

Contaminated Mine Water Amelioration - Study of a Long Established Natural Wetland

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ABSTRACT

A natural wetland area of approximately 2.6 Ha that receives contaminated mine water, with near neutral pH and high levels of copper and zinc, has been studied. Regular water quality monitoring has shown a substantial and consistent reduction of copper in the outflow from the wetland, but a less effective and more erratic reduction in zinc. Removal efficiency for copper and zinc do not correlate with water inflow rate or input loading. Area adjusted mass retention for both copper and zinc are in the order of 0.05 g/m²/day, although complex flow paths mean the removed metal is not distributed evenly throughout the wetland.

Sediment analysis has shown that high levels of zinc are loosely held on exchange sites in the upper, organic matter-rich, layer of the sediment and that this zinc can be relatively easily released into the water. Copper, on the other hand, is held more firmly in the sediment and represents effective removal by the wetland.

Implications of this work for the design of constructed wetland treatment systems and the importance of designing for specific water chemistries are considered.

This work indicates that a suitably designed and engineered wetland should be capable of long term passive treatment of contaminated mine water.

INTRODUCTION

Cornwall, U.K., was the world's leading producer of copper and tin during the 19th century. The legacy of this activity is the numerous and persistent discharges of contaminated mine water from old mine workings, waste rock dumps and tailings dams. These discharges are frequently acidic and have high levels of dissolved metals which have an adverse impact on the biota. Where natural wetlands have become established on rivers receiving contaminated mine water observation indicates a significant improvement in water quality downstream of the wetland area. This study focuses on such a natural wetland area in a former mining district.

Mine drainage treatment with constructed wetlands is gaining popularity and is an attractive option due to its essentially passive nature [1,2,3]. However, there are currently no constructed wetlands for acid mine drainage treatment that have been operating for more than about 10 years [4]. There is therefore uncertainty about the lifespan of such systems. If they reach capacity and cease to function after a certain length of time, the treatment can no longer be considered passive since further expenditure will be required to rejuvenate or replace the wetland.

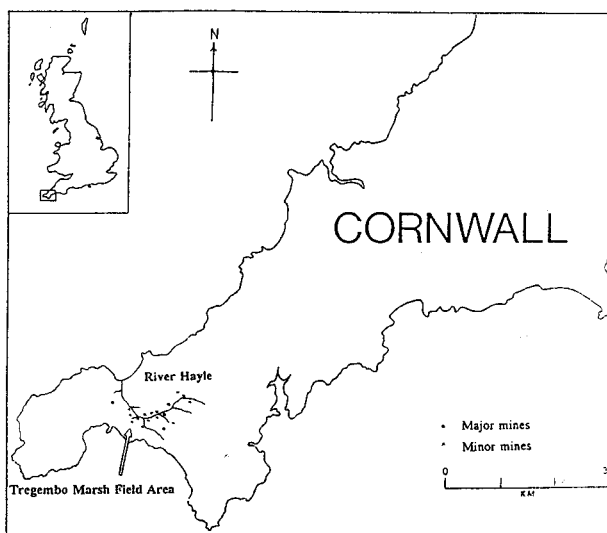
Study of a natural wetland, such as that described in this paper, can provide insight into the long-term functioning of mine drainage amelioration by wetlands.

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SITE DESCRIPTION

Tregembo Marsh is a wetland area of approximately 41 Ha situated on the River Hayle in the Mounts Bay Mining District of Cornwall [5] (figure 1). The River Hayle has a catchment area of about 50 km², within which there are some 50 abandoned mines. The mineralization is dominantly hydrothermal vein type, associated with the Cornubian granite batholith. Mining was carried out during the 17th, 18th and 19th centuries, yielding large quantities of tin and copper ores, with subsidiary amounts of zinc, lead, silver, arsenic and wolfram. The river valley, including Tregembo Marsh, was reworked for tin during the Second World War.

Figure 1 Location Map

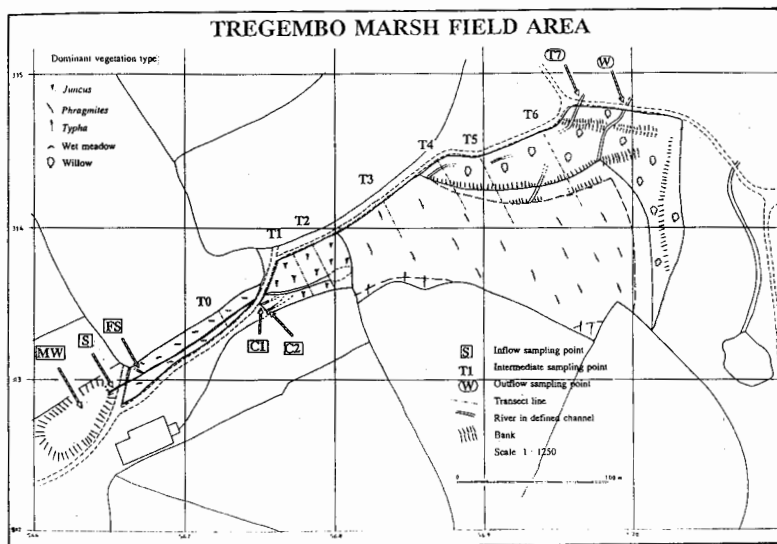


There are four major mine adits draining into the River Hayle. In addition, numerous minor adits occur. There are also seeps, and run-off from extensive areas of waste rock dumps, all of which contribute to the contaminated mine water input to the river.

The field study area is part of Tregembo Marsh (figure 2) which was selected for its accessibility, range of vegetation types and distinct inflows and outflows of surface water and mine water seeps. The study area can be subdivided into 4 areas on the basis of principle vegetation type :- i) wet meadow, ii) *Juncus*, iii) *Phragmites* and iv) Willow carr, although there is considerable species diversity within these areas. There are 5 distinct inflows and two outflow points.

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Figure 2 Field Map



METHODS

Water samples have been taken at approximately fortnightly intervals since November 1993. Analyses carried out on the water samples are summarised in table 1.

Table 1 Analysis of water quality

Parameter	Field/Lab.	Sample prep.	Method
pH	Field	n/a	Whatman μ -sensor
Total Dissolved Solids (TDS)	Field	n/a	Whatman μ -sensor
Alkalinity	Field	n/a	'CHEMets' hand-held titration cells
Dissolved O ₂	Field	n/a	'CHEMets' colorimetric ampoules
Temperature	Field	n/a	Mercury thermometer
'Total' copper*	Laboratory	Acidified	Atomic absorption spectrometry
'Total' zinc*	Laboratory	Acidified	Atomic absorption spectrometry
Sulphate	Laboratory	Unacidified	Barium sulphate gravimetry [6,7]

* 'Dissolved' Cu and Zn was determined on filtered samples; the results were not significantly different from 'total' Cu and Zn determinations.

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Quality control procedures included the use of a synthetic river water reference standard and control charts [8], and analysis of duplicate samples.

Sediment samples were collected in August 1993 using a length of 40mm internal diameter alkathene pipe as a corer. Samples were taken of the upper, organic matter-rich, layer and the lower, predominantly inorganic, layer. Sediment profiles were determined using a standard screw-type soil auger.

Sediment samples were air-dried at approximately 33°C and the < 2mm size fraction was used for the following analyses.

Loss-on-ignition was determined by combusting samples at 550°C for 2 hours in a muffle furnace [9,10]. Weight loss gives an approximation of organic matter content.

'Total' metal content was determined by nitric acid/perchloric acid digestion [11]. The diluted digestate was analysed for metals (copper and zinc) by AAS.

Extractions were carried out to assess the potential mobility and availability of metals in the sediment [12]. The extractants used are shown in table 2.

Table 2 Extractants used in sediment analysis

	Extractant	Fraction extracted	Duration
1.	Water	Water soluble metals	5 hours
2.	Magnesium chloride	'Exchangeable' metals	1 hour
3.	Sodium pyrophosphate	'Organically-bound' metals	15 hours

Extractions were carried out in glass centrifuge tubes, shaken for the time specified and then centrifuged. Metal content was determined in the supernatant by AAS.

Extractions 1 and 2 were carried out sequentially. Extraction 3 was carried out on a separate sub-sample. The use of various chemical extractants to assign soil metal content to specific fractions of the sediment is a useful technique for characterising sediments, but it is by no means a clear-cut process. The possible ambiguities and limitations of these extraction procedures are considered in the discussion section of this paper.

All results were adjusted to a weight of metal/ weight of oven dry sediment basis by determining the moisture content of separate, air-dry sub-samples [9].

Quality control procedures included the use of a certified reference soil standard and duplicate analyses.

RESULTS

Water

Table 3 gives average water quality values of inflow and outflow sampling points for a 6 month period (see figure 2 for the location of these points and figure 3 for a schematic representation).

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Table 3

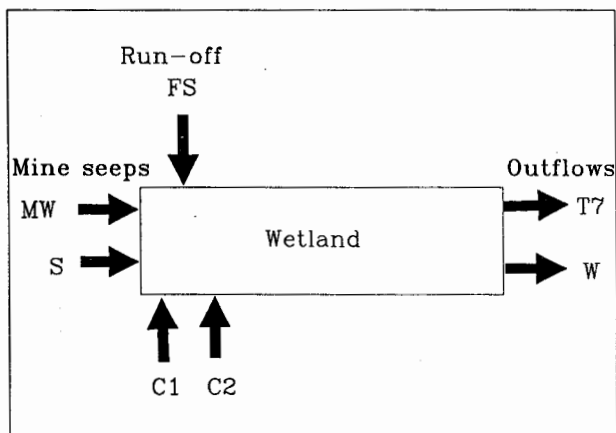
WATER QUALITY
Average for the period 3.11.93-3.5.94
(n = 13, range in brackets)

	Flow L/s	pH	T ¹ °C	Alk. mg/L CaCO ₃	TDS ² ppm	SO ₄ mg/L	DO ₂ ³ ppm	Cu mg/L	Zn mg/L	
INFLOW	MW⁴	4.6 (0.6-11.2)	6.4 (6.3-6.6)	31 (30-35)	240 (230-250)	59.0 (56.5-62.4)	9 (8-10)	1.58 (1.14-1.82)	4.41 (3.78-4.73)	
		5.6 (3.5-8.2)	6.1 (5.7-6.3)	12 (11-13)	18.5 (15-20)	190 (170-220)	50.5 (48.4-53.3)	7 (7-8)	0.88 (0.72-1.06)	3.31 (3.18-3.74)
		3.7 (1.0-13.5)	7.0 (6.7-7.4)	12 (10-14)	48 (35-70)	220 (210-240)	48.4 (43.5-52.4)	9 (6-10)	0.27 (0.12-0.62)	2.15 (1.63-2.66)
		3.0 (1.4-6.0)	6.4 (6.1-6.6)	11.5 (11-12)	27 (20-35)	200 (190-220)	51.1 (45.8-54.8)	7 (5-8)	0.50 (0.43-0.61)	3.14 (2.76-3.50)
C2	6.9 (5.0-11.7)	6.2 (6.1-6.3)	12.5 (12-13)	28 (22-35)	220 (200-230)	54.0 (48.8-57.7)	7 (6-8)	0.64 (0.58-0.76)	3.70 (3.49-3.96)	
OUTFLOW	W	8.1 (3.6-20.0)	7.3 (7.0-7.4)	11 (8-13)	34 (30-40)	210 (190-230)	8 (7-10)	0.05 (n.d.-0.13)	2.74 (2.52-3.10)	
		T7	14.9 (9.3-35.5)	7.4 (7.2-7.5)	11.5 (9-14)	38 (30-45)	210 (190-220)	9 (7-10)	0.11 (0.06-0.20)	2.53 (2.19-2.96)

- 1 31.3.94 to 16.5.94 only, n = 4
- 2 to nearest 10 ppm
- 3 n = 4
- 4 only flowing for period 15.12.93 to 16.3.94, n = 7

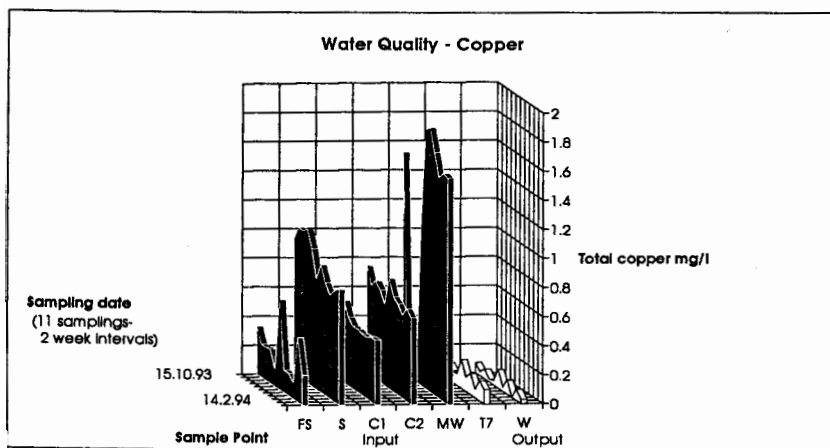
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Figure 3 Schematic representation of field area



The inflows from mine seeps (MW, S, C1, C2) have a pH of between 6.1 and 6.4 whilst runoff from the fields (FS) has a neutral pH. Outflows are always pH 7 or above. Each mine seep has distinctive levels of copper and zinc, with the lowest levels of each found in C1 and the highest levels of each in MW. MW only flowed for a period of about 3 months (when rainfall was particularly high) and the higher concentrations of metals are probably due to the flushing out of the products of mineral oxidation that had occurred since MW last flowed. Outflows had substantially reduced concentrations of copper, and slightly reduced concentrations of zinc. (figures 4 & 5)

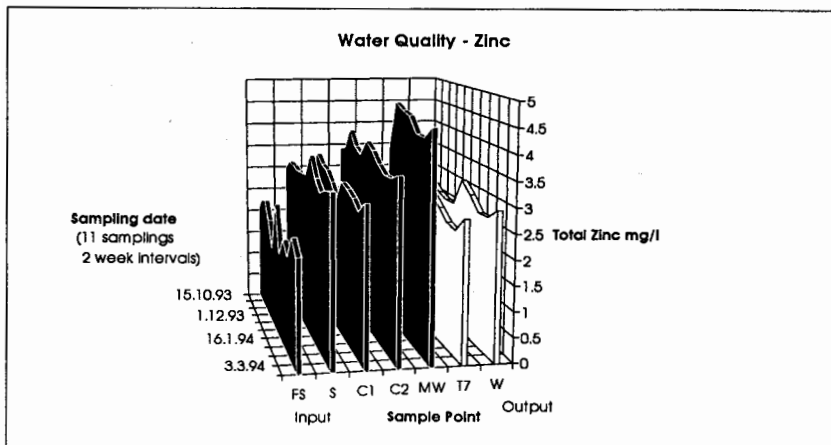
Figure 4



5th International Mine Water Congress, Nottingham (U.K.), September 1994

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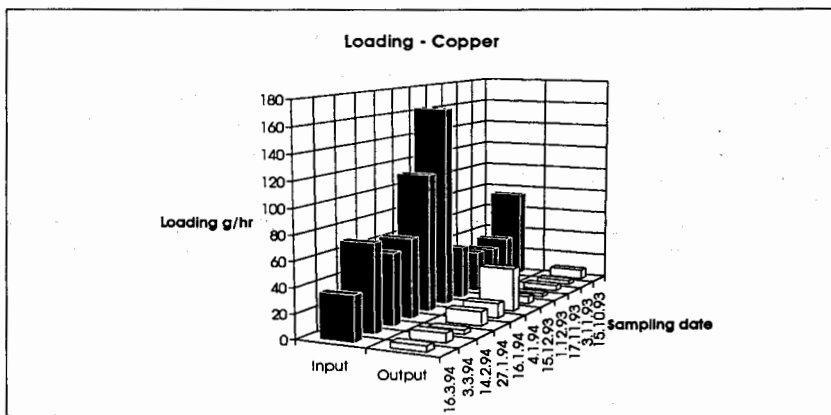
Figure 5



Both copper and zinc concentrations in the mine seeps show a significant positive correlation ($\alpha = 0.05$) with flow rate of the mine seeps. Thus an increasing flow rate through the old mine workings gives an increase in metal concentration in the water, which suggests there is still a plentiful source of soluble metals (i.e. oxidised minerals) within the workings. If this were not the case, increased flow could be expected to give a *decrease* in metal concentrations due to dilution.

Loading levels of copper and zinc (expressed as g/hr) were calculated from metal concentration and flow data to take into account dilution by surface runoff. Figures 6 & 7 and table 4 show that Cu loadings are consistently and substantially reduced whereas Zn shows more erratic behaviour.

Figure 6



5th International Mine Water Congress, Nottingham (U.K.), September 1994

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Figure 7

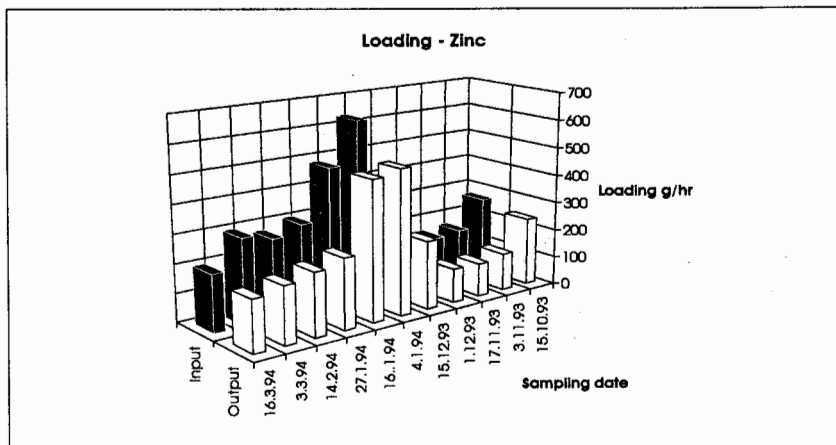


Table 4 Removal efficiency (%)

	Average n = 13	Range	Standard deviation
Cu	87.5	78.7 to 94.1	4.1
Zn	18.1	-0.6 to 35.7	10.9

$$\text{Removal efficiency (\%)} = \frac{\text{Input loading} - \text{Output loading}}{\text{Input loading}} \times 100$$

Removal efficiency does not correlate with water inflow rate or input loading for either Cu or Zn, neither do the removal efficiencies of Cu and Zn show any correlation with each other.

Within the limits of accuracy of the determination of flow rate, and hence the calculation of metal loading, it can be considered that removal of Cu from the water by the wetland system is relatively constant, whilst removal of Zn is very erratic. However, poor removal of Zn does not result simply from increased flow, and neither does increased flow render the removal of Cu less effective.

Area adjusted mass retention of Cu and Zn can be calculated for each sampling date by dividing the difference between input and output loading by the area of the study area, which is approximately 26,000m².

BROWN *et al* Study of a Long Established Natural Wetland**Table 5** Area adjusted mass retention ($\text{g}/\text{m}^2/\text{day}$)

	Average n = 13	Range	Standard Deviation
Cu	0.05	0.026 - 0.119	0.03
Zn	0.04	0 - 0.098	0.03

These results for area adjusted mass retention of Cu and Zn are the same order of magnitude as Eger [13] calculated for Nickel in a cell constructed within a natural wetland in northeastern Minnesota, although his results for Cu and Zn were one to two orders of magnitude lower.

The area adjusted mass retention for Cu has a strong positive correlation with input flow rate and input loading ($r = 0.98$ and 0.99 respectively), which is as Stark [4] found for Iron at Simco #4 constructed wetland, whereas the same figure for Zn does not show such a correlation. This indicates that the wetland system has the capacity to remove the input of Cu but has insufficient area to remove all the Zn.

These figures for area adjusted mass retention assume that removal processes occur evenly throughout the wetland area, which is highly unlikely in a complex natural system with a very heterogeneous water flow pattern through the area. The spatial variation in metal removal by the sediments from the water is further investigated by examining the sediments.

Sediments

A preliminary investigation of the sediments in the field area has been carried out to identify forms in which Cu and Zn are held, and hence allow determination of the removal mechanisms operating.

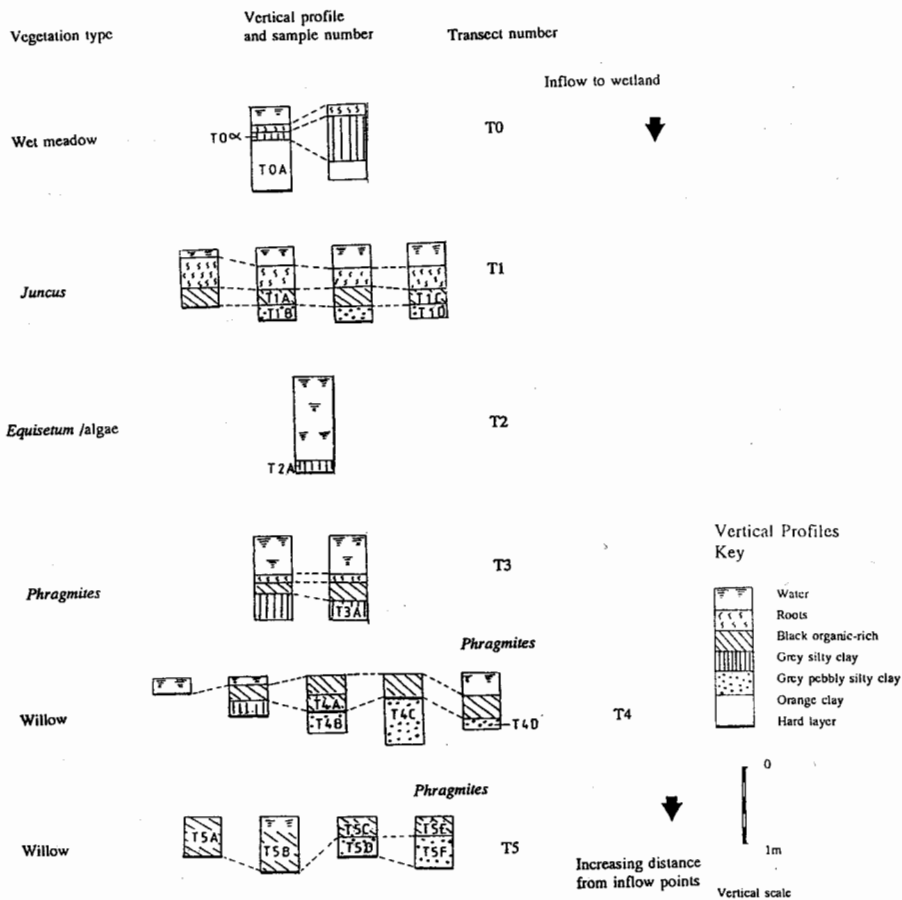
'Total' metal content

Table 6 gives the results of nitric-perchloric acid digests of sediment samples. Sample locations within the profiles can be seen in figure 8. The results have been divided into 'upper layer' (generally the top 15-20 cm, organic-rich) and 'lower layer' (less organic-rich, generally more silty). There is a very great spread of data values, as summarised on the table, although there is a general trend of less metals in the lower layer. Samples T5C and T5E, from the upper layer at two points on transect T5, are notable in that they have much lower levels of Cu than all the other upper layer samples (145 and $174 \mu\text{g}/\text{g}$ respectively), with the next lowest Cu content of an upper layer sample being an order of magnitude greater at $1343 \mu\text{g}/\text{g}$ (sample T0 α). This observation is considered further in the discussion of the results of extractions.

Figure 9 shows the Cu and Zn content of the sediment samples graphically, with loss-on-ignition superimposed. There is a general similarity in the pattern, with high metal content corresponding to high loss-on-ignition. Calculation of the correlation coefficients for metal content with loss-on-ignition shows that both Cu and Zn content have a positive correlation ($\alpha = 0.05$) with loss-on-ignition.

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Figure 8



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Table 6

SEDIMENT METAL CONTENT

Transect	Upper layer				Lower layer			
	Sample	LOI(%)	Cu	Zn	Sample	LOI(%)	Cu	Zn
T0	T0α	9.7	1343	982	T0A	5.9	404	508
T1	T1A	12.6	1872	1261	T1B	12.8	1587	852
	T1C	32.7	12579	8037	T1D	3.4	840	319
T2				T2A	7.9	467	460	
T3				T3A	5.1	300	429	
T4	T4A	68.6	6512	3629	T4B	6.2	148	570
				T4C	4.5	179	1697	
				T4D	3.1	143	282	
T5	T5A	82.4	5302	4858				
	T5B	83.0	3552	4823				
	T5C	32.1	145	1857	T5D	8.2	113	540
	T5E	37.8	174	6603	T5F	6.6	128	1905

Summary statistics

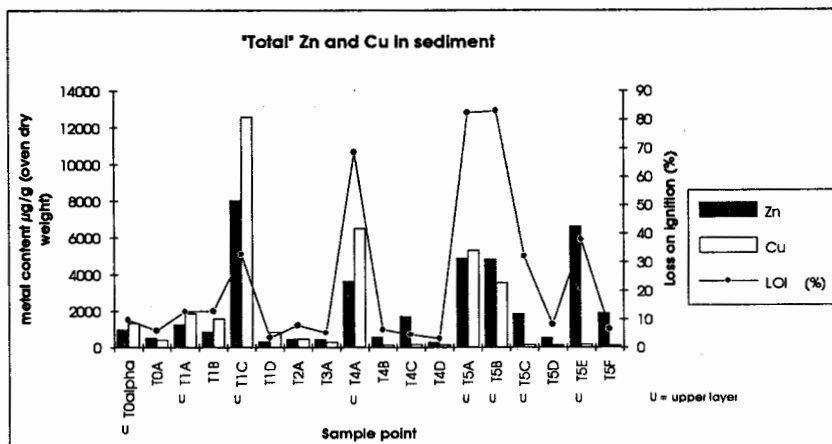
	Upper layer		Lower layer	
	Cu	Zn	Cu	Zn
Average	3935	4006	431	756
Std. deviation	4189	2559	464	574
Range	145 to 12579	982 to 8037	113 to 1587	282 to 1697

Metal content µg/g

Oven dry weights, average of 2 digests

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Figure 9



It thus seems likely that the organic matter plays a significant role in the removal of Cu and Zn from the water, and extractions were carried out to explore this possibility further.

Extractions

The results of extractions are given in tables 7 & 8. The amount of Cu and Zn extracted in each step is expressed both on a weight of metal per weight of oven-dry sediment basis, and a percentage of the 'total' metal.

'Water soluble' Cu is always less than 1.3% of 'total' Cu, whereas 'water soluble' Zn is up to 8.7%, with the highest relative amounts of 'water soluble' Zn found on transect T1, in the *Juncus* and near the mine seep inflows. Figure 10 shows that there are consistently much higher levels of Zn than Cu in the 'water soluble' fraction. Similarly, levels of 'exchangeable' Zn are higher (up to 2 orders of magnitude) than of 'exchangeable' Cu (figure 11), with less 'exchangeable' Zn in the lower layer.

'Exchangeable' Cu shows no correlation with loss-on-ignition, whilst 'exchangeable' Zn shows a significant positive correlation with loss-on-ignition ($\alpha = 0.05$). It can thus be seen that levels of Cu in these two most readily available fractions are low (never more than 7.7% of the 'total' Cu) and not associated with the organic content of the sediment. In contrast, up to 57.3% of Zn is present in these two fractions, with the organic matter playing a significant role.

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Table 7
COPPER EXTRACTIONS*

Transect	Upper layer				Lower layer			
	Sample	Water sol.	'Exch.'	'Org.-bound'	Sample	Water sol.	'Exch.'	'Org.-bound'
T0	T0α	3.2(0.2)		287(21.4)	T0A	2.3(0.6)	1(0.2)	61(15.1)
T1	T1A	2.4(0.1)	39(2.1)	361(19.3)	T1B	1.6(0.1)	23(1.4)	292(18.4)
	T1C	16.9(0.1)	112(0.9)	1188(9.4)	T1D	10.7(1.3)	49(5.8)	179(21.3)
T2					T2A	4.2(0.9)	36(7.7)	158(33.8)
T3					T3A	1.5(0.5)	3(1.0)	46(15.3)
T4	T4A	8.4(0.1)	35(0.5)	1436(22.1)	T4B	0.7(0.5)	1(0.7)	21(14.2)
					T4C	1.2(0.7)	5(2.8)	55(30.7)
					T4D	1.4(1.0)	6(4.2)	26(18.2)
T5	T5A	13.3(0.3)	133(2.5)	379(7.1)				
	T5B	2.1(0.1)	4(0.1)	154(4.3)				
	T5C	0.8(0.6)	n.d. ²	21(14.5)	T5D	0.6(0.5)	n.d.	18(15.9)
	T5E	0.7(0.4)	n.d.	17(9.8)	T5F	0.6(0.5)	n.d.	16(12.5)

Summary statistics

	Water sol.	'Exch.'	'Org.-bound'	Water sol.	'Exch.'	'Org.-bound'
Average	6.0(0.2)	65(1.2)	480(13.5)	2.5(0.7)	16(3.0)	87(19.5)
Std. deviation	6.2(0.2)	55(1.0)	536(6.8)	3.1(0.3)	18(2.7)	92(7.2)

* µg/g metal extracted, oven-dry weights
(figure in brackets is the percentage of 'total' metals)

1 Sample lost

2 n.d. = not detected

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Table 8

ZINC EXTRACTIONS*

Transect	Upper layer				Lower layer			
	Sample	Water sol.	'Exch.'	'Org.-bound'	Sample	Water sol.	'Exch.'	'Org.-bound'
T0	T0α	11(1.1)		236(24.0)	T0A	3(0.6)	28(5.5)	115(22.6)
T1	T1A	43(3.4)	362(28.7)	559(44.3)	T1B	30(3.5)	219(25.7)	499(58.6)
	T1C	696(8.7)	2536(31.6)	1553(19.3)	T1D	17(5.3)	35(11.0)	69(21.6)
T2					T2A	11(2.4)	118(25.7)	169(36.7)
T3					T3A	6(1.3)	43(10.0)	174(40.6)
T4	T4A	60(1.7)	2019(55.6)	3494(96.3)	T4B	4(0.7)	102(17.9)	233(40.9)
					T4C	30(1.8)	256(15.1)	445(26.2)
					T4D	2(0.7)	22(7.8)	32(11.3)
T5	T5A	98(2.0)	1872(38.5)	4404(90.7)				
	T5B	44(0.9)	762(15.8)	1127(23.4)				
	T5C	7(0.4)	178(9.6)	826(44.5)	T5D	3(0.6)	37(6.9)	138(25.6)
	T5E	21(0.3)	688(10.4)	1517(23.0)	T5F	3(0.2)	112(5.9)	463(24.3)

Summary statistics

	Water sol.	'Exch.'	'Org.-bound'	Water sol.	'Exch.'	'Org.-bound'
Average	123(2.3)	1202(27.2)	1715(45.7)	11(1.7)	97(13.2)	234(30.8)
Std. deviation	234(2.8)	923(16.7)	1470(31.1)	11(1.6)	83(7.7)	172(13.5)

* µg/g metal extracted, oven-dry weights
(figure in brackets is the percentage of 'total' metals)

1 Sample lost

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Figure 10

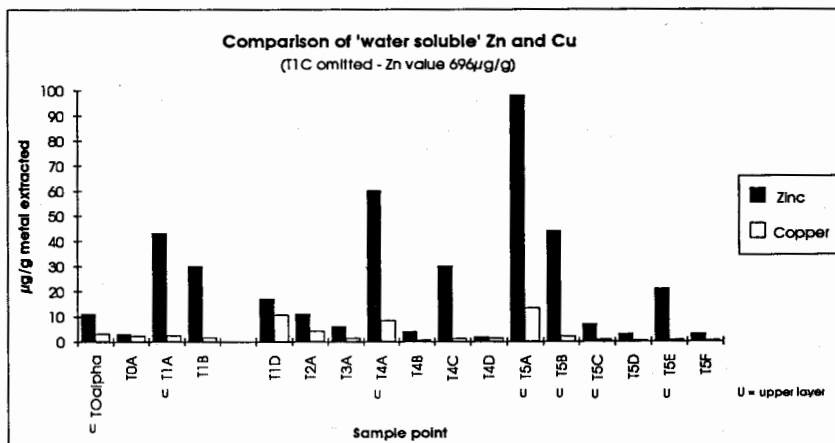
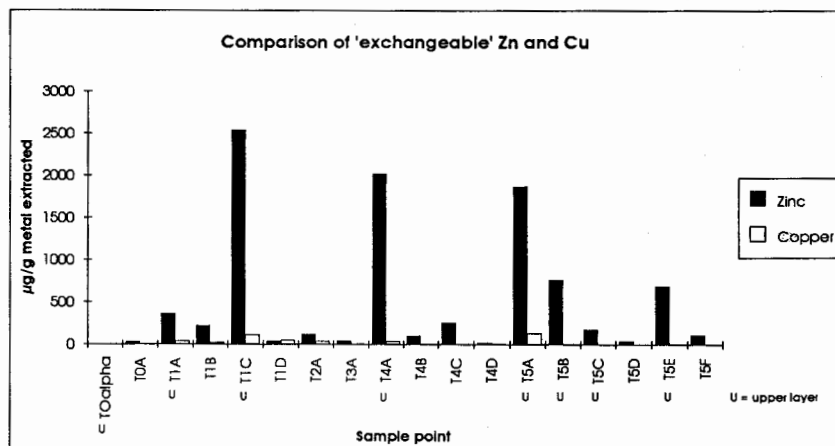


Figure 11

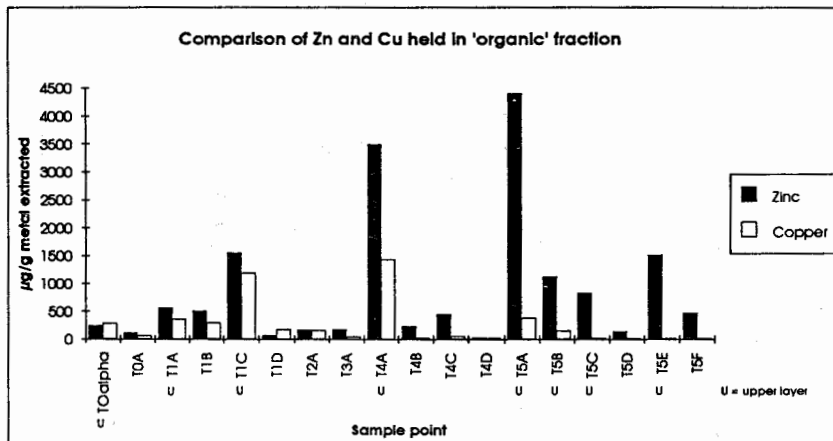


The environmental significance of these results for water soluble and 'exchangeable' Cu and Zn is that there are high levels of Zn loosely held on exchange sites in the upper, organic matter-rich layer of the sediment which can easily be released and thus re-enter the aquatic environment. This means that the wetland area is potentially a significant *source* of Zn as well as acting as a partial *sink*. Cu, however, is held more firmly in the sediment and thus more effectively removed by the wetland from the water course.

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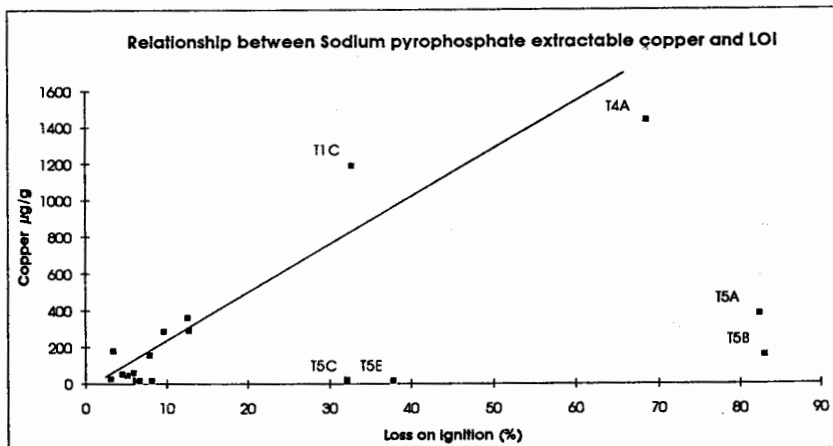
Cu and Zn that are 'organically-bound' are depicted in figure 12. There is more Zn than Cu in this fraction, with the difference between the amount of each metal increasing further into the study area.

Figure 12



Since sodium pyrophosphate is meant to extract the 'organically-bound' fraction [12] one would expect a strong correlation between loss-on-ignition and the results for this extraction procedure. This is indeed the case for Zn, especially if sample T5B, which plots below the trend line of a scatter plot of sodium pyrophosphate-extractable Zn against loss-on-ignition, is omitted ($r = 0.98$).

Figure 13



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However, sodium pyrophosphate extractable Cu shows no significant correlation with loss-on-ignition. Examination of a scatter plot (figure 13) reveals that samples from transect T5 plot well below the general trend line of increasing sodium pyrophosphate-extractable Cu with increasing loss-on-ignition. Indeed, if data for transect T5 is omitted, there is a strong positive correlation ($r = 0.95$). This, in conjunction with the low levels of 'total' Cu in samples T5C and T5E noted previously, would seem to support the supposition that Cu is being removed so efficiently by the wetland system that insufficient is getting as far as transect T5 to interact with, and be bound by, the organic matter. Thus the organic matter further into the wetland is 'undersaturated' with Cu. This contrasts with the case for Zn, which indicates that the organic matter throughout the system is 'saturated' with Zn.

It is intended in future work to investigate the levels and form of iron in the sediments as iron may play a role in binding other metals.

It is proposed on the basis of this work that organic matter is an important factor in removing both Cu and Zn from the water, and that the wetland has plenty of spare capacity to remove Cu whilst it has reached a state of dynamic equilibrium as regards Zn.

DISCUSSION

Extractions

This initial investigation into the partitioning of metals in different fractions of the sediment has revealed that there is considerable variation throughout the study area. Some preliminary observations can be made on the basis of this work about the likely forms in which metals are held but it is also important to consider the limitations and ambiguities of the extraction process.

The use of water as an extractant is quite straight forward. However, the water used for the extraction was de-ionized water, at pH7, whereas the water naturally flowing through the sediments has a pH of between 6.2 and 7.4 and contains both anions and cations. Thus, the leachability of metal cations from the *in situ* sediments will not be precisely as determined in the laboratory extraction process, but a reasonable indication of mobility can be obtained.

A simple salt, such as magnesium chloride, acts as a source of cations to displace trace metals held on inorganic and/or organic sites, predominantly by electrovalent forces - hence the categorization of metals extracted by magnesium chloride as 'exchangeable'.

Sodium pyrophosphate has been used as a dispersing agent for soil organic matter. It is conjectured [12] that this reagent may act in one of two ways:-

- i) by removing trace metals from sites on organic material due to formation of stronger, soluble, complexes;
- ii) by mobilizing those parts of the organic matter, with trace metals still attached, that were flocculated by iron, aluminium or calcium. This is achieved by the sodium pyrophosphate forming complexes with the flocculant cations.

Sodium pyrophosphate was chosen in preference to EDTA as it extracts more colloidal organic matter [14]. This extractant was used at its natural pH (pH 10 for 0.1M solution); at this pH it has been found to extract 'freshly precipitated hydrous ferric hydroxide' but very

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little 'partly crystallized oxides', whereas at pH7 it appears to extract both these [12]. There have been conflicting reports on its ability to dissolve copper sulphides.

It can thus be seen that the use of extractants is not a clear-cut process giving easily definable results, and whilst useful information can be derived from such work, the results should always be interpreted with caution and full awareness of the limitations.

Copper is largely held in the organic fraction of the sediment, although never more than 33.8% of the total. Thus the majority of the Cu is associated with sediment fractions not investigated in this extraction process. It is intended in future work to extend the extraction process to investigate a wider range of fractions. In particular, a step to extract metals held as sulphides will be included which should provide useful data regarding metal availability and stability within the wetland.

Zinc shows a trend of being 'more available' than copper - that is, a higher proportion of Zn was found to be 'water soluble' and 'exchangeable'. Also more of the 'total' Zn was extracted by the three extractants used, with up to 96.3% of total being allocated to the 'organic' fraction. The results for Zn show the limitations of not carrying out the extractions sequentially, since, for example, sample T4A is found to have 55.6% 'exchangeable' and 96.3% 'organic' zinc. This means that the extractants are not mutually exclusive and future extractions will need to be carried out sequentially to allocate metals more reliably to specific sediment fractions.

It must be noted that these extractions were carried out on air-dried sediments that had been stored for several months. Both the drying and the storage are likely to affect the chemical and physical characteristics of the sediment. The precise chemical effects of drying are not known in detail but two examples from the literature, if somewhat contradictory, give an indication of what can be expected. Kersten and Forstner [15] found that zinc is particularly susceptible to changing fraction upon air-drying, with the amount of zinc in the more available fractions being substantially increased. However, Otte *et al* [16] found that it was copper, not zinc, that was thus effected by drying, with Cu that is bound to chelating components of the soil being mobilized into the exchangeable and water soluble fractions. The reason for this apparent discrepancy between these two different studies may be that different sediment types were involved. The former study [15] used anoxic freshwater sediments whilst the latter [16] used salt marsh soil. This would seem to be borne out by the present work on anoxic freshwater sediments, since Zn was found to be present at relatively high levels in the more available fractions, although of course without comparative extractions carried out on fresh sediments, that this is an artifact of the drying process can only remain speculation.

The relevance of carrying out extractions on dried sediments is called into question by these observations. It could be argued that examination of dried sediments gives a closer approximation of plant-availability of metals due to oxidative action of plant roots in the rhizosphere [16]. Furthermore it may give an indication of the likelihood of release of metals into the environment in the event of the water table falling and the sediments becoming dry and aerated. However, this may be of limited use if different metals are effected in different ways.

BROWN *et al* Study of a Long Established Natural Wetland**Implications for design of constructed wetlands**

The study area is a natural wetland system that has evolved naturally over a period of at least 50 years, which is considerably longer than any constructed systems have been in operation. It is therefore of interest to compare the functioning and efficiency of this system with constructed systems. The extent to which this can be done, however, is limited by the fact that the majority of constructed systems are treating coal mine drainage, in which acidity, Fe and Mn are the parameters of interest, rather than Cu and Zn.

Some data for metal mines do, however, exist. Big Five wetland in Colorado [17] is a constructed wetland receiving metal mine drainage input, although the low pH (around pH 3) and small area (total area of 800 ft²) makes the relevance of direct comparisons dubious. Experimentation at Big Five wetland has shown that 100% removal efficiency of Cu and Zn is achievable in cells engineered to have subsurface flow, and with a loading factor (area of wetland per volume of input flow) of above 1000 ft² per gallon/minute. The Tregembo Marsh field site is achieving 79% to 94% removal efficiency of Cu, and -1% to 36% removal efficiency of Zn. Based on the maximum recorded input flow rate of approximately 50 L/s (approximately 800 U.S. Gal./min.) the loading factor for the field site is in the order of 350 ft² per gallon/minute (520m² per L/s).

Considering the very significant differences in scale, water chemistry and homogeneity between an engineered system and a natural one, it is interesting to speculate on these efficiencies and loading factors. It was found in the investigation of sediments at Tregembo Marsh, that Zn is held in relatively available fractions of the upper, organic-rich layer, whereas Cu is also held predominantly in the upper layer, but in less readily available fractions. This suggests that water flow is generally over the surface, in contrast to the subsurface flow in the engineered wetland. Cu is so effectively removed by the sediment that such a surface flow system is adequate to treat the water, and even at a lower loading factor than that proposed from the results from Big Five wetland, the system has spare capacity to remove Cu. Zn, however, is apparently held in the sediment by different mechanisms and a surface flow system provides inadequate treatment. It seems reasonable to propose that if the natural system could be modified to encourage subsurface flow, then the treatment efficiency for Zn could be improved.

This highlights the importance of designing constructed systems with due regard for the water chemistry, in order to avoid incurring unnecessary expense by 'over-engineering' a system whilst also avoiding the possibility of unacceptably low treatment efficiency due to an 'under-engineered' system. This work does indicate that a *suitably* designed wetland has the ability to function as a passive treatment system for a period of at least 50 years, and having evolved over this time scale, the system is likely to be in a state of equilibrium and will continue to function for a considerable period.

Future work on this natural wetland area will investigate further the mechanisms involved in removing metals from the contaminated mine water and assess the importance of the complexity of the flow regime, substrate and the ecology.

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CONCLUSIONS

1. Even after mines have been abandoned for several hundred years and subjected to regular throughflow of water, there is still sufficient oxidised material within the workings to ensure that increased flow rate does not decrease the metal concentration.
2. In the present study the removal efficiency for Copper is significantly better than for Zinc and is also more constant than for Zinc. Removal efficiency does not appear to be simply related to flow rate.
3. The area adjusted mass retention for Copper and Zinc in this study is one or two orders of magnitude higher than some previous studies [13] and the causes for this need to be investigated.
4. Initial work suggests that high levels of Zinc are loosely held on exchange sites in the upper, organic matter-rich layer of the sediment in a wetland and that this Zinc can be relatively easily released into the water. Copper, on the other hand, is held more firmly in the sediment and represents effective removal by the wetland. The wetland area described in this paper would appear to have plenty of spare capacity for removing Copper, but has reached a state of dynamic equilibrium as regards Zinc.
5. More work needs to be done to define how such a natural wetland may assist in the design of constructed wetland treatment systems but these initial results indicate that such systems could be designed to suit specific water chemistries and that long term passive treatment is possible.

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