

**Chapter 9: Modelling the Transport of Trace Metals through
Blelham Tarn**

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9.0 *Modelling the Transport of Trace Metals through Blelham Tarn*

The object of this chapter is to apply the model developed in Chapter 8, using the depositional fluxes given in Chapter 7, and to validate the model where possible, using data from the sediment records and from the data on stable lead isotope ratios.

The first section will consider transport from the catchment, and will attempt to distinguish inputs of minerogenic lead from delayed inputs of atmospherically deposited lead stored in the catchment. The second section will consider transport through the water column, including the impact of solubility and losses via the outflow. The third section will compare the sediment record with the theoretical calculation. The impact of sediment focussing will be assessed using ^{210}Pb . Finally, stable lead isotope ratios in peat, catchment soils and lake sediments will be used to help identify contributions from the various sources to the sediment record. A site description and table of basic morphometric parameters are shown in Chapter 3, *Table 3.1*.

9.1 *Inputs from the Catchment to the Lake*

Inputs to the lake, from direct catchment erosion and/or subsequent runoff, contain trace metals from both atmospheric deposition and an erosional component from minerals present in the soil. Comparison of the ^{210}Pb calculated sedimentation rates versus calendar year of five cores from the Blelham basin (*Fig. 6.5*) has shown a relatively similar rate of accumulation from the 1800's to the present day, with the exception of site J in the SE corner of the lake which shows above average accumulation of material, with significant differences occurring after 1980.

The Blelham Tarn catchment soil lead profiles show enrichment in the upper layers (*Fig. 5.3*) presumably from atmospheric deposition. In a study designed to monitor hill-slope erosion Kitching (1996) also found elevated levels of lead in the sub-surface layers of two hill-slope transects, the longest 255 m in length extending parallel to Wray Beck. The results showed evidence of an erosive catchment with a pattern of mid-slope removal, followed by deposition at the lowest sites.

Due to the number of data points, the stable lead isotope results for the BLS 96 soil cores are inconclusive as to whether they contain similar records of changes in atmospheric deposition to those shown in the sediment and peat cores. Soil core 5 shows a surface decrease (11.5 cm to 5.5 cm) in the $^{206}\text{Pb}/^{207}\text{Pb}$ signature occurring at the same depth as the surface enrichment due to atmospheric input. Core 4 only shows a slight decrease from 1.184 ± 0.014 at 30.5 cm to 1.168 ± 0.012 at 2.5 cm. A likely $^{206}\text{Pb}/^{207}\text{Pb}$ signature of minerogenic lead is thus 1.183 ± 0.002 (average of BLS 96/4 and 96/5 deepest sections). This ratio is a little higher than the value for minerogenic lead given in section 7.5.2 of 1.176, however these cores are from peaty soils which are susceptible to partial leaching. Assuming that the concentration of minerogenic lead in the catchment soils can be approximated by the concentration of lead in the catchment before the onset of the industrial revolution (*i.e.* reduction in the $^{206}\text{Pb}/^{207}\text{Pb}$ signature), a best estimate of the minerogenic concentration for the catchment is 40.7 mg kg^{-1} (section 6.5.1)

9.1.1 Transport Rates for ^{210}Pb

Since ^{210}Pb has a very simple fallout record and is assumed to have a constant depositional flux when averaged over periods of years, transport parameters are easier to measure than for substances with more complicated fallout records. It is also a good environmental tracer for stable lead and other strongly particle reactive trace metals (Benninger *et al.*, 1975; Dominik *et al.*, 1984).

There have been a number of studies of ^{210}Pb transport rates. Calculated transport parameters from previously published studies are shown in *Table 9.1* (Appleby, 1997).

Catchment	Response coefficient η_s	Transport coefficient κ_c (yr^{-1})	Residence Time T_c (yr)	Reference
Alpine Rhône	0.023	0.00072	1400	Dominik <i>et al.</i> (1987)
Mississippi	0.012	0.00039	2580	Scott <i>et al.</i> (1985)
Susquehanna	0.016	0.00052	1930	Lewis (1977)

Table 9.1. ^{210}Pb catchment/lake transport parameters (reproduced with permission from Appleby, 1997)

Since ^{210}Pb is strongly particle reactive (Appleby, 1997) in soils ($K_D = 10^5 - 10^7 \text{ l kg}^{-1}$), taking the upper estimate for K_D the partition fraction, f_D is calculated from equation 8.25 to be 0.96 ($F_{\text{Pb-210}} = 0.81$). It is generally thought that transport rates are low with some authors going as far as stating that all ^{210}Pb is locked in the catchment and is unavailable for transport (Blais and Kalff, 1993).

It is now possible to apply the mass balance equation (*eqn.* 8.41) to the ^{210}Pb results. Since the 1996 sediment core results are biased due to sediment focussing (*Table 7.8*). A better approximation for the sedimentary flux of ^{210}Pb is gained by using a mean of 18 cores taken over the entire basin (Appleby *et al.*, 1999). Therefore $P_s = 203 \text{ Bq m}^{-2} \text{ yr}^{-1}$ whilst the atmospheric flux was determined in section 7.4 ($P_a = 151 \text{ Bq m}^{-2} \text{ yr}^{-1}$). Using these figures it is estimated that 26% of the ^{210}Pb in the sediments derives from catchment inputs. Since the catchment/lake area ratio is 42, the ^{210}Pb transport parameter is calculated to be $\eta_{\text{pb}} = 0.016$. The fraction of the annual fallout onto the catchment delivered to the lake is thus just 1.6%, and the fraction of the catchment inventory delivered annually to the lake, given by *eqn.* 8.15 is just 0.051%. The residence time of ^{210}Pb in the catchment is thus *c.* 1979 years comparable with results from three other studies quoted in *Table 9.1*.

9.1.2 Transport Rates for Trace Metals

Storage in the catchment is a long-timescale process, any recent changes will not have had time to make a significant impact. According to global flux records calculated from natural archives (*Fig. 2.3*) the atmospheric lead flux over the past 1100 years can be roughly approximated by an exponential relation

$$\Phi(t - \tau) = F_a(t) e^{-\xi \tau} \quad \text{eqn. 9.1}$$

where $F_a(t)$ is the present day flux, τ is the age BP, and ξ is an exponential coefficient. From *c.* 1100 BP to the present, the Swiss lead flux increases by a factor of *c.* 200. Fitting an exponential function

to the long-term (1100 yr) atmospheric flux data for Switzerland suggests that ξ has a value of about 0.005 yr^{-1} , whereas for Greenland $\xi = 0.0004 \text{ yr}^{-1}$. At Blelham Tarn, F_a (mean 20th century value) is about $6 \mu\text{g cm}^{-2} \text{ yr}^{-1}$.

Values of the transport parameters η and k (eqn. 8.18) can be estimated from results obtained for the transport of plutonium (Pu) from the catchment of Blelham Tarn (Appleby *et al.*, 1999). Since Pu is strongly bound to particles, its catchment response function $h(t)$ may be assumed to be similar to that for Pb. To a reasonable approximation, Pu can be assumed to have been deposited during a relatively small period of time around 1963. Its transport function will thus be the same as the catchment response function $h(t)$. The Pu results indicated that the integral of $h(t)$ up to 1997 ('total runoff') was 0.029, or 2.9% of total deposition. Further, the present day value of $h(t)$ is $\sim 0.0002 \text{ yr}^{-1}$. These values are only estimates, but the best available. It follows from eqn. 8.18 that

$$\eta(1 - e^{-34k}) = 0.029 \quad \text{and} \quad \eta k e^{-34k} = 0.0002.$$

Solving the equations numerically gives $k = 0.071$ and $\eta = 0.032$. Going back to equation 8.22 and using the established value for ξ of 0.005 yr^{-1} suggests that the rate of transport of particle-reactive trace metals from the catchment to the lake is

$$\psi_c(t) = 0.03 A_c F_a(t) \quad \text{eqn. 9.2}$$

i.e. that *c.* 3% of the annual fallout onto the catchment is delivered to the lake. This is a little higher than the value for ^{210}Pb (1.6%). From equation 8.23 (and using the catchment/lake area ratio of $\alpha = 42$) this shows that atmospherically deposited inputs to the lake coming via the catchment may represent 57% of the total atmospherically derived input. Although some of this may be fresh material, some will be old.

At this stage it is not possible to calculate transport rates for more soluble species. They may penetrate further into the soil making them less available, or they may move quickly in solution. More detailed analysis of the ^{137}Cs data may shed light on this. Although these results are far from perfect, they do establish a methodology for calculating catchment inputs.

9.1.3 Old and New Lead from the Catchment

The sediment record contains a mixture of new and old minerogenic lead from delayed inputs of atmospherically deposited lead stored in the catchment. Calculating a theoretical isotope ratio for the sediments can give an idea as to whether old atmospheric lead in the catchment is a significant contributor to present day inputs.

Assuming that the minerogenic (background) lead in sediments has $^{206}\text{Pb}/^{207}\text{Pb} = 1.176$ and that the

peat bog gives the isotope ratio versus time of atmospherically (excess) derived lead, we can calculate a theoretical isotope ratio for the sediments using weighted averages (eqn. 9.3).

$${}^{206}\text{Pb}/{}^{207}\text{Pb}_{\text{theor.}} = \left[\left(\text{Pb}_{\text{bg}} / \text{Pb}_{\text{meas.}} \right) \times \left({}^{206}\text{Pb} / {}^{207}\text{Pb}_{\text{bg}} \right) \right] + \left[\left(\text{Pb}_{\text{exc}} / \text{Pb}_{\text{meas.}} \right) \times \left({}^{206}\text{Pb} / {}^{207}\text{Pb}_{\text{exc.peat}} \right) \right] \text{eqn. 9.3}$$

The theoretical isotope signature (Fig. 9.1) is generally lower than the actual signature since older lead deposits contributing to the actual lead isotope signature have a higher ${}^{206}\text{Pb}/{}^{207}\text{Pb}$ signature *cf.* lead isotope ratio in the soil cores of 1.183.

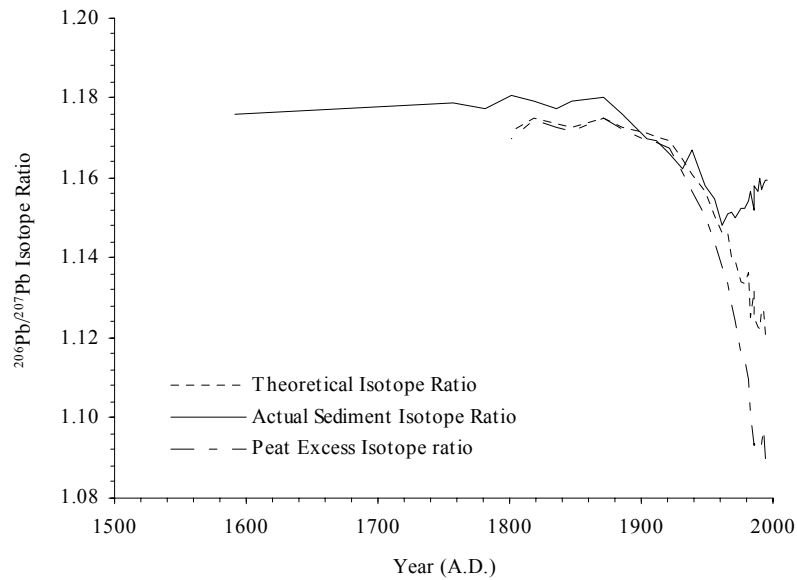


Fig. 9.1: Sediment core BLT 96/A ${}^{206}\text{Pb}/{}^{207}\text{Pb}$ isotope signature, peat core excess (anthropogenic) ${}^{206}\text{Pb}/{}^{207}\text{Pb}$ isotope signature and calculated theoretical isotope ratio vs. calendar year.

9.2 Water Column Transport

The fraction of inputs transferred to the sediment record (as opposed to being lost via the outflow) is given by eqn. 8.37. This equation involves three key parameters, T_w , T_s and f_D . The water residence time T_w (eqn. 8.39) is estimated from the parameters in Table 3.1 to be 32 d. The mean settling velocity for particles in Blelham Tarn is 0.99 m d^{-1} (calculated from a recent accumulation rate of $0.083 \text{ g cm}^{-2} \text{ yr}^{-1}$ and a suspended solids concentration of 2.3 mg l^{-1} (Smith, 1993)), thus the typical settling time T_s (eqn. 8.28) is estimated to be 7 d. The partition fraction, f_D of pollutants is calculated from equation 8.25. And T_L is calculated from equation 8.31. Calculated transport parameters are shown in Table 9.2.

For trace metals such as Zn and Cu a general K_D for suspended particles is 10^4 and $2 \times 10^5 \text{ l kg}^{-1}$ respectively (van den Berg, *pers. comm.*). K_D for lead is taken to be the same as for ${}^{210}\text{Pb}$. In reality, trace metal partitioning in lakes is more complicated and is a function of the metal ion characteristics,

particle size, organic matter content and sediment concentration (Rygwelski, 1984). These factors are beyond the scope of this model and the distribution coefficient represents a simplification of these processes.

Trace Metal	K_D ($l\text{ kg}^{-1}$)	f_D	T_L (d)	F
Pb	$10^5 - 10^7$	0.19 - 0.96	6 - 17	0.46 - 0.81
Zn	10^4	0.02	29	0.10
Cu	2×10^5	0.32	13	0.60

Table 9.2: Model parameters for trace metals Pb, Zn and Cu.

9.3 Comparison with the Sediment Record

Although catchment inputs to Blelham Tarn may be significant, they are concentrated in the southeast corner around the inlet streams. Concentrations around these streams are high, as shown by site J. At sites A and D, well away from inlet streams the flux to the sediments is dominated by direct fallout onto the lake (Appleby, 1999). Even so the calculated fluxes (Fig. 6.7) are not true atmospheric fluxes due to sediment focussing. For lead, catchment inputs (*c.* 3% per annum) do not significantly affect the Pb/ ^{210}Pb ratio and we can use ^{210}Pb to normalise and reconstruct the atmospheric flux from the sedimentary flux. Hence the sediment records normalised against ^{210}Pb give a good record of the atmospheric lead flux. Therefore the lead fluxes shown in Fig. 9.2 are a good estimate of the atmospheric fluxes at Belham Tarn.

Comparison between metal ratios in direct deposition and the ratio in sediments can give a general idea of the quantity of Zn and Cu transferred from direct deposition to the sediments. In Blelham Tarn, anthropogenic lead core concentrations in surface samples are around 60 mg kg^{-1} , for Cu the anthropogenic contribution is 30 mg kg^{-1} , and so the Cu/Pb ratio is 0.5. The ratio Cu/Pb in rainwater is 1.1 (Table 7.2), and so a large fraction of the atmospherically deposited Cu is not transferred to the sediment record. Similarly for Zn, anthropogenic Zn concentrations are around 100 mg kg^{-1} , and so the ratio of Zn/Pb is 1.7, in rainwater it is 5.9 showing a loss of 3 times as much Zn as Pb.

These estimates show a loss of 50% of Cu and 70% of Zn from direct deposition. This is what we would expect since lake water chemistry predicts that Zn and Cu are more soluble than Pb. A theoretical value for K_D can be calculated from these ratio comparisons. From Table 9.2 F_{Pb} is 0.46-0.81. F for Zn should be 30% of this value whilst F for Cu should be 50% of that value. A theoretical K_D for Zn calculated from the model is therefore $9 \times 10^4 - 2 \times 10^5$, for Cu it is $2 \times 10^5 - 4 \times 10^5\text{ l kg}^{-1}$ slightly higher than the quoted values.

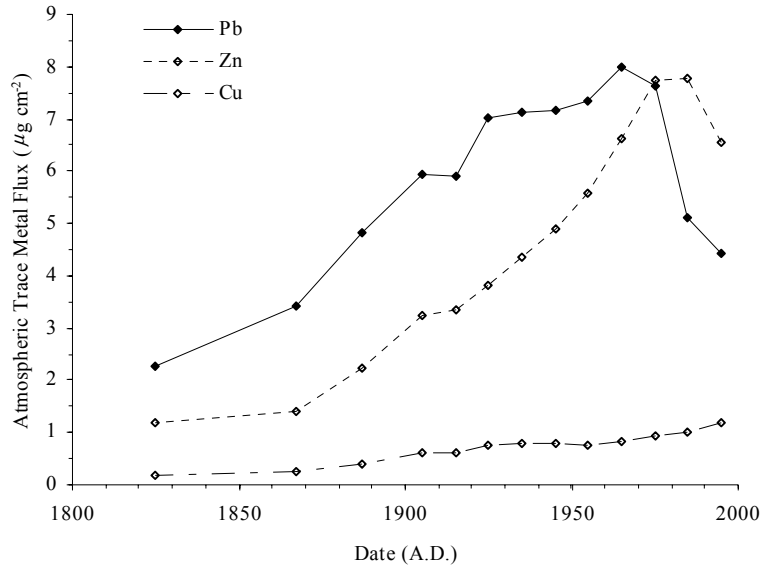


Fig. 9.2: Estimates of atmospheric fluxes to Blelham Tarn ($\mu\text{g cm}^{-2} \text{yr}^{-1}$) for the period 1825-1995.

9.4 Lead Isotopes as Source Indicators

A significant decline in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of excess lead during the 20th century is attributable to the introduction of ^{206}Pb depleted leaded petrol (Farmer *et al.*, 1997). It is possible to determine the quantity of lead derived from emissions from petrol burning relative to that from industrial emissions. Each lead ore deposit has its own characteristic isotopic composition which is fixed during mineral genesis. Lead produced by automobile exhaust ($^{206}\text{Pb}/^{207}\text{Pb} = 1.06\text{-}1.12$) is clearly different from lead coming from other anthropogenic ($^{206}\text{Pb}/^{207}\text{Pb} = 1.18\text{-}1.19$) and natural sources ($^{206}\text{Pb}/^{207}\text{Pb} = 1.20\text{-}1.30$) (Petit *et al.*, 1984).

9.4.1 Source Calculation

The percentage of petrol derived lead to the anthropogenic lead flux for each section of core is normally (Farmer *et al.*, 1996; Shotyk, 1995) calculated assuming an additive nature of lead isotope ratios, using the formula (Shirahata *et al.*, 1980):

$$Pb_{\text{Petrol}}(\%) = \frac{\left[\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}} \right)_{\text{Indus.}} - \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}} \right)_{\text{excess}} \right] \times 100}{\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}} \right)_{\text{Indus.}} - \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}} \right)_{\text{Petrol}}} \quad \text{eqn. 9.4}$$

In 1826, Australian lead was imported to England for the first time. From the middle of the 19th century onwards, the main share of lead used in England was derived from Australian ore (Day and Tylecote, 1991). The exact $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio of British sold petrol is unknown due to the variety of ores used in its production. Known lead isotope ratios for Australian ore and estimates for UK sold petrols are shown in Table 9.3.

Lead Isotopes in UK Petrol	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	Reference
<u>Component</u>				
Australian Ore	16.08	1.037	2.2396	Chow et al. (1975)
<u>Estimate</u>				
UK Petrol		1.07		Farmer et al. (1996)

Table 9.3: Isotope ratios in Australian ore and lead isotope ratio estimates for UK petrol.

Taking 1.17 ± 0.007 as an average (1836-1927) excess or anthropogenic signature and a $^{206}\text{Pb}/^{207}\text{Pb}$ signature of 1.07 to be the average $^{206}\text{Pb}/^{207}\text{Pb}$ value for UK petrol the Pb flux from petrol was calculated using equation 9.5 and the results used to derive an industrial flux (Fig. 9.3).

$$Pb_{\text{petrol}}(\%) = \frac{\left[(1.17 - ^{206}\text{Pb}/^{207}\text{Pb}_{\text{excess}}) \times 100 \right]}{(1.17 - 1.07)} \quad \text{eqn. 9.5}$$

The resulting plot shows that lead pollution from mining, smelting and other industrial practices has been around since the 1600's whilst the contributions from automobiles started in the early part of the 20th century and have been in continual decline since the 1980's. Statistics from the Department of Transport records of U.K. vehicle emissions show that emissions peaked in 1976 (Framer *et al.*, 1997), whereas the normalised sediment record shows the peak lead flux for the lake district to occur in 1969 and the peat record shows peak deposition to have occurred in 1972.

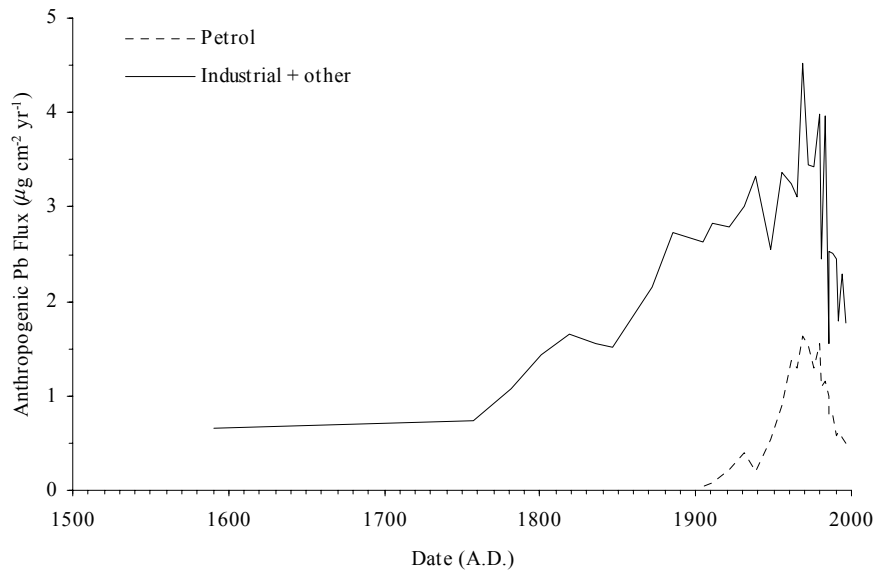


Fig. 9.3: Petrol and industrial derived Pb fluxes derived from Pb isotope ratio measurements.

The fine detail in these profiles is probably distorted. The low industrial flux of $2.55 \mu\text{g cm}^{-2}$ in 1948 (*i.e.* originating from a normalised Pb flux of $3.09 \mu\text{g cm}^{-2}$) is a direct result of the concentration of this core depth (171 mg kg^{-1}) being 12-18% less than the surrounding sections. The corresponding ^{210}Pb corrected BLTW 97/A 1945 Pb flux is $3.22 \mu\text{g cm}^{-2}$. Similarly the high industrial flux of 4.51

$\mu\text{g cm}^{-2}$ in 1969 (*i.e.* originating from a normalised Pb flux of $6.15 \mu\text{g cm}^{-2}$) is a direct result of this core depth concentration (161 mg kg^{-1}) being 12-15% more than sections either side. Whereas in 1969 the BLTW 97/A flux when normalised is $5.25 \mu\text{g cm}^{-2}$.