Chapter 8: Modelling Sediment Records of Atmospherically Deposited Contaminants

8.0 Modelling Sediment Records of Atmospherically Deposited Contaminants

The results given in Chapter 7 confirm that lake sediment cores may contain high quality records of atmospheric deposition. The qualitative validity of these records is demonstrated by the high level of consistency between dates calculated from ^{210}Pb and those determined using independent chronostratigraphic markers such as fallout ^{137}Cs and ^{241}Am. Transport processes following deposition on the catchment or in the lake can however create significant quantitative differences between atmospheric fluxes and supply rates to sediments.

Quantitative models that can be used to reconstruct atmospheric fluxes from sediment records are increasingly being demanded in programmes using sediment records as environmental archives, and also in studies of the environmental impact of atmospheric pollutants. The purpose of this chapter is to review a simple first-order model of transport processes in lake-catchment systems which will then be applied to Blelham Tarn using the data on atmospheric fluxes and sediment records.

Significant differences between atmospheric fluxes and their records in lake sediments may be due to:

(i) inputs from the catchment,
(ii) losses from the water column via the outflow, and
(iii) sediment focussing.

The main objective of simple first order models is to establish a framework for quantifying the first two of these processes. Redistribution over the bed of the lake by sediment focussing depends on detailed hydro-dynamical models of flow within the lake and its interaction with the bottom sediments and will not be considered in this thesis.

The basic elements of the model are relatively well known (*e.g.* Appleby and Smith, 1993) and are illustrated in a very simplified way in *Fig.* 8.1. A part of the atmospheric flux deposited on the catchment will be transported into the lake via runoff or erosion. Fallout entering the lake directly via atmospheric deposition or indirectly via transport from the catchment will eventually be lost from the lake via the outflow, or transported to the bed of the lake and incorporated in the sediment record.

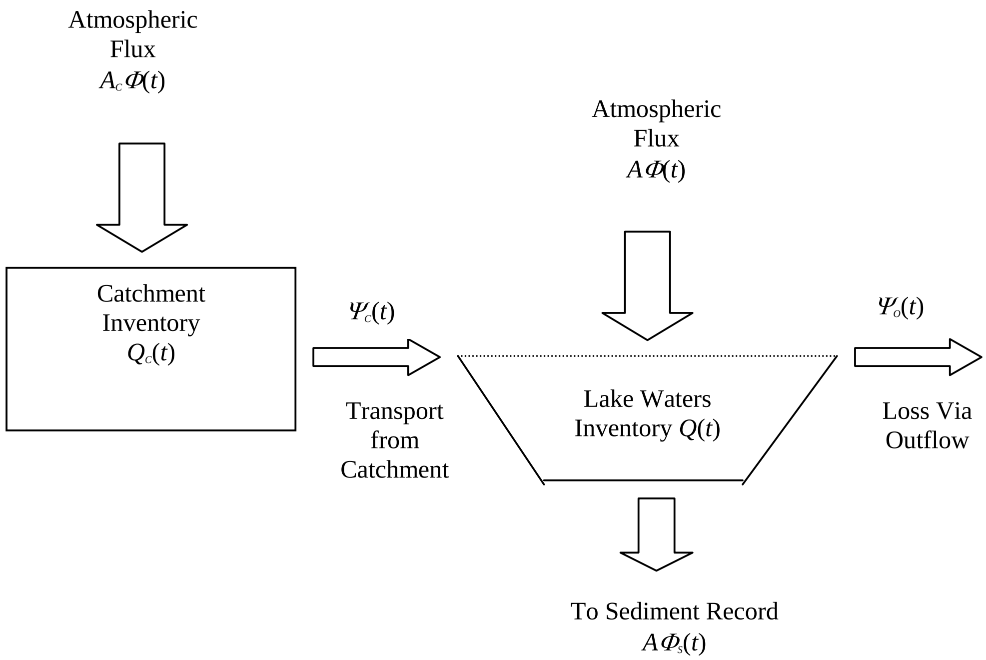

Fig. 8.1: Schematic diagram of the lake catchment model.

The supply of a pollutant to the sediments is immediately controlled by processes in the water column. Letting

$\Phi(t)$ = atmospheric flux (per unit area),

$\Psi_c(t)$ = transport rate from catchment,

$Q(t)$ = inventory stored in water column,

$\Psi_o(t)$ = loss rate via outflow,

$\Phi_s(t)$ = mean flux per unit area to sediments, and

the mass balance equation for the pollutant in the water column may be written

$$\dot{Q} = A\Phi + \Psi_C - A\Phi_S - \Psi_o - \lambda Q, \qquad \textit{eqn}.\ 8.1$$

where A is the lake area and (in the case of a radioactive substance) λ is the decay constant. For non-radioactive pollutants λ = 0. To make use of this equation to determine a relation between the atmospheric flux $\Phi(t)$ and the flux $\Phi_s(t)$ to the sediments we need a means for representing the catchment inputs Ψ_c(t) and outflow losses Ψ_o(t).

8.1. Catchment Transport

Soil zone or catchment modelling is significantly more difficult than water or air modelling since the physical and chemical dynamics are governed by external (out-compartmental) forces such as precipitation, whereas water and air modelling is governed by internal (in-compartmental) forces (Bonazounta *et al*., 1988). Regardless of the detailed processes, two useful parameters for characterising transport from the catchment are (Appleby and Smith, 1993):

(i) the *transport coefficient*

$$\kappa_C = \Psi_C / Q_C \qquad eqn.\ 8.2$$

relating the rate of transport Ψ_c to the catchment inventory Q_c; and

(ii) the *catchment/lake transfer function*

$$T\Phi = \Psi_C / A \qquad eqn.\ 8.3$$

expressing indirect inputs via the catchment as an augmentation of the direct atmospheric flux onto the lake surface. The total input can then be written

$$A(1+T)\Phi. \qquad eqn.\ 8.4$$

The reciprocal

$$T_C = 1/\kappa_C \qquad eqn.\ 8.5$$

is a measure of the residence time of pollutant in the catchment, though this will not be constant since the value of κ_c may be expected to be lower for older deposits which have penetrated further into the soil column making them less available for transport. This time dependence may be represented more precisely using the concept of a unit response function *h(t)*, defined as the transport rate (decay corrected in the case of radionuclides) due to a unit amount of fallout on the catchment. The transport rate due to an arbitrary fallout history can then be written

$$\Psi_C(t) = A_C \int_0^\infty \Phi(t-\tau)h(\tau)e^{-\lambda t}\,d\tau \qquad eqn.\ 8.6$$

where A_c is the catchment area. The catchment/lake transfer function is

$$\{T\Phi\}(t) = \alpha \int_0^\infty \Phi(t-\tau)h(\tau)e^{-\lambda t}\,d\tau \qquad eqn.\ 8.7$$

where $\alpha = A_c/A$ is the catchment/lake area ratio.

Precise determination of the response function is impractical. Representation is possible using an appropriate function, typically exponential, involving a small number of parameters to be estimated from experimental or theoretical considerations. From a palaeolimnological point of view the essential parameters are:

(i) the ultimate fraction transferred to the lake,

$$\eta = \int_0^\infty h(\tau)\,d\tau, \qquad eqn.\ 8.8$$

(ii) the time-scale over which this occurs.

8.1.1 ^{210}Pb

Steady state transport of radionuclides with a constant atmospheric flux $\Phi = P_a$ (*e.g.* ^{210}Pb) is characterised by just a single parameter. The transport rate in this case is the product of the area of the catchment, the atmospheric flux, and the percentage transferred from the catchment. It can be written

$$\Psi_C(t) = A_C \eta_S P_a \qquad eqn.\ 8.9$$

where

$$\eta_S = \int_0^\infty h(\tau) e^{-\lambda t}\, d\tau \qquad eqn.\ 8.10$$

is the decay-weighted area under the unit-response function. There is thus a constant transfer function

$$T\Phi = \alpha \eta_S P_a. \qquad eqn.\ 8.11$$

The balance equation for the catchment is

$$\dot{Q}_C = A_C P_a - \Psi_C - \lambda Q \qquad eqn.\ 8.12$$

and an equilibrium state is reached in which

$$A_C P_a - \Psi_C - \lambda Q = 0. \qquad eqn.\ 8.13$$

Since we also have

$$\Psi_C = A_C \eta_s P_a \qquad eqn.\ 8.14$$

eliminating P_a between these two equations leads an expression for the transport coefficient κ_C

$$\kappa_C = \frac{\lambda \eta_S}{1 - \eta_S}. \qquad eqn.\ 8.15$$

The parameter η_S represents the fraction of the annual fallout onto the catchment that is delivered to the lake.

The expression for the total input of radionuclide with a constant flux P_a to the lake is therefore:

$$A(1 + \alpha \eta_s) P_{a.} \qquad eqn.\ 8.16$$

8.1.2 Trace Metals

For trace metals with an atmospheric flux $F_a(t)$ the balance equation for the atmospherically derived component in the catchment is

$$\dot{Q}_C = A_C F_a - \Psi_C \qquad \textit{eqn}. \ 8.17$$

Assuming an exponential response function

$$h(t) = \eta k \, \mathrm{e}^{-kt} \qquad \textit{eqn}. \ 8.18$$

the transport rate can be written

$$\Psi_C = A_C \int_0^\infty F_a(t-\tau)\eta k \, \mathrm{e}^{-k\tau} \mathrm{d}\,\tau = A_C \eta k \, \mathrm{L}\{F_a(t-\tau)\} \qquad \textit{eqn}. \ 8.19$$

where

$$\mathrm{L}\{\Phi(t-\tau)\} = \int_0^\infty F_a(t-\tau)\mathrm{e}^{-k\tau}\mathrm{d}\,\tau \qquad \textit{eqn}. \ 8.20$$

is the Laplace transform of the atmospheric flux. Assuming for simplicity a long term exponential increase

$$F_a(t-\tau) = F_a(t)\,\mathrm{e}^{-\xi\tau}, \qquad \textit{eqn}. \ 8.21$$

where ξ is determined by fitting an exponential function to the best estimate of the long term history of Pb deposition, the rate of transport to the catchment can be written

$$\Psi_C(t) = A_C F_a(t)\frac{\eta k}{k+\xi}. \qquad \textit{eqn}. \ 8.22$$

Although this model will not adequately represent recent changes since many atmospherically delivered pollutants have a long residence time in the catchment, it may be useful in estimating the impact of long-term inputs. Since trace metals will also have an erosive input via the mineral content of the soils, denoted by Ψ_e, the total input to the lake can be written

$$AF_a(t)\left(1+\frac{\alpha\eta k}{k+\xi}\right)+\Psi_e(t). \qquad \textit{eqn}. \ 8.23$$

(NB: There is an erosive input of ^{210}Pb though since it is easily identified via the supported component (^{226}Ra) it is usually omitted from the modelling).

8.2 Transport Through the Water Column

The following is a review of a transport model originally published in Appleby (1997). Pollutant transport through the water column is dependent on the relative proportion of the species of metal bound to settling particles (often termed suspended solids) to that which remains in the soluble form (Jenne, 1977). The ratio of the concentration of particulate bound to soluble phase ions is commonly characterised by:

(i) the *distribution coefficient*

$$K_D = C_S / C_W \qquad eqn.\ 8.24$$

where C_w = the soluble concentration per unit volume in lake water and C_s = the concentration per unit mass on suspended solids (Evans, 1989; Smith, 1993), or

(ii) the *partition fraction*

$$f_D = sC_S / C = \frac{1}{1+(sK_D)^{-1}} \qquad eqn.\ 8.25$$

characterising the fraction of species on particulates, where *s* is the suspended solids concentration and *C* is the mean concentration in the water column, defined by Q/V where *V* is the volume.

Assuming that pollutant concentrations at the outflow are close to the mean value for the lake, losses from the lake via the outflow may be written

$$\Psi_O = Q / T_W \qquad eqn.\ 8.26$$

where T_w is the lake water residence time. Assuming losses to the bottom sediments are controlled largely by the process of sedimentation, and that diffusion is negligible, the flux to the bottom sediments may be written

$$A\Phi_S = \frac{f_D Q}{T_S} \qquad eqn.\ 8.27$$

where T_s is a typical settling time for suspended particles. To a first approximation

$$T_S = d / \upsilon \qquad eqn.\ 8.28$$

where *d* is the mean water depth and *v* is the mean settling velocity.

Substituting the above expressions into the mass balance equation gives

$$\frac{dC}{dt} + kC = \frac{1}{d}(1+T)\Phi \qquad eqn.\ 8.29$$

where

$$k = \frac{f_D}{T_S} + \frac{1}{T_W} + \lambda = \frac{1}{T_L} + \lambda, \qquad eqn.\ 8.30$$

and T_L is a residence time of the pollutant in the water column, defined by

$$\frac{1}{T_L} = \frac{f_D}{T_S} + \frac{1}{T_W}. \qquad eqn.\ 8.31$$

8.2.1 Solutions for C

Radionuclides such as ^{210}Pb with constant flux P_a can be regarded as being in a steady state, the equilibrium concentration is

$$C_{equ} = \frac{1}{d} T_L (1 + \alpha\eta_s) P_a. \qquad eqn.\ 8.32$$

For trace metals, since the residence time in the water column will usually be small (weeks) compared to the time-scale of changes in the atmospheric flux (years), neglecting short time-scale fluctuations the water column may be assumed to be in quasi-equilibrium with inputs, so that

$$C = T_L \frac{1}{d}\left(1 + \frac{\alpha\eta k}{k + \xi}\right) F_a(t). \qquad eqn.\ 8.33$$

This term only includes the atmospherically derived (exchangeable) component. Assuming that the minerogenic component on eroded particles from the catchment is not exchangeable, there will be an additional component

$$C_e = T_e \frac{1}{V} \Psi_e(t) \qquad eqn.\ 8.34$$

where T_e is a residence time for the non-exchangeable (particulate bound) erosive component, given by

$$\frac{1}{T_e} = \frac{1}{T_S} + \frac{1}{T_W}. \qquad eqn.\ 8.35$$

(*i.e.* $f_D = 1$).

8.3 Water Column to Bottom Sediment Transfer

Precise time dependent and concentration solutions to the mass balance equation are irrelevant to paleolimnological studies. Except on time-scales comparable to the residence time T_L the flux to the sediments can be estimated from the residence times alone. Losses to the bottom sediments and via the outflow are in the ratio

$$\frac{A\Phi_S}{\Psi_O} = \frac{f_D T_L}{T_S}. \qquad eqn.\ 8.36$$

Hence the fraction of any input ultimately transferred to the sediments is

$$\mathcal{F} = \frac{f_D T_L}{T_S}. \qquad eqn.\ 8.37$$

On this quasi-equilibrium time-scale the flux to the sediments is equal to the fraction transferred to the sediments multiplied by the total input to the lake

$$\Phi_s = \mathcal{F}\ (1+T)\Phi. \qquad eqn.\ 8.38$$

Assuming all water falling on the catchment passes through the lake, the approximate formula,

$$T_W = \frac{d}{R(1+\alpha)} \qquad eqn.\ 8.39$$

for the water residence time, where R is the mean annual rainfall, we obtain the approximate equation for the transfer fraction

$$\mathcal{F} = \frac{f_D}{f_D + \frac{R}{\nu}(1+\alpha)}. \qquad eqn.\ 8.40$$

8.3.1 Flux to the Sediments

The mean flux of unsupported (atmospherically supplied) ^{210}Pb to the sediments is

$$P_s = \mathcal{F}_{Pb\text{-}210}\,(1+\alpha\eta_{Pb\text{-}210})P_a. \qquad eqn.\ 8.41$$

For trace metals or contaminants with a variable flux it is

$$F_s = \mathcal{F}\left(1+\frac{\alpha\eta k}{k+\xi}\right)F_a(t) + F_e\Psi_e(t). \qquad eqn.\ 8.42$$

F_e corresponds to $f_D = 1$. Where the trace metal is soluble and there is a weak atmospheric signal, the result could be a damping of the atmospheric signal compared to the minerogenic supply.