

RETENTION OF METALS AND LONGEVITY OF A WETLAND RECEIVING MINE LEACHATE¹

by

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Abstract. Data on metal concentrations in soil and porewater of a marsh receiving leachate from an abandoned lead-zinc mine in Ireland were used to estimate the retention and accumulation of metals by the marsh. Iron concentrations did not vary according to a consistent pattern throughout the marsh. Levels of Zn, As, Pb and Cd decreased with increasing distance from the mine site. The marsh was estimated to retain 95 % of Zn and 65 % of As from porewater. Up to 30 % of the estimated total capacity of the marsh to retain metals had been used so far. Longevity of the marsh is estimated to be in the order of several centuries.

Additional Key Words: marsh, *Molinia*, Ireland, zinc, lead, iron, cadmium, arsenic.

Introduction

The use of wetlands for treatment of contaminated water has become increasingly popular during the past decades (Brix and Schierup 1989, Hammer 1989). Where the application of the technique to persistent contaminants, such as heavy metals in mine leachate, is concerned, questions about the effects of accumulation of the contaminants on the filtering efficiency and longevity of the wetlands still remain unanswered (Walski 1993). It is argued that accumulation of potentially toxic metals could affect the viability of the vegetation and the integrity of the system. If the longevity of treatment wetlands would be reduced to only a few decades, in which case the systems would have to be replaced regularly, this approach might not be economically acceptable for mining companies. Hedin (1996) and Williams and Stark (1996) estimated the longevity of treatment wetlands to be at least in the order of several decades.

The reason that the longevity of treatment wetlands cannot be estimated with certainty is that artificial systems for treatment of mine leachate have not been available long enough, while natural, so-

called volunteer, wetlands are rare. We have been studying metal concentrations in porewater and soil of one such volunteer wetland since 1993, and the results of this study were recently published (Beining and Otte 1996). Here, the findings of that study will be discussed in relation to the following questions: (1) To what extent has the wetland accumulated metals? and (2) What is the expected life-span of this wetland?

Site Description

A detailed description of the study site, including maps, can be found in Beining and Otte (1996). The wetland consists of a marsh of about 100 m x 500 m. It is situated in Wicklow Mountains National Park at the upstream end of a lake (6°23'W, 53°00'N), which is part of the Glenealo - Glendasan - Avonmore River system in County Wicklow, Ireland. The marsh is dominated by the grass *Molinia caerulea* (50 - 100%) and *Juncus acutiflorus* (0 - 20%). An abandoned lead-zinc mine is adjacent to the marsh, opposite the lake. The mine was in operation from 1824 until 1889; the most intensive period of activity occurred between 1850 and 1880. It opened again for short periods between the 1910s and 1950s. The mines, sorting floors, mine spoil heaps and remains of buildings can still be clearly identified. Drainage from the mines and spoil heaps partly flows into a small tailings pond. This pond measures 45 m x 55 m. During periods of high precipitation the pond overflows into the marsh. The hydrology of the marsh has not been accurately described yet, but the marsh appears to be hydrologically separated from the Glenealo River

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running along the marsh, separated by river banks. Thus, water runs from the abandoned mine site into the marsh and then has to pass the full length of the marsh before it enters the lake.

Metal Concentrations in Soil and Porewater

Porewater and soil samples were collected in December 1994, and in February, March and June, 1995. Porewater was sampled using dialysis vials covered with a 20 μm mesh nylon membrane, which were left to incubate in the soil at 10 cm depth for at least five weeks. Soil samples were taken by hand or using a stainless steel spade from about 10 cm depth. Soil samples were acid-digested in Teflon bombs. Details of the materials and methods, as well as the original data from which the data presented here were derived, were described in Beining and Otte (1996). Detection limits were 0.8 $\mu\text{mol Zn L}^{-1}$, 0.4 nmol As L^{-1} and 1.6 $\mu\text{mol Fe L}^{-1}$ (porewater samples), 0.03 $\mu\text{mol Zn g}^{-1}$, 0.1 nmol As g^{-1} , 0.5 $\mu\text{mol Fe g}^{-1}$, 0.1 $\mu\text{mol Pb g}^{-1}$ and 6.5 nmol Cd g^{-1} (soil samples). Because no consistent trends were observed between sampling dates for any of the metals, values were pooled ($n = 2 - 24$).

Table 1. Ranges of concentrations of metals in porewater and soil of the marsh at Glendalough, Co. Wicklow, Ireland. nd = non-detectable, dw = dry weight.

Metal	Porewater	
	$\mu\text{mol L}^{-1}$	mg L^{-1}
Fe	nd - 2250	nd - 126
Zn	nd - 51	nd - 33
As	nd - 2.05	nd - 0.15
Metal	Soil	
	$\mu\text{mol g}^{-1}$ dw	mg kg^{-1} dw
Fe	nd - 2050	nd - 115000
Zn	nd - 300	nd - 19600
As	0.1 - 7.5	7.5 - 560
Pb	2 - 85	400 - 17600
Cd	nd - 1.9	nd - 200

Ranges of metal concentrations in porewater and soil of the marsh are given in Table 1. Average metal concentrations in porewater showed the following patterns. Iron concentrations in porewater did not differ significantly between sampling sites, and varied between 70 and 260 $\mu\text{mol L}^{-1}$ (Figure 1). Iron concentrations in soil were significantly (1-way analysis of variance, $P < 0.01$) different between sampling sites.

Values ranged from 41 to 947 $\mu\text{mol g}^{-1}$, with peak values near both ends of the marsh (Figure 1). The lack of a consistent pattern for iron concentrations in porewater and soil with distance from the mine indicates that iron concentrations have not been altered by the activities of the mine.

Different patterns emerged for the other metals investigated in the study, showing a significant ($P < 0.01$) decrease from the mine site towards the lake (Figure 2). Zinc concentrations in porewater decreased from 28.5 $\mu\text{mol L}^{-1}$ at the mine site to 1.3 $\mu\text{mol L}^{-1}$ at the lake. Concentrations of zinc in soil decreased from 250 $\mu\text{mol g}^{-1}$ at the mine site to 12 $\mu\text{mol g}^{-1}$ at the lake. Arsenic concentrations in porewater decreased from 0.4 $\mu\text{mol L}^{-1}$ at the mine site to 0.14 $\mu\text{mol L}^{-1}$. Concentrations of arsenic in soil decreased from 5.4 $\mu\text{mol g}^{-1}$ near the mine to 0.08 $\mu\text{mol g}^{-1}$ at the lake. As porewater concentrations of lead and cadmium are usually below the detection limits of flame atomic absorption spectrophotometer these were not determined in the study. In soils, lead concentrations decreased from about 100 $\mu\text{mol g}^{-1}$ at the mine site to 2 $\mu\text{mol g}^{-1}$ at the lake. Cadmium concentrations in soil decreased from about 1.1 $\mu\text{mol g}^{-1}$ near the mine site to 0.1 $\mu\text{mol g}^{-1}$ near the lake.

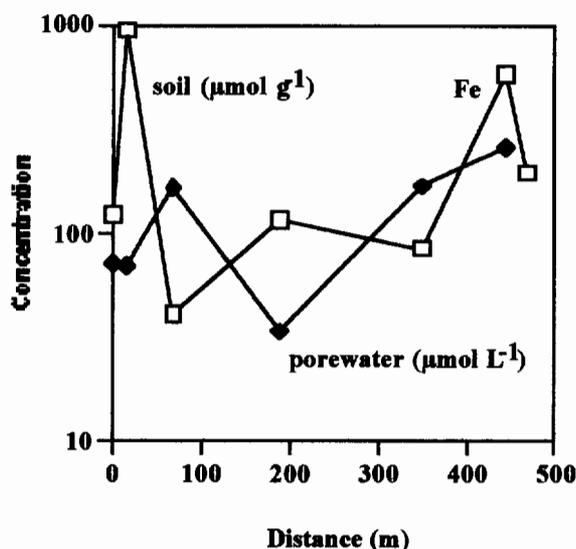


Figure 1. Mean concentrations of iron in soil and porewater of the marsh as a function of distance from the tailings pond.

Metal Retention by the Marsh

If it is assumed that metals are retained from solution by precipitation and binding to the soil, and given that no major inflow of unpolluted water into the marsh appears to exist, and therefore no significant dilution of metal concentrations would be

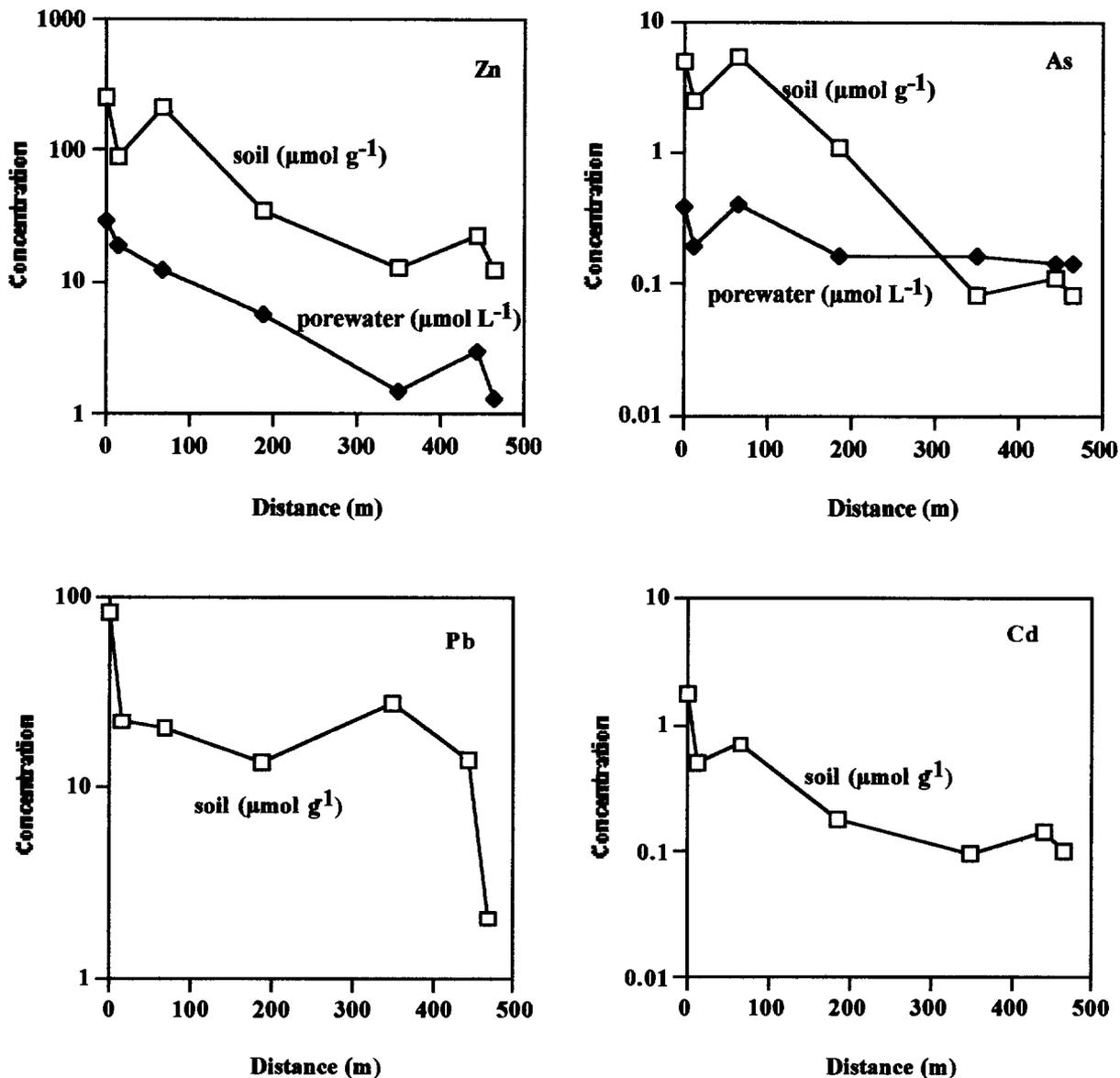


Figure 2. Average concentrations of Zn (top left), As (top right), Pb (bottom left) and Cd (bottom right) in porewater (Zn and As only) and soil of the marsh at Glendalough, Co. Wicklow, Ireland.

expected to occur, the changes in metal concentrations in porewater along the length of the marsh can be used to estimate the instantaneous retention of metals by the marsh. In contrast to iron, concentrations of Zn and As decreased from the mine towards the lake. Zinc concentrations in porewater decreased from about 28.5 to $1.3 \mu\text{mol L}^{-1}$, indicating a retention of 95% of the metal. Arsenic appeared to be retained to a lesser degree, with a decrease in concentrations from 0.4 to $0.14 \mu\text{mol L}^{-1}$ indicating a retention of 65%. Karathanasis and Thompson (1993), Tang (1993), and Noller et al. (1994) reported similar retention rates.

Accumulation of Metals in the Marsh

The variation in concentrations of metals in the soil can be used as an indication of accumulation of metals in the marsh. The lowest concentrations observed in the marsh are comparable to concentrations in similar, unpolluted marshes in the area (Beining and Otte 1996). Organic matter content of the soil is uniformly high across most of the marsh and the vegetation is homogeneous in composition across the length of the marsh, indicating that the soil

composition is similar throughout the marsh. If it is assumed that the marsh soil has the capacity to accumulate metals at least to the highest concentration observed, the integrated values of the metal concentrations as shown in Figures 2 - 5 give an indication of the capacity of the marsh to accumulate metals. Integrated values were calculated according to the following formulas:

$$CT = x_{\max} * d_{\text{total}} \quad (1)$$

and

$$CU = \sum \left(\frac{x_i - x_{i-1}}{2} \right) * (d_i - d_{i-1}) \quad (2)$$

where: CT = total capacity of the marsh to accumulate metals, CU = capacity used, i = the number of the sampling site counting from the mine site ($1 = 0$ m from the site, $2 = 13$ m from the site, etc., x = the concentration of the metal at the site, x_{\max} = the highest average concentration observed across the marsh, d = distance from the mine site, and d_{total} = the total length of the marsh. Following this approach the capacity used, CU , for Zn is about 26 % of the total capacity (CT), while these values are about 30 % for As, 25 % for Pb and 16 % for Cd. These values are based on data from the top 10 cm of soil. No information is available about the changes in the marsh elevation since the mine closed down or about its structure during the operation of the mine. However, for the top layer of soil at least, it appears that for the metals investigated about 70 % of the total capacity to bind metals still remains.

The Longevity of the Marsh

This marsh has been receiving metal-contaminated water for well over a century. Its current retention rate of metals is very high and its capacity to bind metals has not been used by far. One question that remains to be unanswered for this marsh is the current loading rate of the marsh with metals. As Williams and Stark (1996) emphasise, it seems logical that the loading rate is the only important factor determining the longevity of the marsh. For this marsh it appears that the size is sufficient to deal with the present loading rates, and that the longevity is in the order of several centuries, rather than decades.

Another important issue is that of maintenance of treatment wetlands. Hedin (1996) states that "it is likely that well-vegetated organic substrate wetlands will require periodic maintenance in order to maintain the retention times for which they

aredesigned". The marsh at Glendalough has never been maintained. It is a natural organic-substrate wetland and still retaining metals very effectively. The bulk of the organic matter now present in the marsh was most likely already there before the mine became active. How much present-day production of organic matter contributes to increase the metal-binding capacity of the marsh is unknown. Again, the size of the marsh relative to the loading rate seems to be the key factor. It appears that as long as a wetland, volunteer or artificial, is big enough, retention will be satisfactory and maintenance will be minimal.

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