Possible Effects of Losses of Drainage Water on the Copper and Zinc Status of Scottish Upland Soils and their Sustainability

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1. Introduction

Numerous investigators have attempted to quantify rates of release of base cations by biogeochemical weathering, by both laboratory- and field-based techniques. There have been far fewer attempts to quantify long-term rates of release of essential trace elements by weathering, however. This is surprising in some respects, because trace nutrient removal in harvested crops has to be sustainable in the very long term if soil fertility is to be maintained. It seems likely that continued growth and harvesting of high yielding crops, and the associated permanent depletion of soil trace element supplies, must ultimately result in increasing occurrence of trace element deficiency problems, which will need to be rectified. The time scale over which problems will start to arise will depend upon rates of removal in crops and drainage waters, rates of release by biogeochemical weathering, and inputs from external sources such as the atmosphere, sludges and fertilizers.

Because inputs of elements such as Zn from pollution sources are often high, work on concentrations in drainage waters has often concentrated more upon the potential pollution of ocean waters from anthropogenic activities (Martin *et al.*, 1980). Studies on cycling in forest ecosystems have often focussed upon concentrations in biomass and soil compartments (van Hook *et al.*, 1980). Until relatively recently, this was partly because of the difficulties in determining trace nutrient elements at concentrations down to the sub ng ml^{-1} range in fresh waters compartments (Martin *et al.*, 1980). Probably also it was partly because the concentrations in unpolluted drainage waters were thought to be sufficiently low to be of little consequence. For example, *ca.* 2 ng Cu ml^{-1} for rivers without significant industrial contamination (Wedepohl *et al.*, 1991), and between 0.2 - 0.6 ng Zn ml^{-1} (Kennedy and Sebetich, 1976) and 7 ng Zn ml^{-1} (Wedepohl *et al.*, 1991) for supposedly uncontaminated rivers. Values of 0.2 - 2 ng Cu ml^{-1} and 1 - 15 ng Zn ml^{-1} have been reported in rainwater (Grimshaw *et al.*, 1989), suggesting a near balance with outputs in river waters. Sometimes quite high concentrations of Cu and Zn have been reported for allegedly unpolluted river water, for example, 44 and 590 ng ml^{-1} in a section of the River Carnon in England reputedly uncontaminated by acid mine drainage (Johnson, 1986).

2. Aims and Objectives

The two major objectives of the present study were:

- To investigate the mobility of two selected trace nutrient elements, Zn and Cu, in soil solution, with respect to estimation of potential losses in drainage water, and to relate this mobility to concentrations in river water samples in northeast Scotland.
- To estimate the possible range of effluxes of Cu and Zn from Scottish catchments, in the context of long-term trace nutrient element balance sheets.

3.   Methodology

Two approaches were adopted. In the first approach, an investigation was made of the factors influencing concentrations and outputs of Cu and Zn in drainage waters from 59 sub-catchments, covering a range of sizes, topographies, land use distributions, and soil parent materials, of the River Dee catchment in north-eastern Scotland. It was anticipated that hydrological flow path effects might be important for Cu and Zn. When water drains through or over near-surface horizons, it generally is contacting more acidic and more organic matter-rich soils. Thus it might be expected that the combined effects of lower pH and greater chelation at an elevated soluble organic matter concentration could result in increases in Zn and Cu concentrations under high discharge conditions. It was decided to test this hypothesis by analyzing river water samples collected under low flow and high flow conditions.

It was further decided to supplement the river water data obtained by analyzing soil solution taken from a range of depths in the soil profile of typical podzols in the Dee catchment. The most reliable way to do this is to use intact soil core monoliths and small, hollow fibre tension lysimeters (rhizon samplers) inserted horizontally into the microcosms at the required depths. Such an approach has the added benefit of allowing the effects of land use and of harvesting of vegetation to be studied relatively easily and cost effectively. Soil solution concentrations of Cu and Zn would be measured as a function of depth in a typical *Calluna* moorland podzol profile, using intact core microcosms, each fitted with rhizon samplers at three different depths. Zinc availability to plants is strongly related to soil pH, and this is likely to be directly reflected in a pH effect on Zn mobility in drainage water. It was therefore decided to examine, in addition, the effects of prior liming upon soil solution Zn concentrations and mobility. Liming also influences organic matter solubility and turnover rate, and is therefore likely to directly affect Cu solubility and mobility too. Therefore Cu and soluble carbon concentrations also would be monitored. It was also decided to analyze free drainage water from the bottom of the microcosms whenever this was obtained. The concentration results from the microcosm experiments would be compared with those of the river water analysis, and both sets of data used to estimate effluxes of Cu and Zn on a ha^{-1} basis.

4.   Materials and Methods

4.1   Microcosm Collection, Preparation and Application

On careful examination of land use of soils derived from granitic parent materials, which abound along Deeside, it was found that a suitable series of sites with the three required land uses, *Calluna* moorland, slightly improved pasture and improved pasture, was available on the Craibstone Estate, approximately 10 km west of Aberdeen. The granitic parent material in this region would give sufficiently acidic soils for liming effects on Zn and Cu mobilities to be likely to be substantial. Therefore an unlimed soil, and two further soils derived from the same parent material, but which had already been limed in the field for a substantial period of time, were selected. This approach was chosen because penetration of the liming effect to depth is such a slow process (Sanyi, 1989), and the longer-term effects of

liming, rather than the short-term response, were more relevant here for assessing land use/soil management effects.

Triplicate intact soil core microcosms and immediately adjacent loose soil were collected from each of three locations on the Craibstone Estate. The first site was a slightly improved pasture (SIP) on a gentle north-facing slope. Although the grass was well established, some *Calluna Vulgaris* plants remained, but at low density. The site is used periodically for grazing, but lack of faeces suggested that it had not been grazed immediately prior to sampling. The second site was a fully improved pasture (IP), on a flatter area down-slope from the first site. Its vegetation consisted of grass predominantly, but with some clover and the pasture had been recently grazed. The third site was also in the area of the Craibstone Estate, but on the western side of Brimmond Hill. The vegetation was predominantly *Calluna vulgaris.*

From each site, after a preliminary survey by augering to establish that the horizon delineation was as expected and that the local stoniness was not so great that intact core sampling would prove impossible, three intact soil cores were collected. The cylindrical core collection tubes were each 15 cm in diameter (internal) and 50 cm in depth. They were fabricated from heavy-duty plastic drainpipe, the lower edge of which was beveled to facilitate insertion. Prior to using the tubes, a sample of the plastic had been soaked overnight in demonized water, and the water analyzed to confirm that the tubing material did not introduce any measurable Zn or Cu contamination. The tubes were pushed into the soil by hitting gently with a sledgehammer while a plank of wood was held across their top. They were driven down to 30 cm depth below the surface. The intact cores were removed by digging out and removing the external soil surrounding them, and then digging underneath the bottom of the cores, to facilitate their removal. Loose soil from adjacent to the cores was taken for analysis as well. A polyethylene bag was tied around the bottom of each of the cores, to prevent the loss of soil and soil drying during transport and storage. The cores were taken to the laboratory where they were prepared as follows. The soil at the base of the cores was trimmed until it was flush with the core tube beveled rim, and secured by using 1M nitric acid-washed glass fiber matting supported on 1 mm nylon mesh netting, which was in turn secured tightly to the outside of the cores. The 1M nitric acid washes from both of these materials were tested to check for significant Cu or Zn contamination. For the glass fiber matting, a hot 1M nitric acid wash was essential prior to use, to reduce Zn contamination to an acceptable level. Three Rhizon samplers were sealed into the side of each core at the depths specified below. The cores were positioned on purpose-built supports, which securely retained the cores above large plastic funnels, through which leachate was collected in a glasshouse.

The sampling was done in July, 1996. This gave nine microcosms in total (three replicates × three soil treatments). With three rhizon sampler depths and free drainage water collection too, this yields up to 36 samples on each sampling date, or potentially 900 samples for Cu and Zn determination by graphite furnace AAS.

The pH of soil solution, and therefore possibly the solubilities of Cu and Zn, are influenced by the mobile anion concentration of the solution. It was therefore decided to water the microcosms with simulated precipitation with an appropriate composition for north east Scotland, rather than with deionised water. The latter could have resulted in artificially high soil solution pH in the longer term. Rhizon samplers were inserted horizontally through small holes drilled in the side of the microcosm tubes at depths of 5 (H1), 15 (H2) and 25 (H3) cm, to sample the soil solution.

The cores were watered periodically with a simulated rainfall formulation. The rain water composition was based upon the known composition of rain water from the area. The water was applied twice a week, as a fine spray from a calibrated commercial pesticide spray gun. This allowed apparently uniform wetting of the surface. The amount of water to be applied was calculated to match the amount usually received by the sampled area. However, because of the high temperature in the glasshouse, particularly in the late summer and early autumn, more water was necessary to compensate for the increased evapotranspiration and sample removal. About 150 ml was usually applied at each simulated rain shower, instead of the 110 ml that would have been required to match field precipitation. Ca. 30 - 40 ml of this was removed by the rhizon samplers. No water samples were collected over the first three weeks in the glasshouse, to allow the cores time to readjust after the core collection and to their new environment, and to make sure that the rhizon samplers were functioning correctly.

Soil solution and leachate collection was carried out for 4 weeks from August 16th, as described below, at which stage the vegetation was cut down to about 2 cm above the soil. The intention in doing this was to see the effect of vegetation on the concentrations of cations and anions leached out with the regular application of rain water. It is important to know whether the uptake of nutrients by plants will affect the amounts lost by leaching. The experiment was continued for a further 10 weeks. The experimental phase during which water samples were collected and analyzed lasted from the mid August to the end of November. It was noticed that *Calluna* showed little sign of re-establishment after it was cut down in the middle of September. The grass, however, appeared to be growing even better than before the first cutting, probably because it was no longer experiencing any of the several possible types of damage encountered in the field situation.

Leachate from the bottom of the intact cores was collected in plastic bottles *via* the funnels under every core. Soil solution was sampled using rhizon samplers, connected *via* hypodermic needles to 10 ml capacity vacutainers following each water application. Samples were collected twice a week Free draining water samples were collected twice a week as well. The first batch of samples collected each week was usually stored in the refrigerator until the second batch had been collected, at which stage they were analyzed together.

4.2   Catchment Selection

In total, 59 sites were selected for water sampling in the River Dee catchment, as illustrated in Fig. 1. The main geographical characteristics of the catchment have been summarized elsewhere (Langan *et al.*, 1997). The sites were selected to represent, as fully as possible, all of the diverse geological materials in the catchment, in such a way that they could be safely sampled in a single day, even in winter, using two vehicles. The rivers in the 59 catchments or sub-catchments were sampled on four occasions. Two sampling dates were in August, both for base flow conditions, the first following an extended period of very dry weather. The second two were in October and December, and both corresponded to high discharge conditions.
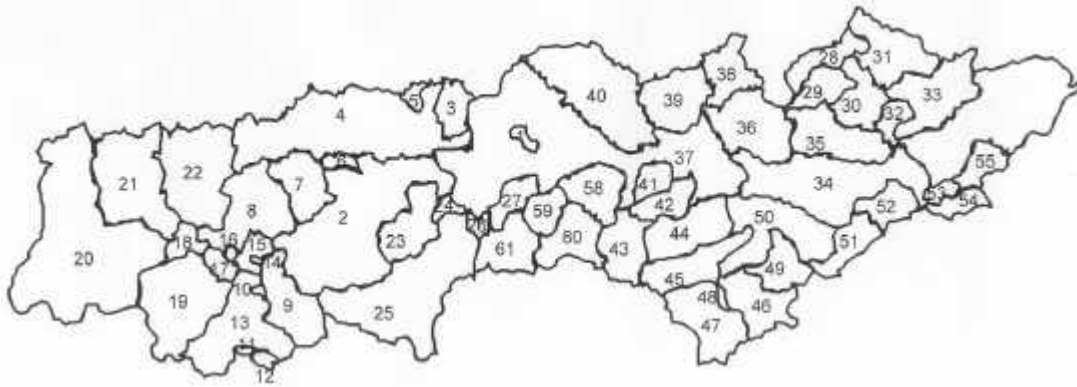
Figure 1. **River Dee catchment map showing numbered sub-catchments.**

4.3 Analytical techniques

The analysis of the water samples was completed as soon as possible after collection, always within the week of sampling. The samples were analyzed for Zn and Cu using graphite furnace atomic absorption spectrometry, with a L'vov platform and matrix modifiers as recommended by Perkin Elmer. Anions (sulphate, chloride, nitrate and phosphate) were measured with a Dionex 4010i Ion Chromatograph, and Total Carbon (TC) and Total Organic Carbon (TOC) using a Labtoc carbon analyzer.

5. Results

5.1 Soil microcosm experiment

The horizons and horizon depths observed are recorded in Table 1.

Table 1. **Profile descriptions for Craibstone and Brimmond Hill sites.**

Site	Area	Horizon	Depth (cm)
Site 1	Craibstone (Semi-improved)	O	0-6
		A/E	6-7
		B	7-13
		Bh	13-25
		C	25+
Site 2	Craibstone (Improved pasture)	A	0-26
		B	26+
Site 3	Brimmond Hill (*Calluna* moorland)	LFH	0-5
		A	5-10
		E	10-15
		Bh	15-20
		B	20-42
		C	42+

5.1.1 Soil solution and drainage water analysis

The results of the Cu and Zn determinations in the extracted soil solutions and in the free drainage water from the bottom of the cores are summarized in Figs. 2 and 3. These bar charts show representative changes over time in the mean (of 3

replicates) Zn and Cu concentrations at 5, 15, and 25 cm, from the three sites (improved and semi-improved pastures and *Calluna* moorland).
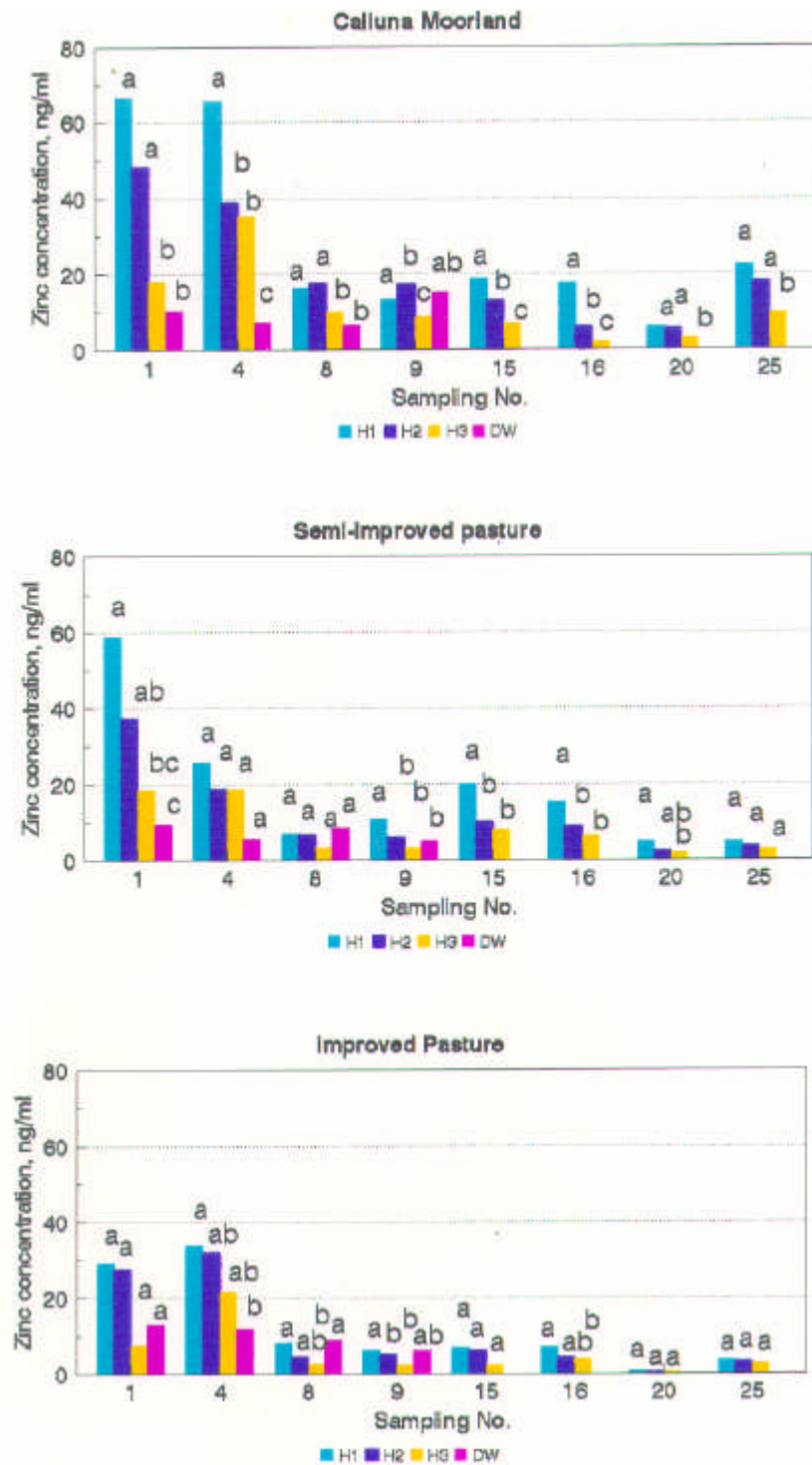

Figure 2.   Zinc concentrations at 3 depths in soil solutions and in drainage water.
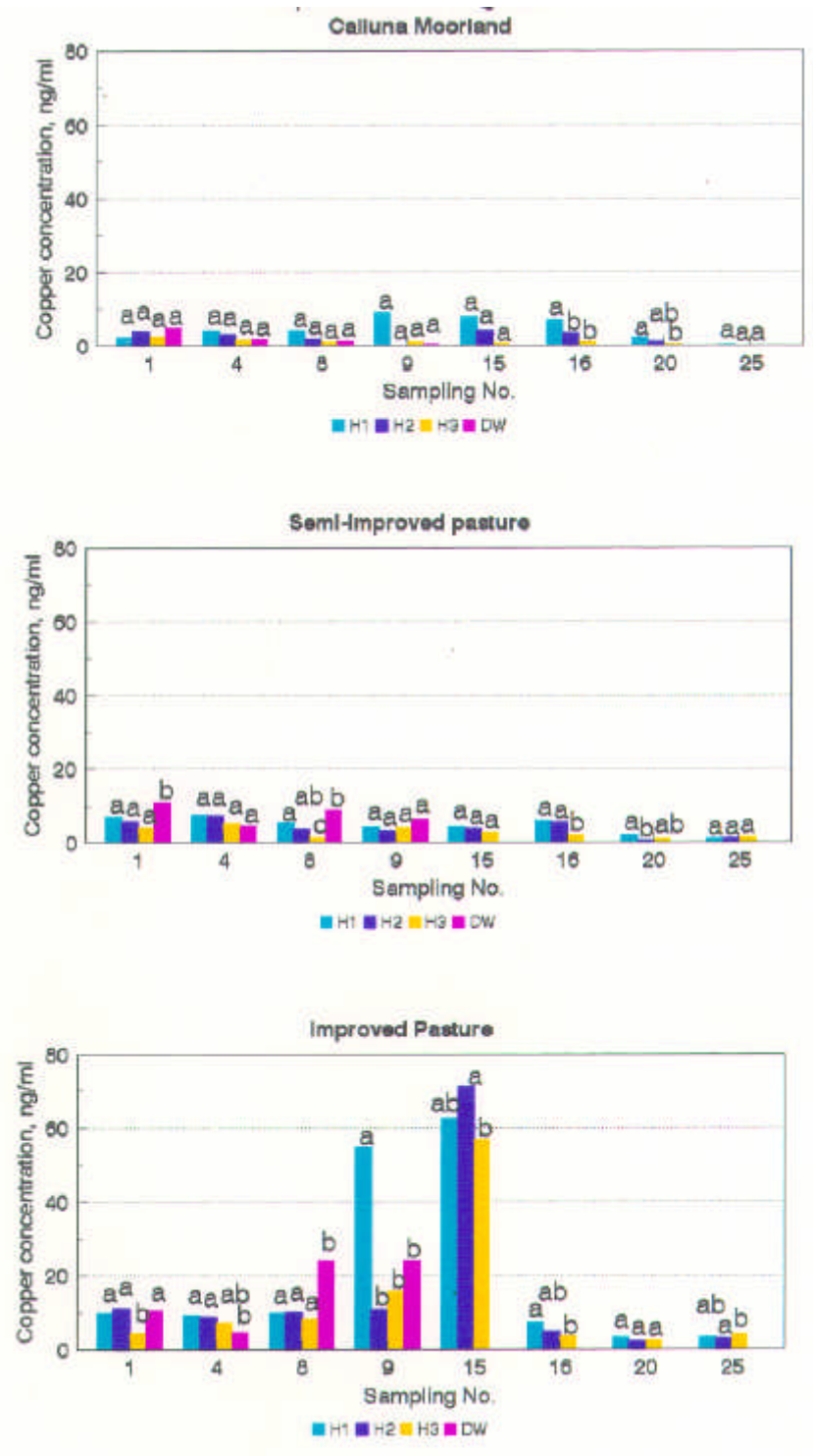
Figure 3.   **Copper concentrations at 3 depths in soil solutions and in drainage water.**

5.2   Analysis of river water samples

Figure 4 shows the Cu concentrations throughout the River Dee catchment on two of the sampling dates, 19th August (baseflow) and 28th October (High flow). Similar concentration distribution maps have been prepared for Zn and for all sampling dates. Figures 5 and 6 illustrate the Cu and Zn data for all catchments and sampling dates, plotted in order of decreasing % broadleaf tree cover (for Cu) and decreasing

% improved grassland cover (for Zn), respectively. Figure 7 shows mean Zn concentrations for all four sampling dates (two low flow and two high flow) plotted separately, split into three blocks according to % heather moor and peat bog cover.

Distribution of Copper Concentration (ng/ml) in River Waters Throughout the River Dee Catchment
19/08/96
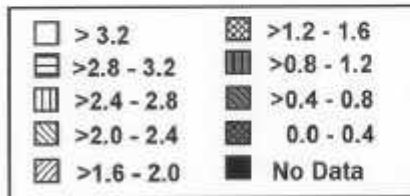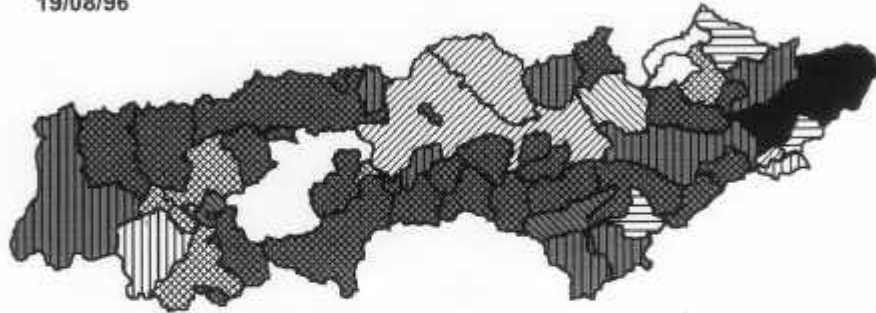
☐	> 3.2	▥	>1.2 - 1.6
☰	>2.8 - 3.2	▥	>0.8 - 1.2
▥	>2.4 - 2.8	▩	>0.4 - 0.8
▨	>2.0 - 2.4	▦	0.0 - 0.4
▨	>1.6 - 2.0	■	No Data

Distribution of Copper Concentration (ng/ml) in River Waters Throughout the River Dee Catchment
28/10/96

☐	> 6.4	▥	>2.4 - 3.2
☰	>5.6 - 6.4	▥	>1.6 - 2.4
▥	>4.8 - 5.6	▩	>0.8 - 1.6
▨	>4.0 - 4.8	▦	0.0 - 0.8
▨	>3.2 - 4.0	■	No Data
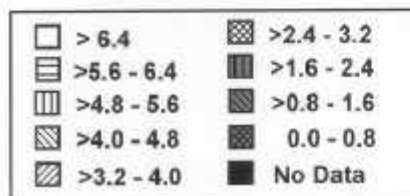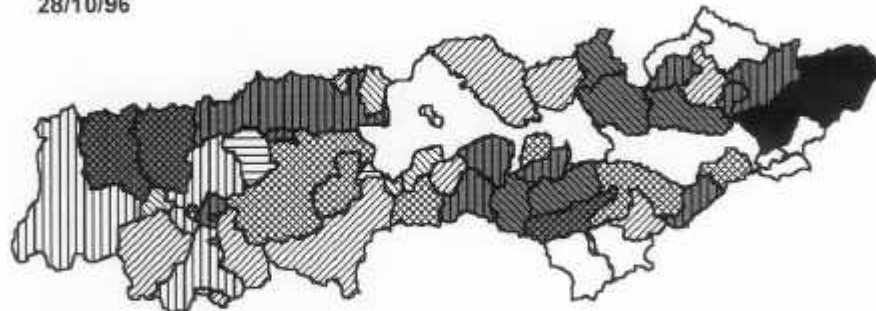
Figure 4.   Copper concentrations throughout the River Dee catchment on two sampling days.

Copper concentration, ng/ml

05/08/96
19/08/96
09/12/96
28/10/96

S7 S28 S31 S37 S39 S55 S53 S58 S35 S38 S41 S29 S46 S15 S18 S10 S13 S20 S46 S59

Decreasing broad leaf woodland cover ------->

Order of Decreasing % Broadleaf Woodland Cover

7,1,26,28,30,32,31,33,42,37,34,40,39,60,2,55,54,36,53,44,
23,58,56,57,35,25,4,38,50,49,41,8,3,29,27,51,46,22,52,15,
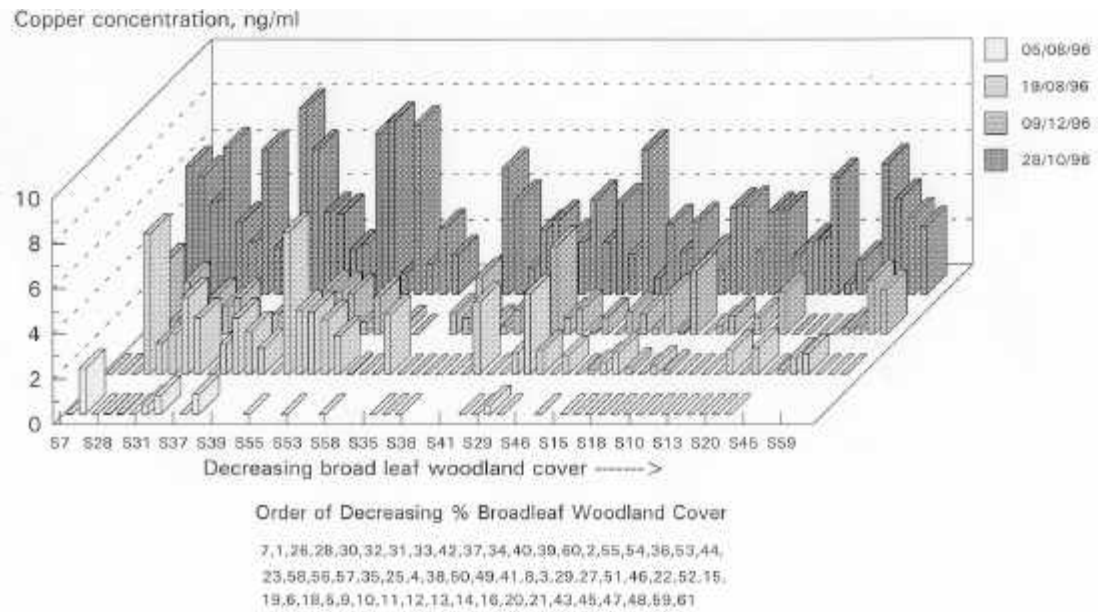19,6,18,5,9,10,11,12,13,14,16,20,21,43,45,47,48,59,61

Figure 5.   The relationship between the Cu-concentration (ng/ml) in river waters and the % of broadleaf woodland cover in decreasing order of cover from 9.8 to 0 %.

Zinc concentration,ng/ml

05/08/96
19/08/96
09/12/96
28/10/96

S53 S56 S55 S28 S42 S51 S34 S37 S3 S4 S2 S23 S25 S13 S18 S47 S5 S11 S16 S21 S60

Decreasing improved grassland cover ------->

Order of Decreasing % Improved Grassland Cover

53,38,57,56,39,36,55,40,33,28,31,54,42,32,30,51,35,29,34,52,50,37,44,
41,3,7,27,4,49,43,2,58,45,23,15,8,25,46,61,13,59,17,18,6,26,47,22,1,
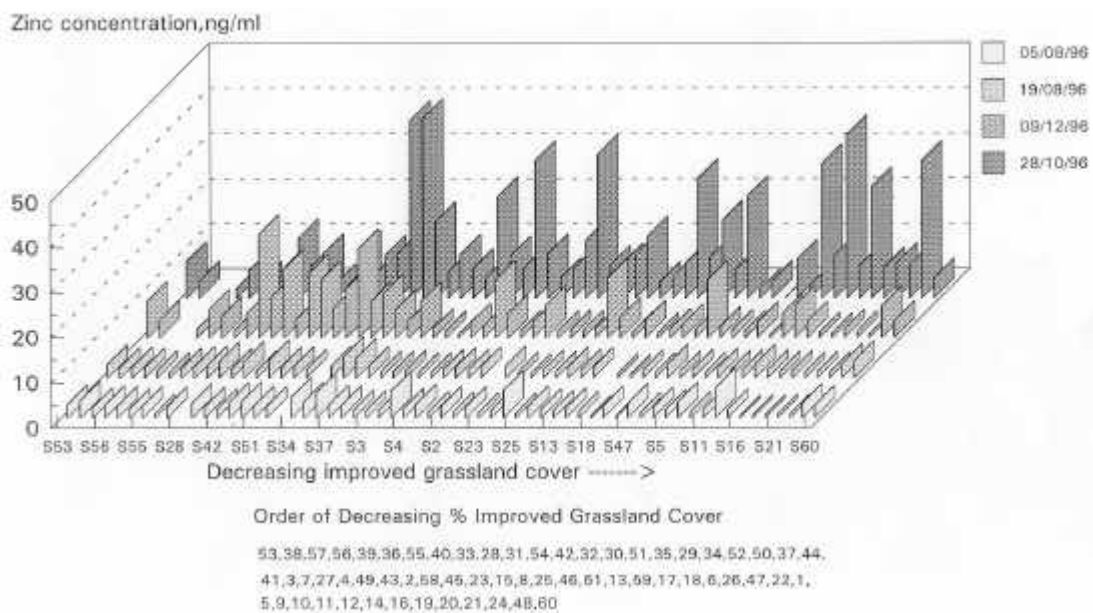5,9,10,11,12,14,16,19,20,21,24,48,60

Figure 6.   The relationship between the Zn-concentration (ng/ml) in river waters and the % improved grassland cover in decreasing order of cover from 46.5 to 0 %.
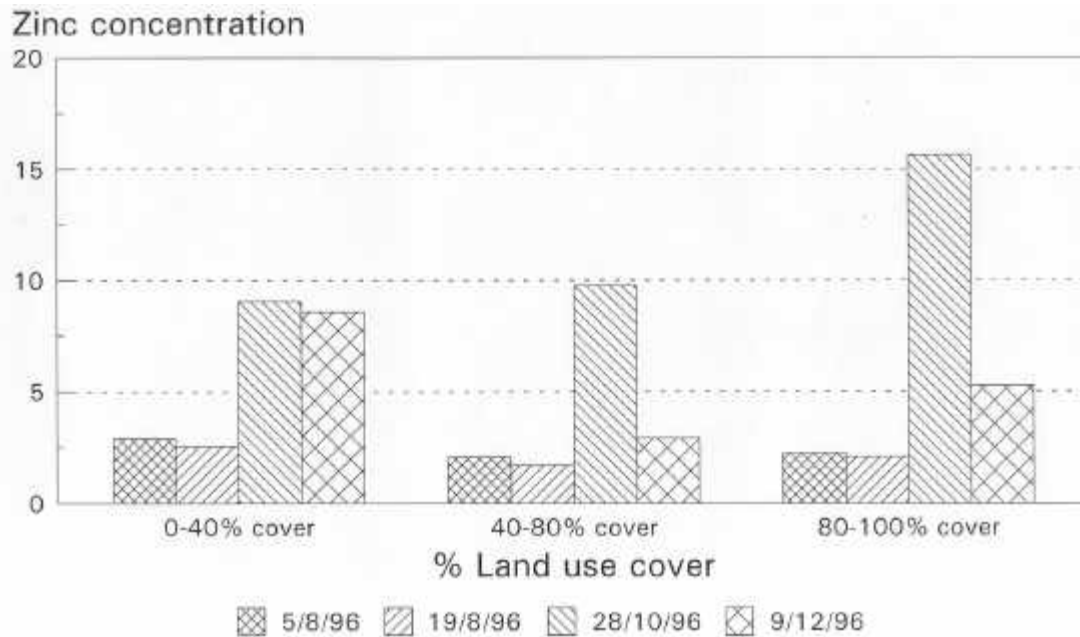
Figure 7.   **Increasing Zinc concentrations in river water (µg/L) with increasing % heather moor and peat bog**

6.   Discussion

6.1   Soil microcosm experiment

6.1.1   Effects of soil depth upon zinc concentrations

From the introduction, it might be expected that the solubility of zinc would be influenced primarily by two factors, viz. soil pH and the amount of labile zinc associated with the soil solid phase. For example, for an unimproved *Calluna vulgaris* moorland podzol soil, pH might be expected to increase with increasing soil depth and thus zinc concentration in soil solution might be expected to decrease with depth. Two-way analysis of variance for individual dates confirmed that the decrease in Zn concentration with depth was significant at $p < 0.001$ at samplings 1, 4, 15 and 16, and at $p = 0.02$ at sampling 25. The depth effect was significant. Table .2 confirms that soil pH does indeed increase systematically with depth for the *Calluna* moorland soil, regardless of whether the soil pH was measured in water or in 0.01M $CaCl_2$. An initially surprising observation about Fig. 2 is that the Zn concentration in water draining from the bottom of the cores sometimes, e.g. for sampling 9, exceeded the concentration of the soil solution extracted by suction a few cm above the bottom of the core. It should be pointed out, however, that the vegetation was harvested after sample 8 was taken. This could result in Zn, which had hitherto been removed by plant uptake from soil close to the bottom of the microcosms, suddenly remaining in solution, although it is by no means obvious why this should happen only at the bottom of the core. Perhaps a more likely explanation is that some evaporative concentration effect was occurring from the surface of the fiber matting at the warm glasshouse temperatures, giving rise to artificially increased concentration values for free drainage water.

For the semi-improved pasture, the systematic decrease in Zn concentration with depth in the soil profile is again readily apparent (Fig. 2). This is in spite of the observation that, for this soil, the highest pH was in the surface horizons (Table 2),

which are presumably reflecting the direct effects of recent liming. The penetration of the effects of lime when the latter is applied to highly organic soils is very slow, taking several years if the lime is not cultivated in (Sanyi, 1989). From the B1 horizon downward, the pH in this profile followed the expected trend, increasing with depth. Thus some factor other than pH must be contributing to the greater Zn concentrations in the water samples taken from closest to the surface (H1 in Fig. 2). There are several possible contributory factors. The most probable is Zn inputs in the field from the atmosphere *via* polluted precipitation and dry deposition or from manure. Calcium would be effective in displacing Zn^{2+} from exchange sites in the soil, which could mean that in the short to mid term, Zn concentration in solution increases following liming. It is also possible that the high pH close to the surface could be adversely affecting *Calluna vulgaris* growth, resulting in mineralization of some organically bound Zn in near-surface litter. Over the period for which free drainage water could be collected, the drainage water Zn concentration followed the expected trend, being lower than the concentrations observed in water from H3, except around samplings 8 and 9.

Table 2. **Soil pH values of the microcosm soils, measured at a 1:5 soil:solution ratio, with water and with 0.01 mol l^{-1} $CaCl_2$.**

	Horizon	pH_{water}	$pH_{Calcium\ chloride}$
Craibstone (Semi-improved pasture)	O	6.23	5.58
	A/E	5.66	4.38
	B	5.31	4.09
	Bh	5.54	4.35
	C	5.63	4.46
Craibstone (Improved pasture)	A (0-15 cm)	6.54	5.66
	A (15-26 cm)	6.55	5.65
	B	6.58	5.62
Brimmond Hill (*Calluna* moorland)	LFH	4.29	2.95
	A	4.44	3.02
	E	4.50	3.11
	Bh	4.55	3.29
	B	6.50	4.53
	C	6.48	4.66

For the improved grassland site, the soil pH (see Table 2) hardly varied with depth. The trends for Zn concentration change with depth were, perhaps as a consequence of the more uniform soil pH, rather less striking and more variable (Fig. 2) than for the other two sites, although the trend H1>H2>H3 for mean Zn concentration was still apparent. It is possible that soil solution pH could be increasing slowly with depth, as a result of a decline in mobile anion concentration caused by increased extent of anion uptake with depth. Free drainage water after the sixth sampling began to exhibit higher Zn concentrations than the soil solution samples. This may be attributed to the evaporation concentration effect occurring on the fibre matting, as discussed earlier for the *Calluna* moorland soil.

6.1.2 Effect of land use on soil solution zinc concentration

From Fig. 2, it is very clear that the sequential improvement of the *Calluna* moorland through semi-improved pasture to improved pasture resulted in a marked decline in the Zn concentration in soil solution. Analysis of variance confirmed that the mean Zn

concentrations for the *Calluna* moorland and semi-improved soils were significantly (at $p<0.05$) higher than the mean Zn concentration for the improved pasture soil. A number of mechanisms may be contributing to this effect. The most obvious is a direct pH effect upon solubility and/or Zn adsorption by iron hydrous oxides. It is also possible that surface soil labile Zn concentrations could be higher in the more acid soils as a consequence of atmospheric deposition of Zn. Inputs from this source would be less mixed in to depth in a very acidic podzol. Another possible cause could be collection of silage from the improved pasture, or removal by heavy grazing. This could lower the labile zinc pool.

6.1.3   Effects of soil depth upon copper concentrations

Whereas from the introduction it would be expected that the solubility of Zn would be influenced primarily by soil pH and the amount of labile Zn associated with the soil solid phase, the situation is rather different for Cu. The findings of earlier workers indicate that while Zn is mobilized into soil solution by acid pH, Cu is much less affected (Sanders, 1982, 1983; Jeffrey and Uren, 1983). This is because while substantial amounts of Zn probably occur in ionic form (Sanders and Kharbawy, 1987) adsorbed onto charged inorganic surfaces in the soil, Cu is mostly complexed by small organic ligands and is held on charged organic surfaces (Sanders, 1983). Even a brief examination of the data for Zn and Cu included in Figs. 2 and 3 shows that the two elements exhibit quite different behaviour. Nevertheless, analysis of variance showed significant depth effects on many individual sampling dates for Cu concentration in soil solution and drainage water. For example, the decrease with depth was significant at $p<0.001$ at samplings 1, 4, 8, 9, 15 and 16, and at 0.014 at sampling 20.

Figure 3 suggests that Cu concentration in soil solution declines with depth in the *Calluna* moorland podzol profiles, but the variability between replicates is such that most of the differences between means were not significant. In spite of the rather undulating nature of the time series plots for Cu, a similar trend over time was discernible when the data for the three individual replicate cores are compared, however, so the trend is apparently a genuine one. Total organic carbon (TOC) concentrations for these profiles decreased much more markedly with depth, suggesting that the Cu is probably not predominantly being regulated by dissolved organic matter. Moreover, there was no obvious correlation between soil solution (at any depth) or drainage water Cu concentration and TOC concentration. Thus it is too simplistic to assume that TOC concentration regulates the Cu concentration in soil solution.

Sometimes the mean Cu concentration in free drainage water was higher than that in soil solution at H3 (25cm). As for Zn, this is probably because some evaporative concentration occurs from the surface of the fibre matting at the warm glasshouse temperatures.

For the semi-improved pasture soil cores (Fig. 3), a decrease in Cu concentration with depth in the soil profile is apparent, but the effect is not totally consistent and is often not significant. In this soil, the highest pH was in the surface horizons (Table 2), which are presumably reflecting the direct effects of recent liming, so pH is not the driving force regulating Cu concentration. In fact there is some similarity between the time series plots for Cu and TOC concentrations for this set of soil cores, and these two parameters were significantly correlated. The strongest correlation was observed at soil depth H2, and the significance of the correlation declined markedly at H3, and dramatically for the free drainage water.

The most remarkable feature of the soil solution Cu concentration time series plots for the improved pasture profile (Fig. 3) is the sharp and immediate response to harvesting the grass at sampling 8. When the data for the three individual replicate cores were considered, it was clear that this is a genuine and reproducible effect. The effect was especially pronounced at H2. However, it is particularly interesting to note that this sharp rise was not associated with a concurrent increase in TOC concentration in the soil solution. Nevertheless, there were significant correlations between soil solution Cu and TOC concentrations for this soil.

6.1.4 Effect of land use on soil solution copper concentration

From Fig. 3, it appears that liming has rather variable effects upon the mobility of Cu. Nevertheless, analysis of variance for selected individual sampling dates showed the effects of site were significant, for example at $p < 0.001$ at samplings 1, 4, 8, 9, 15 and 25, and at $p = 0.003$ at sampling 20.

6.2 River water results

Figures 5 and 6 show that Cu and Zn tended to be more concentrated in river waters under high flow conditions than at low flow, values also varying with antecedent moisture conditions. Attempts to find relationships between Cu or Zn concentrations in river water and pH or TOC were unsuccessful, and the search for correlations between the trace element concentrations and % cover of a range of types of land use met with limited success.

6.2.1 Copper

For the later August and October samplings, but with few notable exceptions, high % broadleaf woodland cover appeared to increase Cu concentrations, perhaps because of the frequent occurrence of such trees in the riparian zone, and a litter fall/degradation effect. In stream processing of litter entering the stream cannot be ruled out as a possible contributing factor. Overall, land use did not appear to be the major factor driving Cu concentrations in the river network.

Only when the Cu concentrations were represented in terms of their spatial distributions did obvious trends become apparent (Fig. 4). If the maps in Fig. 4 are compared with the sediment Cu concentration maps for the East Grampians, published by the British Geological Survey (BGS, 1991), the relationships between the maps are immediately clear. The darker zones in Fig. 4, corresponding to lower concentrations of Cu in river water samples, coincide with river sediments with low Cu concentrations in the BGS maps. Comparison with geological maps for the area shows that these are associated with acid igneous intrusions. The lighter, less shaded zones of higher Cu concentrations, running from the north east to the south west of the Dee catchment, are associated with mica schists and gneisses and graphitic schists in the geological maps, and sediments with higher Cu concentrations. Thus it appears that copper concentration of parent materials is probably the major factor regulating copper concentrations in the river waters.

6.2.2 Zinc

For Zn also, there are relationships between the sediment maps (BGS, 1991), and concentrations in river water samples, but they are less immediately obvious than those for Cu, and land use seems to be having more of an effect. It might be expected from the microcosm experiments that, where there is a substantial proportion of improved grassland in a catchment, even under high discharge conditions Zn concentrations in river waters would remain relatively low. Improved

grassland tends to be on lower lying parts of the catchments, close to the riparian zones. This appears to fit with the data on 28/10/96, but not with that on 09/12/96 (Fig. 6). Possibly close grazing and other animal activities may be having a localized effect on grassland soil solution chemistry and runoff in December. The increase in mean Zn concentration with increasing % heather moor and peat bog cover for the October storm event (Fig. 7) agrees with the microcosm results in so far as Zn concentration tends to be higher in soil solutions at 5 cm for this type of land use (Fig. 2).

6.2.3   Comparison of microcosm and river water concentration values

Figure 7 suggests mean base flow river water Zn concentrations of *ca.* 2.5 ng ml^{-1}. This compares favourably with the values indicated for lower horizon soil solutions in Fig. 2 (0.4 - 10 ng ml^{-1}), provided the initial high values, which may be reflecting a disturbance effect, are ignored.

Copper concentrations in the lower horizon soil solutions ranged from 8 to 24 ng ml^{-1} for the *Calluna vulgaris* moorland microcosms. These values were higher than the typical base flow Cu concentrations after very dry weather on 05/08/96, but similar to base flow values when the soils were initially wetter on 19/08/96 (Figs. 4 and 5). However, the high discharge Cu concentrations (Fig. 5) were appreciably lower than the soil solution Cu concentrations associated with the surface horizons of the microcosm soils (Fig. 3). This almost certainly reflects large Cu inputs *via* animal feed supplements/manure at the sites from which the microcosms were taken.

6.2.4   Estimation of copper and zinc effluxes in river water

It is possible to use the data obtained to estimate approximate effluxes of Cu and Zn from soil in river water. If it is assumed, to a first approximation, that runoff is 20% storm flow and 80% base flow, and that storm flow and base flow contain 4 and 0.5 ng ml^{-1} Cu and 10 and 2.5 ng ml^{-1} Zn, respectively, then for 50 cm of runoff, the Cu and Zn losses are 6 and 20 g ha^{-1} yr^{-1}, respectively. Since the precise Cu concentrations vary significantly with parent material, the Cu value probably indicates a mean value. For arable soils, these losses are small compared with corresponding estimated typical crop offtakes of 100 and 250 g ha^{-1} yr^{-1}.

Analysis of 6 samples of rainwater in the Dee catchment gave a mean Cu concentration of 1.1 ng ml^{-1} (ranging from 0 - 3.6 ng ml^{-1}). This corresponds to an input in precipitation of 11 g Cu ha^{-1} yr^{-1}. Bearing in mind the simplifying assumptions made, this suggests that inputs in rain and outputs in river water are more or less in balance for Cu for natural and semi-natural ecosystems in the region, with some sites accumulating and some sites losing Cu. Billett *et al.* (1991) have reported a mean annual accumulation rate of Cu in surface organic horizons of forest soils of 39 g ha^{-1} at sites close to the study area. Similar calculations for Zn suggest an input in precipitation of 173 g Zn ha^{-1} yr^{-1}, or a net accumulation rate in the absence of crop removal of 153 g ha^{-1} yr^{-1}. This compares with values of 144 and 68 g ha^{-1} yr^{-1} for accumulation rates over the period from 1949/50 to 1987 in surface organic horizons of maturing forest and forest planted on moorland, respectively, reported by Billett *et al.* (1991).

7.   Conclusions

In terms of the longer-term trace element supplying power of soils, the losses in drainage waters for mineral soils appear to give little cause for concern. A soil with a

bulk density of 1.8 g cm^{-3} and 30 mg Cu kg^{-1} to a depth of 50 cm would contain 270 kg Cu ha^{-1}. This is very large compared with an estimated annual loss in river water of only 6 g, and in any case the latter might be more than replenished by atmospheric inputs. As Zn appears to be exhibiting net accumulation in natural ecosystems, its loss in river water might even be regarded as beneficial.

8. Acknowledgements

9. References

Billett, M.F., Fitzpatrick, E.E. and Cresser, M.S. (1991) Long-term changes in the Cu, Pb and Zn content of forest soil organic horizons from north-east Scotland. *Water, Air and Soil Pollution*, **59**, 179-191.

British Geological Survey (1991) *Regional Geochemistry of the East Grampians Area*, BGS, Keyworth, Nottingham, 95 pp.

Grimshaw, H.M., Allen, S.E. and Parkinson, J.A. (1989) Nutrient elements. In: *Chemical Analysis of Ecological Materials*, ed. E.A. Allen, Blackwell, Oxford, pp. 81-159.

Jeffrey, J.J. and Uren, N.C. (1983) Copper and zinc species in the soil solution and the effects of soil pH. *Australian Journal of Soil Research*, **21**, 479-244.

Johnson, C.A. (1986) The regulation of trace element concentrationsin river and estuarine waters contaminated with acid mine drainage: The adsorption of Cu and Zn on amorphous Fe oxyhydroxides. *Geochimica et Cosmochimica Acta*, **50**, 2433-2438.

Kennedy, V.C. and Sebetich, M.J. (1976) Trace elements in northern California current. In: *Marine pollution Transfer*, ed. H.L. Windon and R.A. Duce, D.C. Heath, Lexington, pp. 159-184.

Martin, J.H., Knauer, G.A. and Flegal, A.R. (1980) Distribution of zinc in natural waters. Chapter 6 in: *Zinc in the Environment*, ed. J.O. Nriagu, Wiley, New York, pp. 193-197.

Sanders, J.R. (1982) The effect of pH upon the copper and cupric ion concentrations in soil solutions. *Journal of Soil Science*, **34**, 679-689.

Sanders, J.R. (1983) The effect of pH on the total and free ionic concentrations of manganese, zinc and cobalt in soil solutions. *Journal of Soil Science,* **34**, 315-323.

Sanders, J.R. and Kherbawy, M.I.El. (1987) The effect of pH on zinc adsorption equilibria and exchangeable zinc pools in soils. *Environmental Pollution*, **41**, 165-176.

Sanyi, H.A.R. (1989) Effects of Liming Upland Soils on Nutrient Mobilities in Relation to Water Quality, unpublished PhD Thesis,University of Aberdeen, UK.

Van Hook, R.I., Johnson, D.W. and Spalding, B.P. (1980) Zinc distribution and cycling in forest ecosystems. Chapter 12 in: *Zinc in the Environment*, ed. J.O. Nriagu, Wiley, New York, pp. 419-437.

Wedepohl, K.H. (1991) The composition of the upper earth's crust and the natural cycles of selected metals. In: *Metals and their Compounds in the Environment*, VCH Weinheim, pp. 3-17.