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A model for lead, zinc, and copper in lakes

Brian Rippey, Catherine L. Rose, and Richard W. Douglas
School of Environmental Sciences, University of Ulster, Cromore Road, Coleraine, Northern Ireland BT52 1SA

Abstract

We present a budget for lead, zinc, and copper in Lough Neagh, Northern Ireland, and use the results from this and seven other lakes in Europe and the United States to develop two simple, generic models for heavy metals in lake water. The models, based on retention coefficient and sedimentation coefficient, are assessed by comparing the modeled and measured steady-state lake concentrations. The results show that deposition from the atmosphere is an important source of contamination of the lakes by Pb (56.3% of total inputs) and Zn (34.8%), but not Cu (8.3%). The mean retention coefficient in five of the lakes is 0.70 (RSD = 29%), 0.72 (24%), and 0.24 (133%) for Pb, Zn, and Cu, respectively; mean total residence time is 0.21 (RSD = 64%), 0.36 (61%), and 0.77 (97%) yr; and mean sedimentation residence time 0.34 (RSD = 73%), 0.91 (99%), and 0.05 (95%) yr. The goodness of fit of the two models are similar, with root mean square error of prediction of ± 0.14, 1.9, and 1.6 μg L^{-1} for Pb, Zn, and Cu, respectively. The magnitude of the errors in relation to the ranges of concentration suggests that the models for Pb and Zn can be used as fate models for these metals in lake water.

The amount of research into the fate and effects of heavy metals at the surface of the Earth has increased over the last 5 yr. There are three reasons for this. First, the 1998 Protocol on Heavy Metals, one of eight in the United Nations Economic Commission for Europe's Convention on Long-Range Transboundary Air Pollution, has 30 signatories at present and so emissions of heavy metals need to be managed to ensure that there are no adverse effects on human health and the environment. Second, representatives from many member states of the European Union agreed, at Bad Harzburg, Germany, in 1997, that effects-based critical limits and critical load models for heavy metals in soils and freshwaters should be developed (UN ECE 1998). Finally, research into acid deposition has developed to incorporate the fate and effects of heavy metals in soils (Binder et al. 1999; Ukonmaanaho et al. 2001) and freshwaters (Chen et al. 2000; Lydersen and Lofgren 2002).

There is a long and considerable history of research into the loading and fate of heavy metals in lake water (e.g., Baccini 1976; Skjelkvale et al. 2000). While almost all of this work has been qualitative, our understanding of the behavior of heavy metals needs to be quantitative in order to develop a fate model that can be used to evaluate the effect of emission control strategies on lakes. Since there are fewer than 10 heavy metal budgets for lakes and the fate models published only apply to the lake studied (Baccini 1976; Imboden et al. 1980; Sigg et al. 1982; Hamilton-Taylor and Willis 1990; Sigg et al. 1996), the aim of this investigation was to develop and evaluate a simple fate model for heavy metals in lake water. The objectives were to present a budget for lead, zinc, and copper in Lough Neagh, Northern Ireland; collate the results of other budget studies of these metals in lakes; use the results to develop simple models for heavy metals in lake water; and evaluate the accuracy of the models by comparing the modeled and measured steady-state concentrations. The stimulus for the research was to develop, if possible, a simple, generic model for heavy metals in lake water that could be applied to a population of lakes, for example, the many lakes scattered in the deglaciated areas of northwest Europe (Rippey et al. 2001) and northeast North America. Fate models have been developed for phosphorus in lake water for a similar purpose (Prairie 1989). However, since there are many fewer lakes with heavy metal budgets, compared to the number for phosphorus, the evaluation of the models, a basic test of accuracy, has to be simpler than that used for lake phosphorus.

Materials and methods

Site—Lough Neagh is a large (385 km^2), shallow (mean depth 8.9 m) eutrophic lake (mean total phosphorus concentration from 85 to 149 μg P L^{-1}) with a catchment area of 4,454 km^2 and mean hydraulic residence time of 1.18 yr (Wood and Smith 1993; Heaney et al. 2001). The lake lies on the late Oligocene Lough Neagh clay formation, which is up to 550-m thick, and this is overlain by thick glaciogene formations of Pleistocene age (Carter 1993). There are six major inflowing rivers that drain 86% of the catchment and one outflow (Fig. 1). It is a mainly lowland catchment, with 71% of the land classified as agriculture, mostly permanent pasture. The climate is temperate, and the annual precipitation of Northern Ireland is 1,081 mm. The three sites where bulk deposition was collected, Silent Valley Reservoir, Altnaheglish Reservoir, and the Four Mile Burn; six sites where inflowing river water samples were collected, Moyola River, River Main, Sixmilewater, River Upper Bann, River Blackwater, and Ballinderry River; and the site where samples of the outflow were collected, River Lower Bann, are indicated in Fig. 1.

Methods—A budget for Pb, Zn, and Cu in Lough Neagh was determined by measuring the deposition rate from the atmosphere onto the lake in bulk deposition at three sites,

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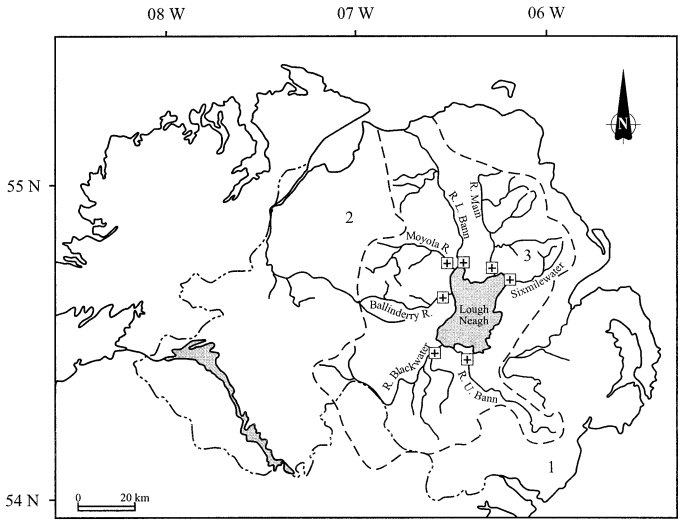

Fig. 1. The Lough Neagh catchment, indicated by a dashed line, and the position of the three sites where bulk deposition was collected, (1) Silent Valley Reservoir, (2) Altnaheglish Reservoir, and (3) Four Mile Burn, the six main inflowing rivers (River Main, Sixmilewater, River Upper Bann, River Blackwater, Ballinderry River and Moyola River), and the outflow, the River Lower Bann.

inputs from the catchment to the lake from the six major inflowing rivers, and output from the lake to the outflow from 1987 to 1989. The concentration of total Cu and Pb was measured in the water column of Lough Neagh every 2 weeks from 10 August 1995 to 12 August 1996, and concentration of Zn was measured on four occasions from 21 April 1988 to 8 February 1989. During both periods, between three and five samples were collected at different locations in the lake at 1-m depth below the water surface.

Bulk deposition was collected in a Warren Springs Laboratory collector (Hall 1986), the type used in the Secondary Network of the National Acid Deposition Network, every 2 weeks from 29 September 1987 to 15 March 1989. The collecting funnel was made of polypropylene, 115 mm in diameter, with a 1-mm mesh plug at the base to prevent larger debris from entering the 3-liter capacity polypropylene collecting bottle. The top of the collector was at a height of 1.75 m, and a bird guard extended above the collector. All parts of the collector that came into contact with deposition were acid washed according to the procedures used for sample bottles described below. The volume of bulk deposition was also measured. Water samples were collected in polypropylene bottles every 2 weeks from 29 September 1987 to 21 January 1989 from the six inflowing rivers and outflow, and Lough Neagh was sampled every 2 weeks from 10 August 1995 to 12 August 1996 and four times between 21 April 1988 and 8 February 1989. Daily flow results were available for the six inflowing rivers from the Government's hydrological network, and the outflow was estimated by the sum of the inflows. In estimating the outflow by this method, it was assumed that direct precipitation onto the lake surface and groundwater inputs were negligible. With the lake area (385 km^2) and long-term average values for total river inflow (2.92×10^9 m^3 yr^{-1}) and precipitation (1,081 mm yr^{-1}), it can be calculated that precipitation is 14.2% of river inflow. The net contribution of precipitation will be less than this value because of evaporation from the surface of the lake. Groundwater inputs to Lough Neagh are likely to be small, since the lake overlies thick clays [glaciogene formations (boulder clay), which overlie the Lough Neagh clay formation]. The assumption that outflow equals the sum of the river inflows has been made in budget studies of phosphorus (Gibson et al. 2001) and silicon (Gibson 1981) in Lough Neagh.

The methods and quality assurance procedures used to determine the metal concentrations are described below. This information is presented in detail since improvements to the collection and handling of water samples for the determination of heavy metal concentrations have been made since the time of this study. We used the methods then currently available, methods that have been replaced by the protocols used today (Nriagu et al. 1993; Benoit 1994). The sample bottles used for bulk deposition and river and lake water were cleaned and handled according to Laxen and Harrison (1981) and Her Majesty's Stationery Office (1987) as follows: soak in a solution of 1% HCl and 1% Decon 90 in deionized water; rinse four times in deionized water; soak for 48 h in 10% HNO_3 (AnalaR) in deionized water; rinse three times in deionized water and three times in Millipore Milli-Q water; dry inverted. All samples were acidified to 1% HNO_3 (ARISTAR grade) and stored at 4°C until analysis by flameless electrothermal atomic absorption spectrophotometry, with a L'vov platform and use of matrix modifiers (Perkin-Elmer HGA300 with an AS40 autosampler during 1987–1989 and Perkin-Elmer 4100ZL during 1995–1996).

There were five components to the quality assurance procedures used in 1987–1989: a procedural blank, recording of the peak area of standards for every batch of samples, recording of the concentration of recalibration blanks for every batch of samples, spiking recovery tests on river water samples for every batch of samples, and calculation of the characteristic masses for every batch of samples. The analysis was repeated if the quality assurance failed. Procedural blanks had Millipore Milli-Q water added to a sample bottle in the laboratory before leaving to take samples, and subsequently they were treated identically to water samples. The aim was to check the degree of contamination of samples as a result of loss of metal from the walls of the sample bottle and the addition of preservative acid. This check was completed on two occasions, 26 April 1988 and 17 May 1988, and the means of the procedural blanks ($n = 2$) were -0.20 μg Pb L^{-1}, -0.35 μg Zn L^{-1}, and 0.05 μg Cu L^{-1}. The spiking recovery tests involved adding 50 μL of a 500 μg L^{-1} standard to 1,000 μL of sample, giving an expected increase in concentration of 23.81 μg L^{-1}, and the results were 104% for Pb (78 to 131, $n = 11$), 106% for Zn (78 to 131, $n = 10$), and 96% for Cu (77 to 116, $n = 16$). The characteristic masses (picogram/0.004 absorbance) were found to be 5.74 for Pb (5.0 to 6.6, $n = 13$), 0.91 for Zn (0.69 to 1.27, $n = 13$), and 8.52 for Cu (7.0 to 12.0, $n = 13$).

The deposition rate of Pb, Zn, and Cu from the atmosphere onto Lough Neagh was calculated for each 2-week period using the formula (concentration in bulk deposition $\times$ volume of bulk deposition)/(area of collector). The inputs

of heavy metals from the catchment to the lake and output from the lake by catchment rivers were estimated in two ways. The first method, log load − log flow (Smith and Stewart 1977), is widely used, and the second, mean monthly concentration × mean monthly flow, is simpler and mainly has been used for soluble chemicals (where concentration varies little with flow). Metal loads in the rivers were estimated using the two methods so that the accuracy of the simpler method could be compared to that of the more complex one. Since the six major inflowing rivers drain 86% of the catchment, the measured inputs were applied to the whole catchment using the calculation 1.16 × (measured inputs)([1/0.86] = 1.16).

Simple model for heavy metals in lakes—Two simple models for the steady-state concentration of chemicals in lake water were developed using the results from Lough Neagh and four other lakes. The simplest model for the behavior of a chemical in a lake is a steady-state mass balance, where total input is identical to the sum of the output through the outflow and retention in the sediment (Reckhow and Chapra 1983; Prairie 1989). The two main options used to describe the retention of a chemical in lake sediment are either by a retention coefficient [R, the proportion of the load of the chemical on the lake that is retained (dimensionless); Dillon and Rigler 1974] or a sedimentation coefficient [σ, proportion of the mass of the chemical in the lake water that is retained (yr^{-1}); Vollenweider 1975], and so these two simple models for heavy metals in lake water were developed and their accuracy evaluated.

The steady-state concentration of the heavy metal in lake water (C, g m^{-3}), based on the retention coefficient model, is given by Eq. 1 (Prairie 1989);

$$C = [L(1 - R)]/(z\rho) \quad (1)$$

where L is the loading of metal on the lake (g m^{-2} yr^{-1}), R the retention coefficient of metal in the lake (dimensionless), z the mean lake water depth (m), and ρ the hydraulic flushing coefficient (yr^{-1}; $\tau_w = \rho^{-1}$, where τ_w is the hydraulic residence time).

The steady-state concentration of metal in the lake water (C, g m^{-3}), based on the sedimentation coefficient model, is given by Eq. 2 (Prairie 1989);

$$C = L/[z(\rho + \sigma)] \quad (2)$$

where σ is the sedimentation coefficient of metal in the lake (yr^{-1}; $\tau_S = \sigma^{-1}$, where τ_S is the sedimentation residence time of the metal; Stumm and Morgan 1996). In order to estimate τ_S from the total residence time of the metal in the lake (τ_M), we used the principle of addition of residence times ($\tau_M^{-1} = \tau_S^{-1} + \tau_w^{-1}$; Stumm and Morgan 1996).

The calculation of the annual average retention and sedimentation coefficient was completed as follows. R for each metal in each lake was calculated using (annual load of metal on lake − annual loss of metal from lake)/(annual load of metal on lake) (Dillon and Rigler 1974). The value of σ was calculated using (annual average mass of metal in lake water)/(annual load of metal on lake − annual loss of metal from lake) (Vollenweider 1975).

The accuracy of the models was evaluated by comparing the modeled and measured steady-state lake water concentrations. For the retention coefficient model, the measured loading (L), lake mean depth (z), and hydraulic flushing coefficient (ρ) were used along with Eq. 1 and the arithmetic mean retention coefficient (R) for all the lakes to calculate the steady-state lake water concentration (C). For the sedimentation coefficient model, the measured loading (L), lake mean depth (z), and hydraulic flushing coefficient (ρ) were used along with Eq. 2 and the arithmetic mean sedimentation coefficient (σ) for all the lakes to calculate the steady-state lake water concentration (C). The model errors were estimated by calculating the root mean square error of prediction using the difference between modeled and measured concentrations, $\sqrt{\Sigma[(\text{modeled} - \text{measured})^2]/n}$. Using mean values for the coefficients allows simple, generic models for metals in lake water to be developed and their goodness of fit to be assessed by comparing modeled and measured concentration. This method of using the same data to develop and evaluate the accuracy of a model, although widely used (Birks et al. 1990; Bennion et al. 1996), is not an independent test of the model. It is desirable to use a separate data set to test model accuracy (Bennion et al. 1995).

Results

Deposition rate from the atmosphere—The concentration of Pb, Zn, and Cu in bulk deposition did not vary greatly, and only Zn on 3 and 31 January 1989; Zn, Cu, and Pb on 29 March 1988 at the Silent Valley; and Zn, Pb, and Cu on 13 September 1988 at Altnaheglish were much higher than the other values. These high values may have been due to contamination of the bulk deposition samples. The evidence for this is that the values are so much outside the ranges of the other results, there is no consistency in the high values across all sites, and the quality assurance is good. They were, therefore, removed to calculate the summary statistics (Table 1), but deposition rates were calculated both including and excluding them in order to establish their effect on the estimates of deposition rate from the atmosphere. The concentrations of Pb, Zn, and Cu in bulk deposition in the Lough Neagh catchment (Table 1) are within the ranges found at other rural and remote locations (Barrie et al. 1987; Berg et al. 1994; Lawlor and Tipping 2003), and so they are typical of sites influenced by background regional contamination of the atmosphere, not by specific point source emissions.

There is moderate correlation between the properties in bulk deposition. The average metal–metal correlation coefficient is 0.48 (n = 26–28) for the Silent Valley (maximum is 0.61 for Zn/Cu), 0.34 for Altnaheglish (0.39 for Pb/Zn), and 0.46 for Four Mile Burn (0.83 for Zn/Cu), and the average metal–volume correlation coefficient is −0.34 (maximum is −0.43), −0.17 (−0.29), and −0.27 (−0.46), respectively. The Kruskal-Wallis H-test shows that the null hypothesis, in which there are no differences in the concentration of a metal across the three sites, cannot be rejected ($p > 0.05$, df = 2) for each of the three metals. The rate of deposition from the atmosphere from 29 September 1987 to 15 March 1989 was 6.06, 4.54, and 2.76 mg Pb m^{-2} yr^{-1} at Silent Valley, Altnaheglish, and Four Mile Burn, respective-

Table 1. Summary statistics for Pb, Zn, and Cu concentration (μg L^{-1}) and volume (liters) measured every 2 weeks in bulk deposition at three sites in the Lough Neagh catchment from 29 September 1987 to 15 March 1989. The number of samples is between 25 and 30 and RSD is relative standard deviation ([SD/mean] $\times$ 100).

	Silent Valley				Altnaheglish				Four Mile Burn			
	Pb	Zn	Cu	Vol.	Pb	Zn	Cu	Vol.	Pb	Zn	Cu	Vol.
Mean	2.7	7.1	4.5	0.94	2.1	6.5	5.1	0.99	1.5	8.3	4.1	0.75
Median	1.8	3.7	2.0	0.87	1.4	2.1	2.2	0.91	1.4	6.0	1.8	0.75
Minimum	0.12	0.04	0.11	0.03	0.10	0.04	0.11	0.05	0.10	0.04	0.11	0.04
Maximum	15.1	28.4	22.7	2.30	10.8	25.8	24.4	2.41	7.2	30.1	19.0	1.79
RSD (%)	125	101	130	59	118	114	118	62	89	88	117	54

ly; 14.84, 16.26, and 13.88 mg Zn m^{-2} yr^{-1}; and 9.25, 11.01, and 6.35 mg Cu m^{-2} yr^{-1}, and the average value (and standard error) for the three sites is 4.45 $\pm$ 0.95 mg Pb m^{-2} yr^{-1}, 14.0 $\pm$ 0.68 mg Zn m^{-2} yr^{-1}, and 8.87 $\pm$ 1.36 mg Cu m^{-2} yr^{-1}, excluding the high values. If the high values are included, then the averages are 18, 35, and 37 mg m^{-2} yr^{-1} for Pb, Zn, and Cu, considerably greater than the averages calculated excluding them.

Inputs from the catchment and output from the lake—The concentration of Pb, Zn, and Cu in the rivers also did not vary greatly. As with the bulk deposition samples, there were occasionally very high values that may have been due to contamination. The results were evaluated as follows. The most likely reason for a high metal concentration in a river water sample is that it coincides with a high discharge, which causes resuspension of sediment. Where a high daily discharge value occurred on or 1 or 2 d before a sample with a high metal concentration, the value was retained. These values were for Zn in the Moyola (37 μg L^{-1}), Main (67 μg L^{-1}), and Upper Bann (35 μg L^{-1}) on 26 October 1987; Zn in the Sixmilewater on 7 June 1988 (38 μg L^{-1}); and Pb in the Main on 25 October 1988 (7 μg L^{-1}). Where a high concentration was not associated with a high river discharge, the value was removed. These values were for Zn in the Main on 9 November 1987 (67 μg L^{-1}); Lower Bann on 25 October 1987 (51 μg L^{-1}); Sixmilewater on 4 January (69 μg L^{-1}), 6 June (38 μg L^{-1}), and 24 October (36 μg L^{-1}) 1988; and Pb in the Lower Bann on 7 December 1987 (7 μg L^{-1}). The summary statistics (Table 2) and estimates of river loads do not include these values. The mean metal concentration (and standard deviation) in the six inflowing rivers from 29 September 1987 to 21 January 1989 was 0.7 $\pm$ 0.24 μg Pb L^{-1}, 7.9 $\pm$ 1.5 μg Zn L^{-1}, and 5.9 $\pm$ 0.6 μg Cu L^{-1}, higher than in the outflow, 0.4 $\pm$ 0.6 μg Pb L^{-1}, 2.6 $\pm$ 2.9 μg Zn L^{-1}, and 4.6 $\pm$ 2.5 μg Cu L^{-1}.

The two methods used to estimate catchment inputs and output of Pb, Zn, and Cu, the simple method (mean monthly concentration $\times$ mean monthly flow) and more complex one (log load $-$ log flow), give similar results; the simple method slightly underestimates the Zn and Cu load (by 2.0% to 10.4%), compared to the more complex method, and overestimates the Pb load (13.2% and 35.0%) (Table 3). The coefficients of determination of the log load $-$ log flow models for the metals in the seven rivers are quite high (n = 30–32); the mean value is 0.81, maximum 0.94 (for Zn in the Moyola), and minimum 0.65 (for Pb in the Upper Bann). This finding suggests that the simple and cheaper method may be suitable for estimating Zn and Cu loads in rivers, and this may also be true for Pb, although it depends on the accuracy required.

The inputs from the catchment include a contribution from waste water treatment works (WWTWs) discharges, and an estimate of it was made as follows. Results from a survey by the Department of the Environment for Northern Ireland of the metal concentrations in effluent from nine WWTWs in Northern Ireland, none of which were in the Lough Neagh catchment, were made available. The mean concentration (and range) was 14 μg Pb L^{-1} (1.2–40), 67 μg Zn L^{-1} (34–150), and 22 μg Cu L^{-1} (10–38). The sewered population in the Lough Neagh catchment was 229,600 in 1979 (Gibson et al. 1988), and it was assumed that the waste water produced was 365 liters per sewered person per day. Using these values, it was estimated that the contribution of WWTWs to

Table 2. Summary statistics for Pb, Zn, and Cu and concentration (μg L^{-1}) measured every 2 weeks in the six main inflowing rivers to Lough Neagh and the outflow (Lower Bann) from 29 September 1987 to 31 January 1989. The number of samples is between 32 and 34, and RSD is relative standard deviation ([SD/mean] $\times$ 100).

	Pb			Zn			Cu		
	Mean	Median	RSD (%)	Mean	Median	RSD (%)	Mean	Median	RSD (%)
Main	0.36	0.12	84	6.5	5.9	69	5.3	5.6	58
Upper Bann	0.85	0.60	107	8.9	8.4	50	7.0	7.3	48
Moyola	0.74	0.40	129	6.5	5.7	72	5.8	5.7	48
Ballinderry	0.58	0.40	105	7.5	6.0	62	5.8	5.7	53
Blackwater	1.07	0.90	102	7.4	6.3	68	5.5	6.2	61
Sixmilewater	0.71	0.50	100	10.3	9.3	48	5.8	6.0	55
Lower Bann	0.35	0.12	163	2.6	1.8	112	4.6	5.0	56

Table 3. The annual inputs of Pb, Zn, and Cu from the catchment to Lough Neagh and output from the lake based on measurements over the period 28 September 1987 to 2 January 1989, estimated by two methods, log load − log flow and mean monthly concentration × flow. The loads are also expressed per unit area of Lough Neagh (385 km²) and the difference between the two models is given (log load − monthly)/(log load × 100).

	Pb	Zn	Cu
Inputs			
log load − log flow (kg yr^{-1})	2,030	26,300	19,900
log load − log flow (mg m^{-2} yr^{-1})	5.3	68.0	51.5
Mean monthly concentration × flow			
(kg yr^{-1})	2,740	25,300	19,500
(mg m^{-2} yr^{-1})	7.1	65.4	50.4
Difference (%)	−35	3.8	2.0
Output			
log load − log flow (kg yr^{-1})	1,210	8,910	16,100
log load − log flow (mg m^{-2} yr^{-1})	3.1	23.0	41.5
Mean monthly concentration × flow			
(kg yr^{-1})	1,370	7,980	14,700
(mg m^{-2} yr^{-1})	3.5	20.6	38.0
Difference (%)	−13	10	8.7

the inputs from the catchment is likely to be less than 10% for Zn and Cu and less than 30% for Pb.

Budget for Lough Neagh—The results presented for the deposition rate of Pb, Zn, and Cu from the atmosphere, inputs from the catchment in the six inflowing rivers, and output from the lake in the lake outflow from 28 September 1987 to 2 January 1989 were used to derive a budget for these metals in Lough Neagh (Table 4). The log load − log flow method was assumed to give the most accurate estimate of the river loads, and the deposition rate from the atmosphere was estimated with and without the high concentration values. The loads were expressed per unit area of lake to allow comparison with other lakes.

Lake concentrations—The overall mean concentration of total Cu and Pb from 10 August 1995 to 12 August 1996 and total Zn from 21 April 1988 to 8 February 1989 is presented in Table 5. The concentration of Cu is relatively high. In regional surveys of Pb, Zn, and Cu concentration in over 2,500 lakes in Norway, Sweden, Denmark, and Finland in 1995, Skjelkvale et al. (2000) found that the median concentration varied from 0.14 to 0.38 μg Pb L^{-1}, 1.1 to 7.4 μg Zn L^{-1}, and 0.33 to 0.6 μg Cu L^{-1}, with Denmark always having the highest value.

Discussion

Errors in the budget—Before using the budget for Pb, Zn, and Cu in Lough Neagh to develop the lake models, the possible errors in the budget should be assessed. The main error is whether or not to include the eight high concentration values in bulk deposition. We have reported the budget with and without them (Table 4), but, since our assessment is that they may be due to contamination, the lower values for deposition rate from the atmosphere are used in the analysis below. The 14-d sampling interval for the rivers may produce an underestimate of river loads because of undersampling of high flow events (Stevens and Smith 1977). However, since the concentration of Pb, Zn, and Cu did not vary much with flow and the simple method of estimating river loads gives similar results to the more complex one

Table 4. Budget for Pb, Zn, and Cu in Lough Neagh based on measurements from 28 September 1987 to 2 January 1989, expressed per unit area (mg m^{-2} yr^{-1}) of Lough Neagh (385 km²). The retention coefficient ([total inputs − output]/total inputs) is also shown.

	Pb	Zn	Cu
Inputs			
Excluding high bulk deposition concentrations	9.7	82.8	60.4
Including high bulk deposition concentrations	22.4	103.0	88.2
Output	3.1	23.0	41.5
Proportion of total input from the atmosphere			
Excluding high bulk deposition concentrations	0.458	0.179	0.147
Including high bulk deposition concentrations	0.765	0.340	0.416
Retention coefficient			
Excluding high bulk deposition concentrations	0.680	0.722	0.313
Including high bulk deposition concentrations	0.862	0.777	0.529

Table 5. Concentration of total Pb, Zn, and Cu (μ L^{-1}) in Lough Neagh. Zn was measured from 21 April 1988 to 8 February 1989, Cu and Pb were measured from 10 August 1995 to 12 August 1996, and RSD is relative standard deviation ([SD/mean] × 100).

	Pb	Zn	Cu
Average	0.45	5.5	2.68
Minimum	−0.13	1.6	1.07
Maximum	2.25	9.4	7.68
RSD (%)	92.2	48.1	28.9
Number of samples	113	11	113

(Table 3), this error may not be large. Others studies have found that heavy metal concentrations vary weakly or not at all with stream discharge (Schut and Douglas Evans 1986; Dillon et al. 1988). The input of heavy metals to Lough Neagh from groundwater is likely to be small, since the lake overlies thick clays. There is more direct evidence to support this from the major ion concentrations in Lough Neagh. The major ion concentrations can be predicted from simple mixing of the loads in the six main inflowing rivers (Rippey 1993), and this indicates that there are no large additional sources of major ions, for example, from groundwaters.

The use of lake water Pb and Cu concentration measurements made in 1995–1996 with budget results for 1987–1989 may introduce some errors, although these are likely to be small. The amount of Pb and Cu contamination in Lough Neagh, as a result of deposition from the atmosphere, did not change over this period (Fig. 2), and, since rainfall during the two periods was similar, the amount of Pb and Cu delivered to the lake by rivers is also likely to be similar. Overall, since the total loading of Pb and Cu on Lough Neagh is likely to be similar in 1987–1989 and 1995–1996, the lake water concentrations are also likely to be similar.

Contribution of Pb, Zn, and Cu from the atmosphere—Deposition from the atmosphere onto the surface of Lough Neagh is an important component of the budget of Pb, Zn, and Cu; it is estimated to be 45.8%, 17.9%, and 14.7% of the total input, respectively (Table 4), and is responsible for the contamination of sediment in the lake by these metals (Rippey et al. 1982).

Deposition from the atmosphere is a significant source of Zn and Pb in eight lakes in Europe and the United States

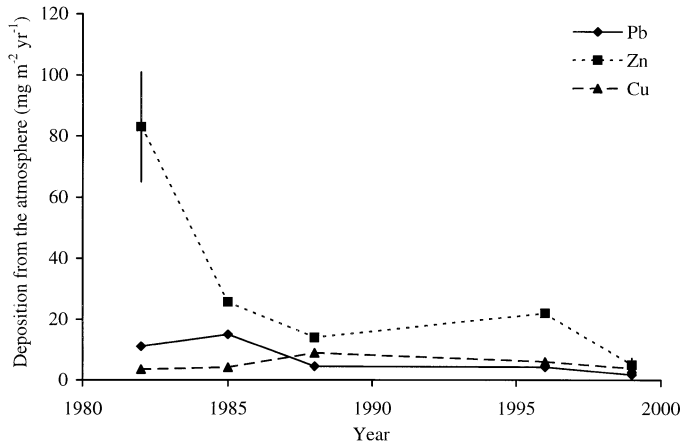

Fig. 2. Variation of deposition of Pb, Zn, and Cu from the atmosphere from 1981 to 1999 in the United Kingdom. These data are from Hamilton-Taylor and Willis (1990), Durand et al. (1994), Alloway et al. (unpubl.), Lawlor and Tipping (2003), and this study, and the standard error of the mean is shown, although most values are very small.

(Table 6); the importance of the atmosphere is always greatest with Pb, least with Cu, and the average of the total input that is deposited from the atmosphere is 56% for Pb, 35% for Zn, and 8.3% for Cu. Catchment inputs are still the most important source of heavy metals to the lakes, contributing, on average, 44%, 65%, and 92% of Pb, Zn, and Cu, respectively (Table 6). These inputs are mostly from the weathering of soils. In most cases, the retention of Pb and Zn deposited from the atmosphere on to the catchment is complete, with increasing losses of Cu, Ni, and Cr in that order (Schut and Douglas Evans 1986; Blais and Kalff 1993). The importance of deposition of heavy metals from the atmosphere has changed over the last 20 yr (Fig. 2).

Simple model for heavy metals in lake water—Two simple, generic models for the concentration of heavy metals in lake water were developed: a retention coefficient model and a sedimentation coefficient model. To develop the models, the results of budget studies of Pb, Zn, and Cu in lakes were collated from the literature and the results from Lough Neagh added (Table 7). This produced a small data set, particularly compared to the 120 lakes for phosphorus (Prairie

Table 6. Proportion of total input of Pb, Zn, and Cu to lakes from the atmosphere. RSD is relative standard deviation ([SD/mean] × 100).

Lake	Reference	Pb	Zn	Cu
Lough Neagh	This study	0.458	0.179	0.147
Alpnachersee	Baccini (1976)	0.301	0.196	0.024
Lake Michigan	Eisenreich (1980)	0.604	0.326	0.135
Lake Constance	Sigg et al. (1982)	0.828	0.267	0.072
Lake Windermere	Hamilton-Taylor and Willis (1990)	0.427	0.512	0.153
Greifensee	Sigg et al. (1996)		0.267	
Lake Erie	Nriagu et al. (1996)	0.647	0.492	0.028
Lake Ontario	Nriagu et al. (1996)	0.674	0.546	0.024
Mean		0.56	0.35	0.083
RSD (%)		32	42	72

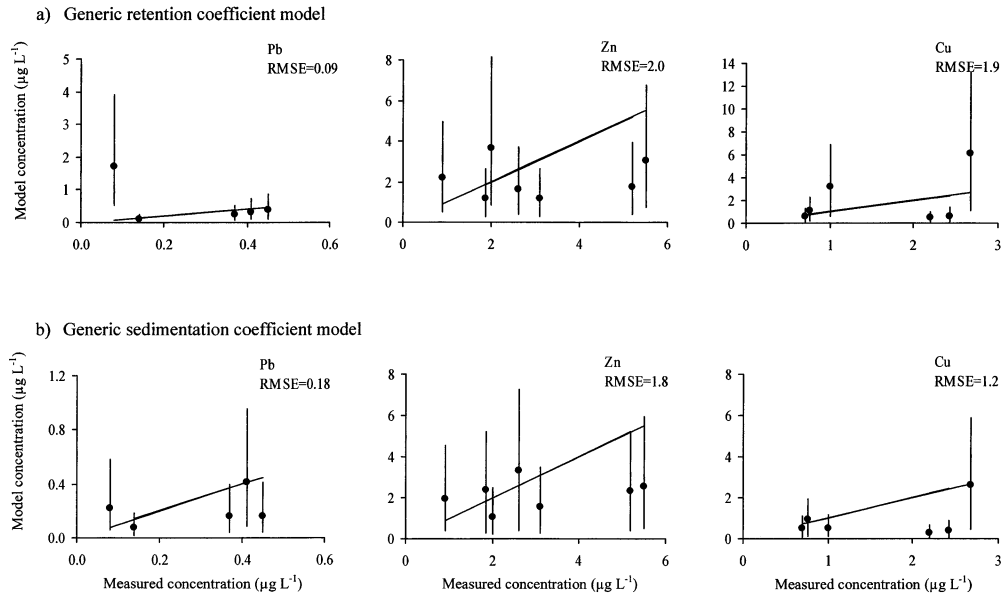

Fig. 3. The relationship between modeled and measured steady-state concentration of Pb, Zn, and Cu in lake water. (a) Relationship for a generic retention coefficient model. For the model, the concentrations were modeled using Eq. 1, the measured metal loading, lake mean depth and hydraulic residence time (Table 7), and the average retention coefficient (0.70 ± 0.09 for Pb, 0.72 ± 0.06 for Zn, and 0.24 ± 0.13 for Cu). (b) Relationship for a generic sedimentation coefficient model. The concentrations were modeled using Eq. 2, the measured metal loading, lake mean depth and hydraulic residence time (Table 7), and the average sedimentation coefficient (5.81 ± 2.34 yr^{-1} for Pb, 2.80 ± 0.90 for Zn, and 1.75 ± 0.54 for Cu). The 1 to 1 line, standard error of the modeled concentration due to propagation of the standard error of the retention or sedimentation coefficient, and root mean square error of model prediction (RMSE, $\mu g\ L^{-1}$) are shown on all graphs.

1989), but it is unlikely that the number of heavy metal budgets for lakes will increase greatly. Any generic model for heavy metals will have to be developed using a small data set.

The variation of retention coefficient for each metal across the lakes is quite low, except for Cu. The mean retention coefficient is 0.70 (RSD = 29%), 0.72 (24%), and 0.24 (133%) for Pb, Zn, and Cu, respectively (Table 7). Although the retention coefficient of the three metals is highest in Lake Constance, the lake with the longest hydraulic residence time, retention coefficient is not correlated with hydraulic residence time, lake mean depth, or loading in this data set. Such correlations are central to lake phosphorus models (Prairie 1989), but a simple arithmetic average retention coefficient for each metal is the only option for heavy metals at present.

There is more variation of total and sedimentation residence time across the lakes than was found with retention coefficient. The mean total residence time is 0.21 (RSD = 64%), 0.36 (61%), and 0.77 (97%) yr for Pb, Zn, and Cu, respectively, and the mean sedimentation residence time 0.34 (73%), 0.91 (99%), and 1.05 (95%) yr. When sedimentation residence time (τ_S) is converted to sedimentation coefficient (σ, $\sigma = \tau_S^{-1}$), before it is used in the sedimentation coefficient model (Eq. 2), the RSD changes a little. As was found with the retention coefficient, the sedimentation coefficient is not correlated with hydraulic residence time, lake mean depth, or loading, and so a simple arithmetic average sedimentation coefficient for each metal is the best way of describing the retention of metal in this type of model at present.

Since the mean value for the coefficients is used in the generic models, it is important to evaluate the accuracy of the models. It was evaluated in two ways. First, the standard error of the mean retention and sedimentation coefficient was propagated through Eqs. 1 and 2, respectively, to calculate a standard error for the steady-state lake water concentration (Fig. 3). Second, the goodness of fit of the models was determined by calculating the root mean square of error prediction between the modeled and measured steady-state metal concentrations in the lakes (Fig. 3). With the retention coefficient model, the modeled steady-state Pb concentration in Lake Constance is very much higher than the measured. Part of the reason for this discrepancy is because the measured retention coefficient is very close to 1.0 and small changes in the value lead to large changes in lake water concentration (Prairie 1989). Even though the mean retention coefficient for Pb (0.70) is not very different from the measured value (0.98), this difference leads to a large change in modeled concentration. The result for Pb in Lake Constance was, therefore, removed before calculating the root mean square error of prediction. The model errors are ±0.09, 2.0, and 1.9 $\mu g\ L^{-1}$ for Pb, Zn, and Cu, respectively, and there is no consistent bias. With the sedimentation coefficient model, the model errors are ±0.18, 1.8, and 1.2 $\mu g\ L^{-1}$ for Pb, Zn, and Cu, respectively, and there is no consistent bias.

There is little difference between the performance of the two models (Fig. 3); the errors are similar (the mean values are ±0.14, 1.9, and 1.6 $\mu g\ L^{-1}$ for Pb, Zn, and Cu, respectively), and there is no difference in bias. However, the performance of the models is better for Pb and Zn and, prob-

Table 7. Lake mean depth (z), hydraulic residence time (τ_w), steady-state concentration in lake water (C), lake loading (L), retention coefficient (R), total residence time (τ_M), and sedimentation residence time (τ_S) of Pb, Zn, and Cu in five lakes. Values are given for total metal and dissolved metal. The data were collated from Baccini (1976), Imboden et al. (1980), Sigg et al. (1982), Hamilton-Taylor and Willis (1990), Sigg et al. (1996), and this study.

	Lough Neagh total	Alpnachersee total	Alpnachersee dissolved	Greifensee total	Greifensee dissolved	Constance total	Windermere total	Windermere dissolved
z (m)	8.9	21		17.7		100	21.3	
τ_w (yr)	1.18	0.28		1.2		4.2	0.63	
C_{Pb} (μg L^{-1})	0.45	0.41				0.08	0.37	0.14
C_{Zn} (μg L^{-1})	5.50	2.62	1.86		0.91	2.00	5.20	3.10
C_{Cu} (μg L^{-1})	2.68	0.76	0.70			1.00	2.43	2.20
L_{Pb} (mg Pb m^{-1} yr^{-1})	9.7	81.0	39.6			135	25.6	12.0
L_{Zn} (mg Zn m^{-1} yr^{-1})	82.8	450	322		129	315	217	144
L_{Cu} (mg Cu m^{-1} yr^{-1})	60.4	104	58.8			99.6	28.6	21.0
R_{Pb}	0.68	0.81				0.98	0.48	0.55
R_{Zn}	0.72	0.51	0.48		0.89	0.85	0.75	0.87
R_{Cu}	0.31	0.42	0.05			0.77	0.05	−0.13
τ_{MPb} (yr)	0.41	0.11		0.13		0.06	0.31	0.25
τ_{MZn} (yr)	0.59	0.12	0.12	0.30	0.13	0.63	0.51	0.46
τ_{MCu} (yr)	0.40	0.16	0.26	0.25		0.99	1.08	2.23
τ_{SPb} (yr)	0.63	0.17	2.69	0.15		0.06	0.60	0.41
τ_{SZn} (yr)	1.18	0.22	0.21	0.42	0.13	0.74	2.68	1.66
τ_{SCu} (yr)	0.59	0.36	2.69	0.32		1.30		

ably, not acceptable for Cu; if the ratio of model error to maximum measured concentration is used to establish the relative performance of the models, then they are best for Pb (≈0.3) and Zn (≈0.3) and worst for Cu (≈0.6). While better accuracy and an independent test of accuracy is desirable, the retention coefficient and sedimentation coefficient models developed here are the best generic models available for Pb and Zn in lake water at present.

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