents.

This paper reviews historical physico-chemical and flow data on the load and retention characteristics of the wetland systems, which was used to polish wastewater exiting the sedimentation dam. Such data is useful for future wetland developments, which can be incorporated into new mining projects. Specifically the objective of investigation is to evaluate the load characteristics of heavy metals, metalloids and soluble constituents of the Woodcutter's wetland and identify aspects, which maximised its efficiency and minimised its downstream impact.
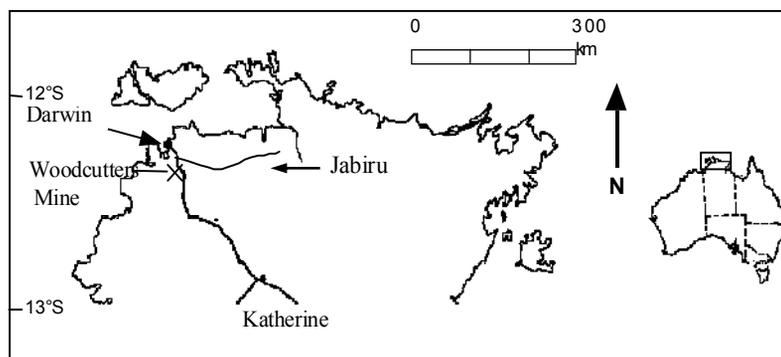

Figure 1. Location of Woodcutters Lead-Zinc Mine

1.2. Tropical monsoonal climate

The Top End of Northern Territory, Australia (Top End) lies within the tropical monsoonal zone, which is the area of Australia north of 15°S (Figure 1). It has an annual high temperature distribution with daily maxima between 29° and 34°C in the shade and temperatures of up to 77°C being measured in direct sunlight. The area experiences a wet-dry seasonal climate with an annual rainfall of around two metres, which falls between the months of December and April.

A maximum average of 21 rain days is reached in January at Darwin whilst the minimum falls to an average of near zero for June-August. The rainfall intensity is high during the wet season with an extreme value of 544mm per day (McGill, 1983). Humidity in the Top End is also high throughout the year with wet-dry maxima ranging between 70 and 100% relative humidity.

1.3. Wetlands for water quality

1.3.1. Historical

Wetlands have been used to treat mine wastewaters in temperate regions since the 1970s (Dunbabin, 1983), including iron and coal mining (August *et al.*, 2002; Butterworth *et al.*, 1997; Tyrrell, 1996). Some successful case studies have been reported in the literature (August *et al.*, 2002; Butterworth *et al.*, 1997; Weider, 1989). There is little data available on the performance of tropical wetland systems for the purpose of wastewater treatment, particularly for minesites. Guidelines for design and management of wetland systems, which are successfully applied in temperate and arid zones, may not be suitable for water pollution control on minesites in the tropics. Tropical hydrological characteristics differ from those of temperate areas and tropical aquatic ecosystems are controlled by the extremely variable wet-dry climatic cycle. The design and management of minesite wetland systems at tropical locations has been derivative rather than innovative. Some wetland systems used for wastewater treatment at minesites in tropical areas are simply natural creek beds or oxidation ponds (Noller *et al.*, 1994). Nonetheless these systems appear to be quite effective.

Ongoing research into minesite wetlands in the Top End has been conducted over the past decade. A number of wetland systems, both constructed and natural, are currently used on operational and rehabilitated minesites for polishing wastewaters before discharge to creeks. The design and success of these systems has been reviewed by various authors (Noller *et al.*, 1994; Ryan and Hosking, 1992). A major conclusion drawn from these case studies is that wetlands can reduce the load and concentration of a number of common mine-sourced contaminants. Some detailed studies have also been undertaken in the Northern Territory (Woods and Noller, 1995; Jones *et al.*, 1995; Shinners, 1996), and preliminary criteria for the design of tropical systems has been proposed (Noller and Parker, 1996).

1.3.2. Attributes of wetlands

While wetland plants are important in creating tortuous routes for water flow, allowing optimal metal retention, as well as acting to filter particulates and create conditions optimal to microbial activity, it is the wetland soils the constitute the major sink for retained inorganic ions (>95%) (Tables 1 and 2). Wetland soils are dominated by anaerobic conditions induced by soil saturation and flooding, as well as accumulation of organic matter (Faulkner and Richardson, 1990). The system under examination tends to remain continuously saturated. The most significant effect of this saturation is the isolation of the soil from atmospheric oxygen, which activates the anaerobic, reducing microbial population (Ledin and Pedersen, 1996).

Clay soils with low hydraulic conductivity values may have large, interconnected pores permitting rapid water movement with little soil-water contact. Saturated flow in organic soils and most clays is slow (Faulkner and Richardson, 1990).

The total charge capacity of a soil can be divided into permanent and pH dependent, or variable charge. Hydroxyl groups form the permanent charge, being unaffected by pH (Faulkner and Richardson, 1990). The sources of variable charge in soils are dissociation of hydroxyl (-OH), carboxyl (-COOH) and phenolic (C_6H_4OH) functional groups, which become more negative as pH rises. Organic matter may account for 20-100% total CEC, become charged with increasing pH. Ca^{2+}, Mg^{2+}, Na^+ dominate in minerals soils while H^+ dominates in organic soils (Faulkner and Richardson, 1990).

Wetlands are often the major reducing ecosystems in a landscape, and thus have great potential for nutrient cycling (Stoltz and Greger, 2002). The overall effect of flooding a soil is to reduce the pH of alkaline soils, due to buildup of CO_2, and increase the pH of acidic soils, due to

$Fe(OH)_3$ reduction to $Fe_3(OH)_8$ (which requires H^+). In reduced soils and sediments, metal reduction (as sulfides) tends to be the most effective retention mechanism (Faulkner and Richardson, 1990). Plant uptake under typical mine drainage loads tends to be less than 1%.

Table 1
General characteristics of mineral and organic soils (Faulkner and Richardson, 1990)

Parameter	Mineral Soil	Organic Soil
Organic Content (%)	< 12-20	> 12-20
pH	6.0-7.0	< 6.0
Water holding capacity	Low	High
Nutrient availability	Generally high	Often low
Cation exchange	Low, dominated by major cations	High, dominated by hydrogen ion

Table 2
Ranges for physical parameters in organic and mineral soils (Faulkner and Richardson, 1980)

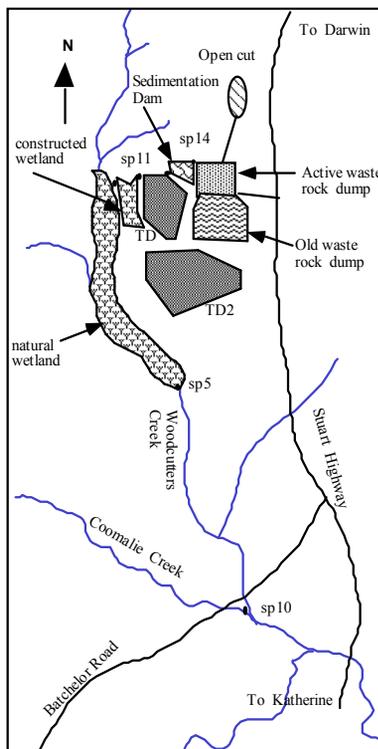| Soil Type	Total Porosity (%)	Hydraulic Conductivity (m/d)	Bulk density (g/cm^3)
Peat	(High)	(High-Low)	(Low)
Fibric	>90	>1.3	<0.09
Hemic	84-90	0.01-1.3	0.09-0.2
Sapric	<84	<0.01	>0.2
Mineral	(Low)	(High)	(High)
Gravel	20	100-1000	≈2.1
Sand	35-50	1-100	1.2-1.8
Clay	40-60	<0.01	1.0-1.6

Figure 2. Woodcutters Mine layout

1.3.3. The Woodcutters project

The layout of Woodcutters Mine is shown in Figure 2. The water pumped up from the underground workings has relatively high salinity (due largely to magnesium and calcium

bicarbonates and sulfates) and is much more turbid than dewatering alone. The concentration of several dissolved metals and metalloids is elevated. This water was first passed through a large sedimentation pond, and thence through a constructed wetland (polishing pond) prior to discharge to the adjacent Woodcutters creek. Although the ore and waste rock are rich in sulfide, oxidation had not led to acidification of waters up to the time mining ceased, as acidity is consumed by reaction with the largely dolomitic gangue.

Woodcutters Creek has been developed in two stages with large areas of *Typha* sp. dominating the wetland system: (i) a constructed ponded area; and (ii) an enhancement of the creek channel. Flow is from (i) to (ii). Water in Woodcutters Creek joins the larger Coomalie Creek some 2km downstream of the mine lease. In some dry seasons all dewatering output was been consumed by evapotranspiration or seepage within Woodcutters Creek prior to its joining Coomalie Creek.

The creek flows through the year (due to discharge of water – it is naturally an ephemeral water body). The wetland is heavily colonised by *Typha orientalis*, as well as other wetland bullrush species, such as *Eliocharis sphacelata* and *Marsilea* sp. to a lesser extent and various algal populations. The creek, in the vicinity of the mine also supported a substantial aquatic macrophyte population with similar species distribution to the wetland filter.

The wetland filter received water from 3 main sources: overflow from the settlement pond (which receives mine dewatering); runoff from the tailings dam catchment; and rainfall direct to the pond. Hydrographic data for flow through the wetland was not extensive, making modelling an "assumptive" process, consisting of inlet and outlet flow data, downstream creek flow data (but no upstream creek flow data, unfortunately), and rainfall data. Evaporation data for the site itself was not available, but evaporation tends to be fairly consistent from year to year and across the Top End, so 20-year average monthly evaporation data from Jabiru Airstrip (near Ranger Uranium Mine, about 300km to the east; Figure 1) has been extrapolated to this site. The tailings dam catchment that drains to the wetland filter from the north-east (the west and south side of the wetland filter is bunded) is 186,255m^2 in area. The wetland surface is 57,000m^2, with a volume of 85,500m^3 when full. Runoff coefficients for the catchments were extrapolated from studies on similar catchments at Ranger Uranium Mine, being 0.6 for the tailings dam catchment, and 1.0 for the wetland filter. An evaporation coefficient of 1.0 has also been assumed.

Sediment analyses have shown that the top 0-5 cm of the wetland filter floor is heavily contaminated, both due to sulfide precipitation, and adsorption onto iron oxyhydroxides (ie. the sulfide-forming metals are in excess of sediment sulfide, thus much adsorption has occurred) (ERAES, 1992). At 30°C the concentration of dissolved oxygen (DO) in water at equilibrium with air at a total pressure of 1 atm is 7.53mg/l (Drever, 1988). Profiles of the wetland filter showed that DO ranged from 5.6mg/l at the water surface, to 1.3mg/l at bottom waters. Hence oxygen-limiting conditions were encountered in the sediments. Possible processes of attenuation/release in a wetland are given in Table 3.

Table 3
Processes of attenuation/release possible in a wetland (Tchobanoglous, 1991)

Processes	Comments
Bacterial conversion	Bacterial conversions are most important in flooded systems where the soils maintain an anoxic environment
Gas adsorption/desorption	The processes where gas is taken up by a liquid (adsorption), such as O_2 uptake, or released by the liquid (desorption), CO_2 release.
Sedimentation	Suspended solids settle to the bottom (enhanced by flocculation)
Natural decay	Such as bacterial mortality or organic decomposition
Adsorption	Adsorption to sediments and suspended particulates, which combined with sedimentation results in much non-decaying constituent removal
Volatilization	Eg. Volatile organic compounds (VOCs)
Chemical reactions	Eg. Hydrolysis, redox and precipitation reactions

The wetland featured in this examination operated under a gravity flow type arrangement, with spillways and channels directing the flow from the wetland to the creek.

1.4. Chemistry, toxicity and impact of dewatering contaminants

The dewatering at the Woodcutters site contains elevated concentrations of antimony, cadmium, lead, zinc and sulfate (Jones *et al.*, 1995; Woods and Noller 1995; Gao and Noller 1997). Of less concern, were marginally elevated concentrations of copper in the dewatering, although these are reduced to less than detection limits at SP12 (Figure 2). The potential toxicity of these elements to aquatic fauna and flora is variable and reviewed in the following paragraphs.

1.4.1. Zinc

Zinc is an important trace element for all living organisms. The toxicity of zinc and zinc-containing compounds is low and generally of minor importance compared with the significance of zinc deficiency in plants, animals and mankind (Ohnesorge and Wilhelm, 1991). Zinc-accompanying impurities more often tend to be much more dominant toxicants.

Zinc's stable oxidation state is +2. Zn^{2+} has a strong tendency to react with acidic, alkaline and inorganic compounds. Because it is amphoteric zinc reacts to form a variety of salts. Zinc oxides, carbonate, phosphates and silicates tend to be insoluble in water, while zinc-chloride, sulfates and nitrates are readily soluble. It is a strong reducing agent; the metal oxidizes in air to form a basic carbonate on the surface, which makes zinc resistant to corrosion (Ohnesorge and Wilhelm, 1991).

Under aerobic conditions, Zn^{2+} is the predominant species at acidic pH, while at pH 8-11 $Zn(OH)_2$ is preferentially formed, and $Zn(OH)_3^-/Zn(OH)_4^{2-}$ predominate at pH>11. Anaerobic conditions lead to the formation of ZnS, regardless of pH (Moore, 1991). Zinc readily binds with many organic ligands, particularly in the presence of nitrogen and sulfur donor atoms.

The normal zinc content of plants ranges from 15 to 100mg/kg dry weight, but can be considerably greater in the vicinity of base metal mines. Zinc deficiencies occur below 20mg/kg Zn in leaves (Ohnesorge and Wilhelm, 1991). Values greater than 400mg/kg are regarded as toxic. Trace elements in freshwater vascular plants have been studied in detail by Outridge and Noller (1991), who found that uncontaminated freshwater plants contained 54-78µg/g. Some emergents in contaminated regions of Australia showed zinc concentrations as high as 7000µg/g in the roots. Roots tended to be the site of highest zinc accumulation. The zinc accumulated from polluted sites was released if plants were transplanted. In general, aquatic plants (as well as alga and bacteria) can assimilate zinc in elevated quantities and show great resilience to zinc contamination. These groups can also develop a genetic tolerance to heavy metals.

Uptake experiments on various aquatic plants have shown that zinc is mainly adsorbed at the cell surface, and only enters the intracellular space via passive diffusion (Weatherley *et al.*, 1980). It has also been found that algal cells accumulate more [65]Zn after they die than when living. This is attributed to internal chemical changes, which occur after respiration has ceased, that facilitate zinc adsorption at certain sites within the cell.

In fish species an acute LC_{50} (lethal concentration 50% population; 48 to 96hr) was reported at zinc concentrations between 1 and 10mg/l (Weatherley *et al.*, 1980). Some fish species show a definite age dependence, with resistance increasing from hatching to 100 days of age (Weatherley *et al.*, 1980). Fish uptake of zinc is mainly through food rather than water, being exponential in rate. In addition, zinc was found to act synergistically with mercury and cadmium. Copper and lead are also thought to act synergistically with zinc.

1.4.2. Cadmium

Like zinc, cadmium is mobile in the +2 oxidation state. Unlike zinc, cadmium is not amphoteric, and is therefore only readily soluble in acidic solutions. Cadmium readily precipitates as sulfide, carbonate, fluoride and hydroxide compounds. Cadmium forms

complexes with halogen ions and organic acids, and cadmium complexes are more stable than zinc complexes (Stoeppler, 1991). Cadmium sources are linked to resources of zinc. Cadmium emissions to the atmosphere tend to be substantially greater than to water, with 90% of the emitted cadmium deriving from anthropogenic activities. Cadmium is readily immobilised on soil particles, and hence soils around sources are often enriched in cadmium. Background cadmium levels in river water range between 0.01 and 0.15µg/l. Sediments in unpolluted water show cadmium levels of 0.04-0.8mg/kg whereas levels in polluted river sediments range from 30 to 400mg/kg. Cadmium is highly toxic, and uptake occurs by ingestion and inhalation in animals. Acute effects can be seen in the respiratory and digestive tracts. Cadmium accumulates predominantly in the kidneys and has a biological half-life of more than 10 years. Bioconcentration factors of cadmium in aquatic organisms are of the order 100-100,000 (ANZECC, 2000).

Acute toxicity of cadmium to freshwater animal species in 44 genera, ranged from 1µg/l in rainbow trout to 28,000µg/l for mayfly (USEPA, 1986). Aquatic plants were affected by cadmium concentrations as low as 2µg/l. The acute toxicity of cadmium to aquatic biota is affected by water hardness, pH, water temperature and the presence of organic compounds. An increase in salinity and/or calcium content and a decrease in temperature both decrease cadmium toxicity. Zinc, cobalt and selenium have an antagonistic effect with cadmium.

Chronic toxicity values for cadmium exposure to 12 fish and 4 invertebrate species ranged from 0.15µg/l for *Daphnia magna* to 156µg/l for Atlantic salmon. Water hardness also affects chronic toxicity: cadmium is less toxic in hard water. Links between cadmium and cancer remain uncertain.

1.4.3. Lead

Anthropogenic outputs to the environment outweigh all natural sources and lead reaches the aquatic environment through precipitation, fall-out of lead dust, street runoff and industrial and municipal wastewater discharges. In the presence of atmospheric oxygen lead becomes susceptible to attack by acids, including very weak acids such as carbonic acid and even water. The dissolution of lead is considerably reduced by small amounts of carbonate, sulfate and silicate in the water, and therefore decreases with water hardness. This has significant impact on the plumbosolvency of lead (Ewers and Schlipköter, 1991).

In most inorganic compounds lead is in the +2 oxidation state. The salts of Pb(II), lead oxides and lead sulfide are not readily soluble in water with the exception of lead acetate, lead chlorate and to some extent lead chloride. Inorganic Pb(IV) compounds are unstable and strong oxidising agents. In anaerobic environments lead is immobilised as a sulfide mineral (galena) while in aerobic waters lead carbonate and lead-organic complexes predominate.

Lead in rocks is often found at concentrations of 10-20ppm, with granitic rocks tending to have higher levels than basaltic ones. Lead values in soils tend to be less than 20ppm except when significantly contaminated. The lead concentration in lakes and rivers is typically in the range 0.1-10µg/l. It is important with lead to distinguish between dissolved and particulate forms.

Most of the lead associated with plants occurs on the emergent surfaces resulting from wet and dry deposition. Lead taken up from the soil by plants is strongly retained in the roots. The impact of lead to plants does not appear to be significant in a direct sense, but affects subsequent components of the food chain. Microorganisms appear more sensitive to soil lead pollution than plants. USEPA data (1986) indicates inhibition of plant growth begins at lead concentrations of less than 1µg/g soil moisture and becomes completely inhibitory at levels between 3 and 10µg/g. Plant populations near to sources become resistant and can tolerate higher levels of Pb. Freshwater algae have shown effects of lead exposure at concentrations of 500µg/l.

The acute toxicity of lead to several species of freshwater animals was greater in soft water than hard water. At a hardness of 50mg/l as $CaCO_3$ the acute sensitivities of ten species ranged from 143µg/l for an amphipod to 236µg/l for a midge (ANZECC, 2000). Acute toxicities for Australian fresh water species ranged from 180µg/l to 500µg/l. The chronic toxicity also

decreased with increasing water hardness. *Daphnia magna* showed reduced reproduction at lead concentrations of 30µg/l in soft water.

1.4.4. Antimony

Antimony is a relatively common toxic trace element normally occurring with sulfur and arsenic. The toxic properties of antimony are similar to those of arsenic (Fowler and Goering, 1991). Trivalent antimonials are generally more toxic than pentavalent forms. Exposure to these agents produces cell injury in a number of organic systems such as the lungs, heart, liver and kidney. Antimony trioxide has been shown to be carcinogenic in animal experiments.
Antimony may exist in –III, +III, +IV or +V oxidation states. More than 3000 organic antimony compounds are known. Antimony is present in the earth's crust at an estimated concentration of 0.2-0.3ppm. There are no known biological functions of antimony. Bioconcentration factors range between 40 and 16,000 for freshwater fish and invertebrates respectively.

Antimony oxides are released into the environment from smelters, coal-fired power plants and volcanoes (Fowler and Goering, 1991). In 1979 it was estimated that 3.8×10^{10} gram/year were released globally into the environment from anthropogenic activities. Plants have been found to contain up to 0.2mg/kg Sb, while freshwater fish contain 3µg/kg on a wet weight basis.

Some plants, mosses, lichen and fungi are able to accumulate antimony compounds. Adsorption from the gastrointestinal tract in animals is relatively slow. Inhalation of antimony compounds results in extensive pulmonary deposition. Uptake and retention of antimony by tissues is highly dependent on chemical form and oxidation state. Excretion of pentavalent antimonials is mainly in urine, while trivalent forms are excreted through faeces. The liver and kidneys are major organs for antimony toxicity.

In natural waters two forms of antimony are found (ANZECC, 2000): antimony (III) occurs under 'moderately oxidising conditions', whereas antimony (IV) predominates in 'highly oxidising environment'. Toxicity to freshwater life occurs at concentrations of 1,600µg/l. Aquatic freshwater plants may be even more sensitive to antimony concentrations than either fish or invertebrates. USEPA (1986) claims that freshwater aquatic organisms should not be affected by antimony (III) if the four-day average concentration does not exceed 30µg/l.

1.4.5. Analysis and speciation

The determination of total and filtered fractions of a particular metal provides very little information about the bioavailability or behaviour of that trace metal in the environment (Florence, 1980). This information can only be gleaned by knowledge of speciation. Anodic stripping voltametry (ASV) techniques are used to provide speciation data, but can be very time consuming (Martin *et al.*, 1980). Analytically, species determination is difficult, and can prove quite costly. In order to gain some kind of an estimation of concentrations and species prevalent in natural waters there are a number of equilibrium models available. However, equilibrium approaches have limited use and may not be appropriate due to kinetic and other considerations. While there are some kinetic codes available, once again they remain largely untested, and, in addition, kinetic data is fairly scant. Both equilibrium and kinetic models also neglect what can be important environmental sinks for metals, such as plant and bacterial uptake. Table 4 uses zinc as an example to indicate the range of species found in different size fractions.

Table 4
Zinc forms in natural waters (Florence, 1980).

Chemical Form	Examples	Approximate Diameter (nm)
Particulate matter	Retained by 0.45µm filter	>450
Simple hydrated metal ion	$Zn(H_2O)_6^{2+}$	0.8
Simple inorganic complexes	$Zn(H_2O)_5Cl^+$, $Zn(H_2O)_5OH^+$	1

(continued)

Chemical Form	Examples	Approximate Diameter (nm)
Simple organic complexes	Zn-citrate, Zn-glycinate	1-2
Stable inorganic complexes	ZnS, $ZnCO_3$, Zn_2SiO_4	1-2
Stable organic complexes	Zn-humate, Zn-cysteinate	2-4
Adsorbed on inorganic colloids	$Zn^{2+}-Fe_2O_3$, $Zn^{2+}-SiO_2$	10-500
Adsorbed on organic colloids	Zn^{2+}-humic acid, Zn^{2+}-organic detritus	10-500

Zinc and cadmium in particular form quite strong complexes with chloride and cysteine, and very strong complexes with fulvic acid and sulfide. Many metals adsorb strongly to ferric hydroxide at circumneutral to alkaline pH, and also on silica and alumina, manganese dioxide, humic acid, clay minerals, organically coated minerals and on algae (Florence, 1980). It is generally agreed that adsorption on particles, both organic and inorganic, is the dominating process controlling equilibrium concentrations of trace metals in waters, hence the use of wetlands for metal removal from wastewaters. In freshwater the extent of adsorption will depend on the pH ie. at pH <5 zinc adsorption to various surfaces sharply declines. Some of the factors that keep metals in solution are summarised as follows (Weatherley *et al.*, 1980):
1. pH – high metal concentrations are characteristically associated with low pH. However, antimony will be strongly adsorbed in acidic solutions;
2. Alkalinity – zinc, cadmium and lead tends to be precipitated at high alkalinities;
3. Solute exposure – following flood episodes, sediments in rivers may greatly increase the amount of pollutants present in solution; and
4. Dissolved Oxygen (DO) – the greater the concentration of DO, the less solute is likely to be in solution.

Regarding speciation of metals in soils, sediments and tailings, the sequential extraction procedure may be used.

2. EXPERIMENTAL

2.1. Measurements

Continuous conductivity loggers (UNIDATA) were installed at SP11 (wetland filter inlet; WF inlet) and SP5 (wetland filter outlet; WF outlet) from June to July 1994 in order to examine the "in" versus "out" load of salts. SP10 corresponds to creek downstream (Figure 2). The mining company has stream-gauging stations at these sites, thereby allowing the calculation of loads. The flow data (flowrate in m^3/day) was supplied by Energy Resources of Australia – Environmental Services. The mining company monitoring data was also coupled with flow allows the examination of soluble load variation for input vs output of the wetland, and the influence of storm events. Historical data from May-July 1993 is given in Figures 3 and 4.
Selected spot sampling for heavy metals, metalloids and major ions was also undertaken during the recorded episodes during 1994. Samples were prepared and preserved in accordance with Australian Standards (2031 - Part 1 Chemical) and dispatched to a NATA registered laboratory (ISO 17025) for analysis. The following parameters were analysed:
- Field measurements – pH, Electrical conductivity, Temperature, Total alkalinity
- Metals and metalloid concentrations
- Total and filtered (<0.45μm fractions) – Sb, Cd, Cu, Pb, Zn
- Total fractions (data supplied by ERAES) – Mn, Fe, Al, Co, Ni, As
- Cations – Ca^{2+}, Mg^{2+}, Na^+, K^+ (data supplied by ERAES)
- Anions – SO_4^{2-}, Cl^-, HCO_3^- (data supplied by ERAES)
- Nutrients - NO_3^-, NO_2^-, PO_4^{3-} (data supplied by ERAES)
- Special analyses – dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), total organic carbon (TOC), total inorganic carbon (TIC). The samples were collected in prepared glass vials and were analyzed by Northern Territory University.

2.2. Calculations

2.2.1. Load data

Loads were calculated via the usual method – concentration at the gauging station x flow rate. No allowance was made for hydraulic retention, because this figure is unknown, and also because during the wet season it was clear that the responsiveness of the polishing pond (ie. difference between inflow and outflow volumes in a day) was almost immediate (Figure 2).

Contact times (τ) are calculated by dividing the water volume in the wetland by the volumetric flow rate Q:

$$\tau = \frac{V \in}{Q} \tag{1}$$

where V is the wetland volume and $\in$ is the porosity.

Water mounding at the inlet may occur if vegetative resistance is sufficiently high. To take account of rainfall (Cueto, 1990);

$$\tau = \frac{V \in}{\dfrac{Q_i + Q_o}{2}} \tag{2}$$

where Q_i and Q_o are inlet and outlet flows (m^3/day) respectively.

Based on average daily inflows and outflows to the wetland hydraulic retention time can be calculated. For example, in January 1994,

$$\tau = \frac{85,500 \times \in}{\dfrac{5090 + 4619}{2}} = 17.61 \in \tag{3}$$

Therefore, the maximum retention time was 17.61 days. The porosity of the wetland is the percentage volume not occupied by wetland plants (Cueto, 1990). The porosity must therefore be low in this wetland since it is clear from the inlet and outlet data that the response time is quite rapid, within a day, rather than over 17 days. A low porosity is consistent with the mineral dominated soil expected for this wetland. Based on a compilation of data for wetlands in the USA (Knight *et.al.*, 1990), the flow for a wetland of this size is elevated over average figures, but by no means extreme. Thus, there is evidence for a short hydraulic retention time.

2.2.2. Retardation ratios

Although sulfate may be reduced in water passing through the wetland due to the production of sulfide minerals, the amount of sulfate reduced is only a small proportion of the total sulfate load, and is often undetectable. Sulfate is typically very low in concentration in local surface waters due to the highly leached landscape, as well as being low in rainfall (0.35mg/l was the geometric mean sulfate concentration in rainfall measured at Jabiru, which is located at a similar latitude and distance from the ocean; Noller *et al.*, 1990).

The retardation ratio of the constituent to sulfate is normalised with respect to the ratio at the source of dewatering water, (at SP11) via the expression:

$$R_i = \frac{(X_i / SO_{4i})}{(X_S / SO_{4S})} \tag{4}$$

where X is the species of interest at site i. As for load calculations, this data assumes immediate passage through the polishing pond, and does not make allowance for hydraulic retention time. At 15 December 1993, sulfate concentration was typically 580mg/l at SP5 reflecting the presence of dewatering undiluted by creek water.

3. RESULTS

3.1. Conductivity, pH and flow characteristics

Plots of mining company data for electrical conductivity, pH and daily discharge volume for the period May to July 1993 are given in Figures 3 and 4. This time frame corresponds to the end of the wet season when the limited influence of wet season rainfall causes less variation in electrical conductivity.
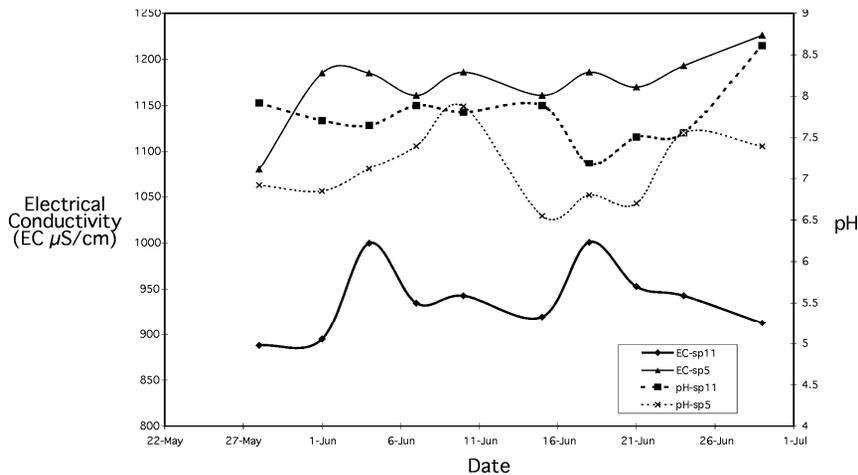

Figure 3. Comparison of electrical conductivity (EC μS/cm left hand scale) and pH (right hand scale) at SP5 and SP11 from May to July 1993

The historical data for electrical conductivity (Figure 3) shows apparently higher readings at SP5, which is downstream from SP11. This indicates a significant, additional source of dissolved salts to the wetland filter apart from the underground dewatering which had a typical sulfate concentration of 580mg/l during the dry season. This anomaly is explained by addition of seepage from the original tailings dam (TD, Figure 2) to the wetland filter (note refer to Figure 6 given later).
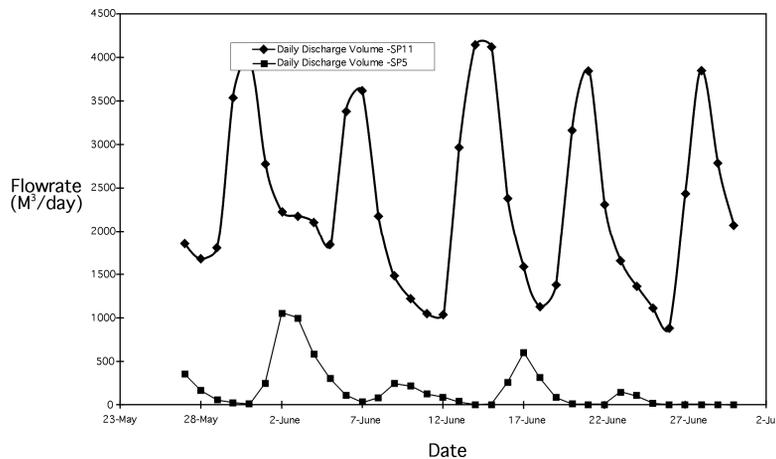

Figure 4. Comparison of flow data at SP5 and SP11 from May – July 1993

Electrical conductivity of tailings supernatant (TD, Figure 2) was 1500-2700μS/cm and sulfate concentration 1500mg/l approx during the time of the experimental study. Seepage from the tailings dam was characterised by electrical conductivity of 1200–3500μS/cm and sulfate concentration 1200–3150mg/l. Thus the higher dissolved salts, which were observed at SP5, can be explained by seepage from the tailings dam entering the wetland.

The pH (Figure 3) showed some variation but tended to remain alkaline.

The daily flow volume for May to July 1993 at the downstream of the wetland at SP5 is significant lower than the upstream (inlet SP11) flow (Figure 4). The maximum difference could lead to over 4000m^3 per day. The flow volume variance at the downstream is also much flatter than the flow in the inlet. The effective evapotranspiration in the tropical wetlands system leads to such flow pattern difference. The strong evapotranspiration is caused by dense wetland vegetation and tropical dry climate (May to Sepember). The wetland vegetation area is about 70% of the total Woodcutters wetland area, which is much more dense than ordinary tropical wetland systems located in the Northern Territory minesites (Noller *et al.*, 1994). The logical result for Woodcutters mine is the remarkable water quality difference between the downstream and upstream. It can be seen from the result that if there is not enough water supply into the wetlands, the water quality improvement may not be achieved. This has been proved by the other similar wetland systems located in similar regions.

Thus tropical wetlands for the purpose of wastewater treatment have to be supported by dense wetland vegetation and have sufficient water supply, especially at the dry season. Otherwise the wetland plants cannot grow so well and therefore the wetland cannot achieve its expected functions.

3.2. Retardation ratios and carbon in water

The results for retardation ratios (Table 4), relative to sulfate concentration (Table 5) show that antimony, cadmium, lead and zinc were essentially attenuated via passage through the wetland system for the period Jan to Feb 1994. Copper, however, showed fluctuation in retardation ratio (Table 4). The highest ratio for copper corresponded to the lowest sulfate concentration measured at SP5 (Table 5) and electrical conductivity (Figure 5) indicating dilution of dewatering by creek water, derived from rainwater runoff.

Table 4
Retardation ratios for antimony, cadmium, copper, lead and zinc at SP5 (Jan-Feb 1994)

Date	Antimony	Cadmium	Copper	Lead	Zinc
11 Jan (f)	0.122	0.013	2.059	0.018	0.118
11 Jan (t)	0.106	0.012	0.995	0.005	0.127
14 Jan (f)	0.179	0.124	12.862	0.132	0.292
14 Jan (t)	0.171	0.071	3.899	0.129	0.188
17 Jan (f)	0.108	0.009	1.380	0.028	0.081
17 Jan (t)	0.151	0.015	1.469	0.023	0.132
28 Jan (f)	0.185	0.010	0.280	0.008	0.069
28 Jan (t)	0.179	0.013	0.258	0.022	0.073
4 Feb (f)	0.084	0.006	1.227	0.005	0.067
4 Feb (t)	0.079	0.009	1.125	0.012	0.057

Note: f = filtered; t = total

Table 5
Concentration data for sulfate and dissolved and total carbon (both inorganic and organic forms) at SP5 (Jan-Feb 1994)

Date	Sulfate (mg/l)	DIC -Inorganic Carbon (mg/l)	DOC-Organic Carbon (mg/l)	TIC- Inorganic Carbon (mg/l)	TOC-Organic Carbon (mg/l)
11 Jan	310	1.6	2.2	1.7	2.0
14 Jan	130	3.0	0.6	3.2	0.5
17 Jan	400	2.0	0.2	1.9	0.2
28 Jan	280	2.9	0.3	2.9	0.3
4 Feb	440	2.0	0.5	2.6	3.7

The results for inorganic and organic forms of carbon are given in Table 5 and show that dissolved and total carbon in water fluctuate with time and flow. Inorganic carbon concentrations were more consistent during the period sampled, being derived from the dewatering and seepage. Organic carbon was derived essentially from decaying vegetation in the wetland.

3.3. Electrical conductivity and total dissolved salts loads at SP5 and SP11 June to July 1994

Figure 5 gives electrical conductivity (EC μS/cm) measured at SP5 and SP 11 using the continuous loggers to record data. These data provide a means of showing the true relationship of dissolved salts at each location through comparison of flow data converted to TDS (Figure 6) using a factor of 0.8x EC (Woods and Noller, 1995).
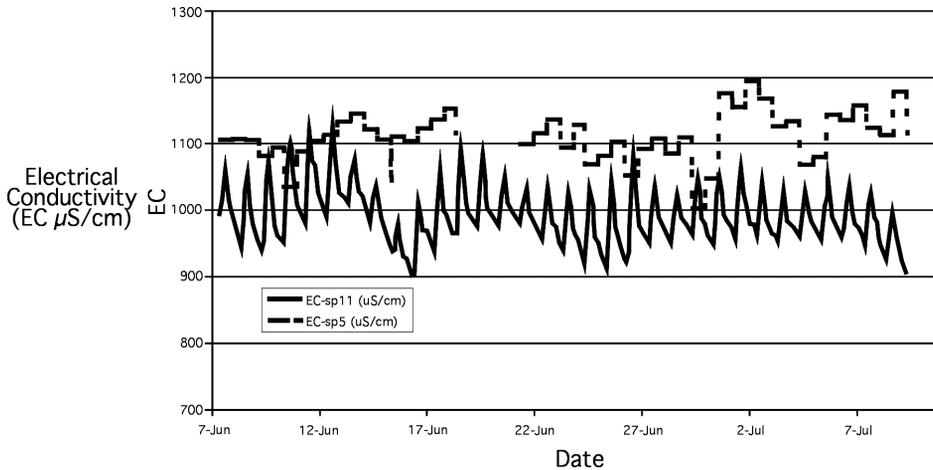
Figure 5. Continuously recorded electrical conductivity at SP 5 and SP 11 from June – July 1994

The electrical conductivity at SP11 clear shows the diurnal cycle associated with daily temperature fluctuation. The changes range from 900μS/cm to1200μS/cm. The data for SP5 show the diurnal fluctuation less clearly than for SP 11. The apparently higher electrical conductivity at SP5, compared to SP11, is demonstrated with the daily measured data and confirms the phenomenon shown in Figure 3.
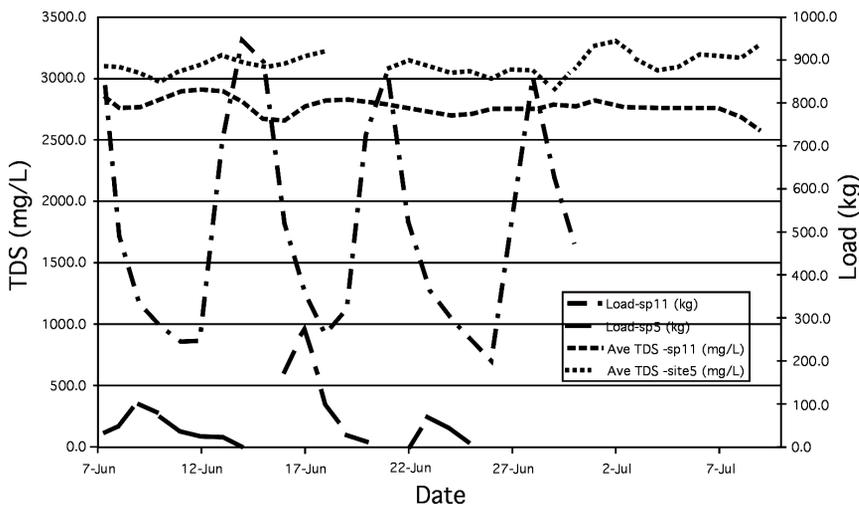

Figure 6. Total dissolved salts concentration and load data at SP5 and SP11 from June – July 1994

The plot of TDS load data (Figure 6) at SP5 and SP11 shows a different phenomenon to that observed for EC data alone (Figure 5). The load of TDS at SP11 (wetland inlet) is in fact higher than that observed at SP5 (wetland outlet). This finding indicates that dissolved salts including sulfate are retained within the wetland or lost by a process other than flow through the wetland. It also indicates the significance of considering loads.

3.4. Load data for specific parameters

The load data was calculated as explained in section 2.2. Selected data has been graphically represented and is displayed below in Figures 7-12. Generally there is a reduction in load for wetland inlet compared to downstream.
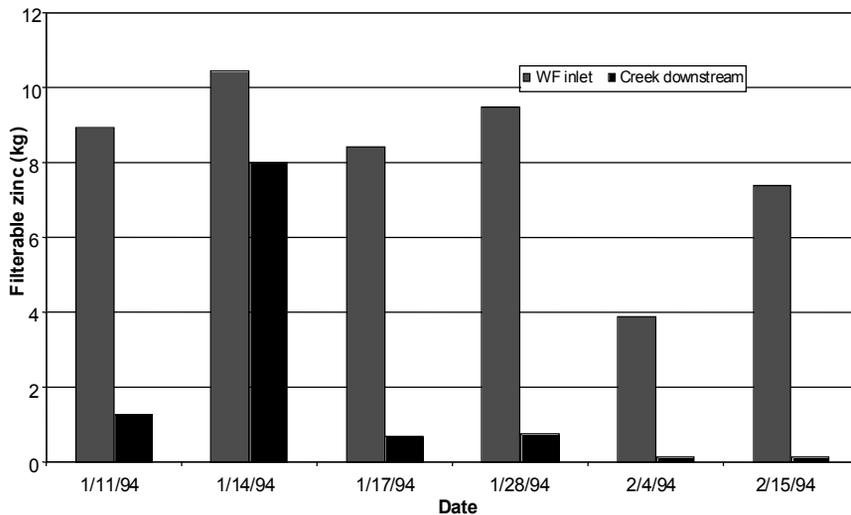
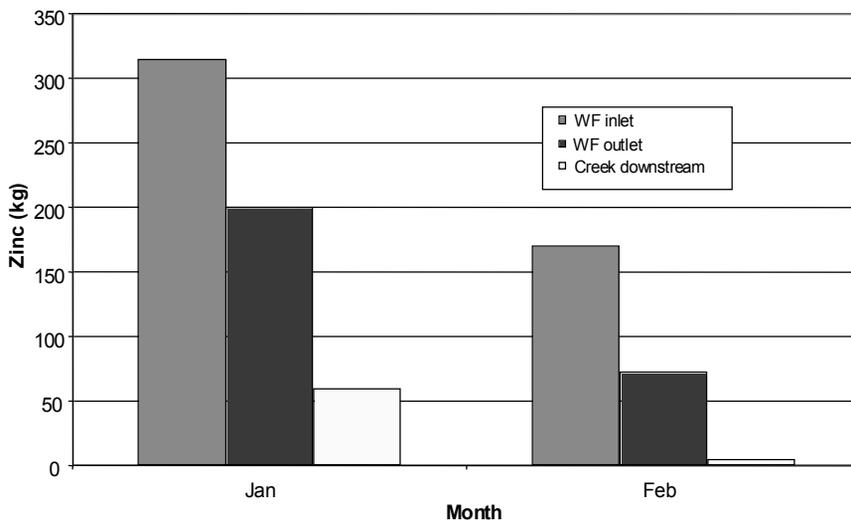Figure 7. Filterable zinc loads to the wetland and Woodcutters Creek in 1994

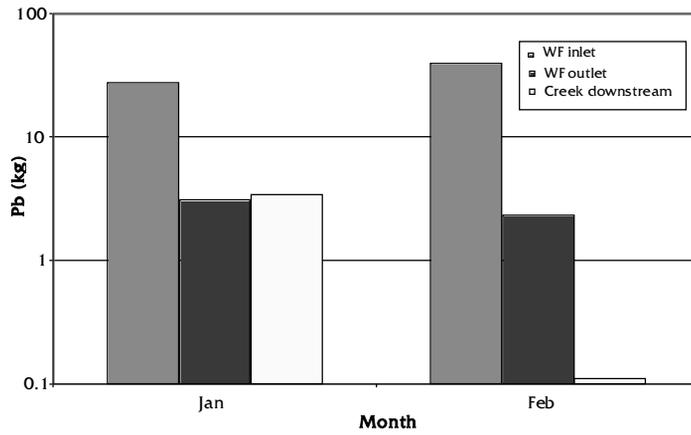Figure 8. Total zinc loads to the wetland and Woodcutters Creek, January and February 1994

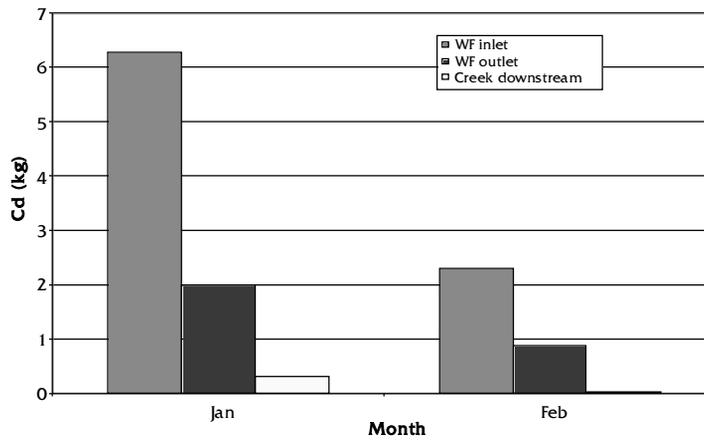Figure 9. Total lead loads to the wetland and Woodcutters Creek, January and February 1994

Figure 10. Total cadmium loads to the wetland and Woodcutters Creek, January and February 1994
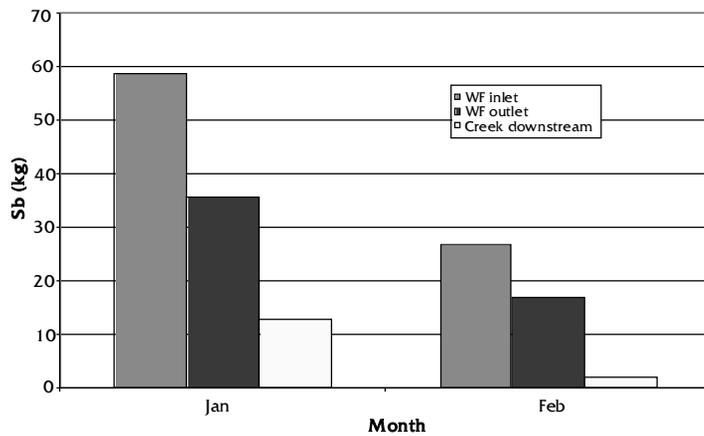
Figure 11. Total antimony loads to the wetland and Woodcutters Creek, January and February 1994
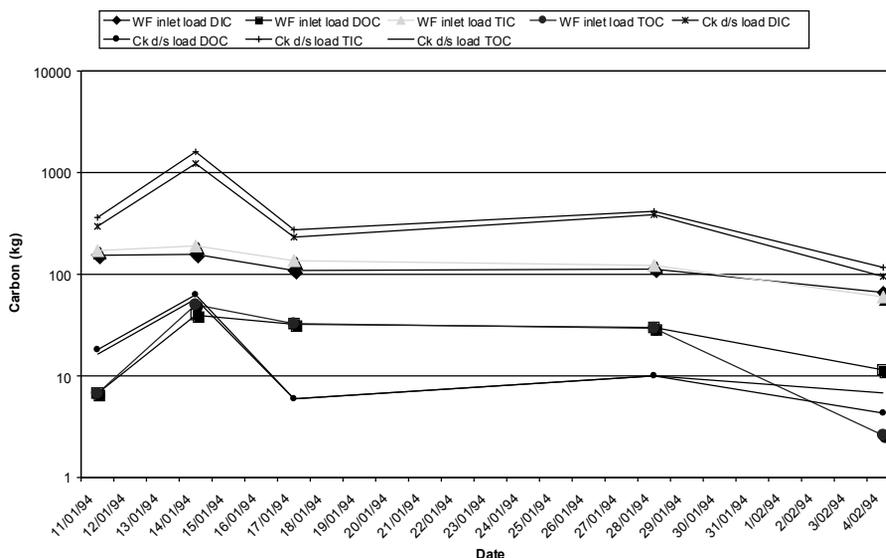
Figure 12. Total carbon loads to the wetland and Woodcutters Creek, January and February 1994

4. RESULTS AND DISCUSSION

4.1. General observations of load

It is clear from loads analysis (Figures 7-12) at the wetland inlet and outlet, that sulfate is not significantly reduced in the wetland. But it must be remembered that sulfate is about 1000X greater in concentration than zinc, the most concentrated of the transition metal contaminants, hence a significant reduction (such as that which could react with the load of transition metals present), would be barely noticeable from a total scale.

While anaerobic pockets appear to be active, much of the wetland remains oxidising and therefore free for aerobic processes, like iron oxide formation and adsorption (August *et al.*, 2002; Eger, 1994), as is evidenced by elevated iron and manganese concentrations in the sediments (ERAES, 1992).

The organic carbon loads to the wetland are, as expected, quite small compared to the inorganic carbon load (Figure 12). While the organic carbon concentrations in the creek are double those at the wetland filter inlet, the load data does not display this variation, due to the lesser flow rate in the creek compared to the wetland filter inlet.

The transition metals show significant reduction in concentration on passage through the wetland, even for zinc and antimony, which were not expected to decrease so significantly. The lack of lead reduction in the creek in January may be due to the apparent increase in organic carbon concentrations. Next to copper, lead has a high affinity for complexation to humic material. It is unusual though that the other metals did not show a similar increase. It should be noted that there was a spike in concentration of lead at SP5 on 14 January 1994, which corresponded to a high-flow period, and hence the high load value. The lead concentration could be due to contamination of sample rather than a real value.

4.2. Chemical characteristics of the Polishing Pond and Woodcutters Creek

The water released to the wetland is high in sulfate ($\approx$500mg/l), similar to upstream sites for inorganic carbon, and slightly greater than upstream for organic carbon, high in zinc ($\approx$ 2000µg/l as total and filtered fractions), about half the creek levels for alkalinity and bicarbonate, and with pH ranging between 7.2 and 8. Copper input to the wetland is low (generally less than 5µg/l), as are all the major cations, except calcium, which is about 10x the

upstream creek concentration. Chloride, nitrate, phosphate, manganese, iron and arsenic are close to or less than natural surface water concentrations in the tropics at the wetland inlet. Other transition metal concentrations entering the wetland are slightly elevated, although not to the same extent as zinc. Total and filtered concentrations tend to be similar. This is what is termed a "low-strength" metal mine drainage.

The oxidising waters would support precipitation of iron and aluminium oxyhydroxides, particularly at the slightly alkaline pH observed in the wetland. Manganese oxyhydroxide precipitation may be supported at this pH, although slightly more alkaline conditions would be more conducive to its precipitation. Of course, iron and aluminium would also be expected to be complexed by dissolved humic matter, but their concentrations are such that they would still give significant quantities of precipitates.

It is evident that early in the wetland filter's life adsorption to clays would have been a mechanism for removal for many cationic species. Unfortunately no silica concentrations in sediments or waters of this wetland were available for the study period, although values from 1992 exist. Silica was quite high, being about 18mg/l at the wetland inlet, and 18mg/l at the outlet. Given the reduction in flow rates at the outlet compared to the inlet, as well as the high silica concentration a number of silica precipitates may have formed, despite the apparently constant concentration; silicate minerals that precipitate usually contain iron, aluminium, sodium, calcium and magnesium in varying amounts (Morel and Hering, 1993). The other transition metals present (zinc, cadmium and lead) do not form silicate minerals (except possibly by ion exchange with the primary ions), but precipitated silicates provide further adsorbing surfaces, although these are generally not as efficient as the oxides. Complex silicate precipitation, however, is generally not very favourable, probably due to the massive entropies involved in such a reaction. Only simple silicates are expected to precipitate, but these could account for some removal of trace metals, although iron and aluminium oxyhydroxides would account for a greater proportion

The sediments are therefore likely to comprise iron/aluminium oxyhydroxides at the surface and sulfides in localised anaerobic pockets – studies subsequent to 1994 by CSIRO (ERAAES, 1992) have shown that the surface sediments of the wetland contain sulfide concentrations of up to 26000mg/kg dry weight. This removal mechanism would be mainly due to the activities of sulfate-reducing bacteria, which speed the kinetics of sulfate reduction, and could survive in the oxygen limiting conditions near the sediment surface. The wetland plants provide the organic substrate sulfate-reducing bacteria require to function (Sobolewski, 1996). Low-strength metal mine drainage appears to favour sulfide formation in wetlands (Sobolewski, 1996), unlike high-strength metal mine drainage (which are frequently acidic) that tends to retard sulfate-reducing bacteria activity. Zinc, lead, cadmium, iron and antimony concentrations in surface sediments near the inlet were 75000, 5090, 106, 42100 and 856mg/kg respectively, compared to 8800, 2250, 48, 31200 and 173mg/kg at the wetland outlet. Clearly reduction of zinc and iron in the wetland is significant. Eger (1994) found sulfate-reducing wetland systems could reduce concentrations of zinc, a recalcitrant transition metal, in mine drainage by 100X. The sediment sites at the outlet appeared to be oxidising, and hence zinc and iron in the porewaters were elevated.

It is clear from the sediment analyses, that precipitation as a sulfide is not the only removal mechanism for zinc, since zinc is present in the sediments at greater concentrations than sulfide. As iron is present in such high concentrations in the wetland soil, despite its rather insignificant concentrations in the inlet waters (being undetectable in January, and $700\mu g/l$ in February) this must be a prime removal mechanism through adsorption, which is essentially an aerobic process (Eger, 1994).

P, OH^- and other ions aid in adsorption of trace metals to iron and aluminium oxides. Application of phosphate can cause zinc uptake to be reduced in plants, leading to zinc deficiencies; low phosphate concentrations (<0.01mg/l) in the study wetland mean this problem is unlikely to be encountered (Shuman, 1980). A fresh oxide surface can adsorb 10x as much trace metal as an aged oxide surface, with fresh aluminium oxides adsorbing more than fresh iron oxides. The iron in the wetland is constantly being precipitated as oxyhydroxide, so should remain fresh and maintain a high adsorption capability, hence good trace metal removal.

The iron and aluminium hydroxide species tend to retain a positive charge at pH<8 (Fe) and pH<9 (Al), thus they 'stick' well to the negatively charged clay surfaces (Pickering, 1980). One effect of the presence of a hydrous oxide coating on sediments is the reduction in pH required for precipitation of heavy metal ions. The selectivity sequence of iron oxide coatings is Pb (3.1)>Cu (4.4)>Zn (5.4)>Ni (5.6)>Cd (5.8)>Co (6.0)>Sr (7.4)> Mg (7.8), while for aluminium it is Cu (4.8)>Pb (5.2)>Zn (5.6)>Ni (6.3)>Co (6.5)> Cd (6.6)>Mg (8.1)>Sr (9.2).

The elevated bicarbonate concentrations in wetland influent suggest also that some of the trace metals will precipitate as carbonates.

As the water moves down the creek, further removal becomes less significant. Tropical creeks tend to be buffered by silicate weathering, rather than by bicarbonate/carbonate, and therefore bear mildly acidic water. The precipitation and adsorption of metals therefore reduces, compared to the mildly alkaline water in the polishing pond and upper reaches of Woodcutters Creek. Tropical creek waters also tend to contain naturally higher levels of dissolved humic materials than their temperate counterparts, which also aids in keeping metals mobile. However, subsequent studies by ERAES have shown that trace metal levels in these downstream sediments are significantly elevated over control sites, so active removal is still clearly occurring, even if not to the same extent as the polishing pond. A proportion of the sediment contains elevated sulfide, so sulfate-reducing bacteria are active in localised anaerobic pockets.

4.3. Role of organic carbon

Despite reasonable dissolved and total organic carbon concentrations (27.5 and 30.5mg/l respectively), at the pH of the wetland water, it is unlikely that humic and fulvic acids will interfere with zinc adsorption, by either chelation with the zinc or monopolising adsorption sites. It is more likely that organic matter, which is negatively charged in natural waters, will form colloids, and/or settled particulates, and that these will provide a further adsorbing surface for metal removal. The decomposing surfaces of dead wetland plants also provide adsorption sites. Doyle and Otte (1997) found that while wetland vegetation and organisms were important in increasing accumulation of arsenic and iron in a salt marsh wetland, that zinc retention was not statistically different whether wetland flora and fauna were present or not. However, zinc concentration in the wetland soil was strongly correlated with iron, therefore wetland organic matter is indirectly responsible for zinc removal via iron species. Zinc has a lower tendency to adsorb to particles than do other transition metals, particularly copper and lead (Kelly, 1988).

In natural systems the organic ligands most likely to be present are humic acids, although some plants also release hydroxycarboxylic acids (Pickering, 1980). These natural organic ligands can both solubilise heavy metal ions and be sorbed on clays, and may therefore significantly affect the sorption/desorption behaviour of trace metals. The water-soluble, low MW component not precipitated on reducing pH is known as fulvic acid; which generally possess three types of functional groups; phenolic, carboxylic and carboxyl groups. The stability of metal humates is a function of the nature and concentration of the metal ion, the pH, Eh and ionic strength. In general, stability constants decrease in the order Cu>Pb>>Cd>Zn, thus is unlikely to affect zinc in solution. Fulvic acid is reportedly a better extractant than humic acid, but both are inferior to synthetic chelating agents like EDTA. Zinc tends to be less easily extracted than manganese and iron. Should the surfaces of the clay be coated in iron or aluminium hydroxides, enhanced bonding of the organic material can occur to the sediment. Increased salinity and acid pH also enhances humic acid adsorption on clay.

In alkaline media, such as Woodcutters wetland, chelating materials become less significant, as the organic functional groups form salts rather than dissociate. Since mine drainage is unlikely to have strong organic chelates present a significant proportion of the trace metals should be removed in the sediments provided the pH is near neutral or alkaline.

Of course a small proportion of the trace metals will be incorporated into organic molecules in plants. Aquatic plants can bioaccumulate significant concentrations of zinc, lead, cadmium and antimony, and so effect some removal (Outridge and Noller, 1991). However, wetland

plants tend to accumulate less than 1% of the trace metals in the wastewater (Kelly, 1988), compared to the sediments, which remove the majority. Therefore the plants effect very little trace metal removal. However, wetland plants play a very important role in increasing the dispersion (and thereby wastewater contact with reactive surfaces), and acting as a filter, removing particulates, which may carry sorbed trace metals. Trace metals accumulated by plants is unlikely to be released upon senescence, rather, it is incorporated into the sediments.

5. CONCLUSIONS

This paper sought to review historical physico-chemical and flow data on load and retention characteristics of the wetland system at Woodcutters mine. This system was used to polish wastewater exiting the sedimentation dam that originated from underground dewatering. The dewatering contains elevated concentrations of antimony, cadmium, lead, zinc and sulfate with lesser concentrations of copper. The potential toxicity of these elements to aquatic fauna and flora has been reviewed. The dewatering was essentially alkaline, limiting the toxicity of heavy metals present. Antimony, however, exists in an anionic form (stibnite) and is not easily removed from solution in such a wetland polishing system. Both organic and inorganic carbon as total and dissolved forms were measured and showed that organic carbon levels were relatively low compared with temperate vegetation runoff and were derived essentially from decaying vegetation.

Continuously-logged conductivity, pH and flow characteristics of the wetland system showed that there was an additional source of dissolved salts to the system, namely the addition of seepage from the original tailings dam. Comparison of upstream vs downstream data, expressed as load, showed the correct relationship of dissolved salts at each location. The electrical conductivity also showed the relationship of the diurnal cycle associated with daily temperature fluctuation.

Consideration of mechanisms for trapping contaminants in the wetland showed that adsorption on to mineral particles in sediments was an important trapping mechanism together with that of detrital matter from decaying wetland vegetation. It was concluded that the role of organic carbon was less likely to affect zinc retention compared with copper, lead and cadmium.

The study demonstrated the value in undertaking more intensive studies over short time duration in order to understand wetland retention performance based on load characteristics as a means of understanding the significance of the individual constituents in the wastewater. Concentration data alone does not provide these answers.

ACKNOWLEDGEMENTS

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