

## Seasonal transformations and movements of iron in a productive English lake with deep-water anoxia

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### ABSTRACT

The seasonal and depth distributions of the concentrations of total and soluble iron in a seasonally anoxic lake basin are described for two years. Transport of iron is related to hydrodynamics and fluxes of iron both within and to and from the lake are calculated. The results enabled the construction of a schematic model for iron movement; it is critically dependent upon the many rate processes involved.

### CONTENTS

1. Introduction .....	196
2. Methods .....	197
3. Results .....	199
3.1 Stratification cycle .....	199
3.2 Depth-time distribution of iron .....	201
3.3 Budgets of iron within the lake .....	207
3.4 Budgets of iron to and from the lake .....	209
3.5 Calculation of fluxes .....	213
4. Discussion .....	217
5. Summary .....	220
References .....	222

### 1. Introduction

It is well established, at least in grosser features [19], that extensive transformations of iron occur in lakes subject to deep-water anoxia. Insight into the nature and control of these processes has developed from a combination of the relevant chemistry (e.g. Stumm and Lee [39] and Stumm and Morgan [40]) with studies of natural patterns of distribution in time and depth [19, 23], supplemented by artificial model systems. Pre-eminent amongst such studies is that of Mortimer [28, 29], based largely upon field observations during 1939–40 of a small productive lake – Esthwaite Water – in Northwest England. The present work, based on the same lake, attempts a finer resolution of events in the depth-time continuum, a quantitative consideration of individual rate processes which govern the observed distributions of

iron forms, and budgets of gains and losses of iron to the water column, or its component strata.

Mortimer's studies [28, 29, 31] provided a valuable link between the iron cycle and other related seasonal conditions in the lake, especially indices of redox conditions and processes of sediment-water exchange. Early in the summer season, before complete anoxia had developed above the sediment, there was an increase in the concentration of total iron, but not of ferrous iron, in these bottom waters. He attributed this to an increased rate of diffusion of ferrous iron from the sediment and its oxidation to ferric hydroxide at higher levels in the water. When oxygen disappeared from the bottom waters free ferrous iron appeared and, as summer proceeded, made up a progressively increasing part of the iron in the hypolimnion. A turbidity maximum was observed in the upper hypolimnion and attributed to freshly oxidised ferrous iron, although the possibility of it being due to phytoplankton was not excluded. Mortimer reported that the restoration of dissolved oxygen to deep water in the autumn effected a rapid oxidation and precipitation of iron, most of which was deposited on the mud surface. Nevertheless the iron concentration in the whole lake remained relatively high during the early part of the winter, and was attributed to suspension by wind-driven circulation – a view supported by the rapid decrease in total iron concentration when ice formed on the lake. Although Mortimer believed that ferrous sulphide formation might be possible near the sediment-water interface, he was unable to measure sulphide quantitatively. He did, however, report a smell of sulphide from the bottom waters in August and September, and a black cloudiness due to colloidal ferrous sulphide in the lower hypolimnion during the latter month.

Since this pioneering work, much published and unpublished information pertaining to chemical cycles in the lake is available [11, 12, 27, 35, 41]. The sampling, analysis and distribution of iron has received special attention in recent years [4, 5, 8, 9]. This paper considers events in 1977–78, separated from Mortimer's observations by 37 years of marked cultural change and eutrophication [25]. Interesting comparisons can therefore be made, and some newer aspects – related to recent techniques and interpretations – developed.

The lake (fig. 1) has a surface area of 1.0 km<sup>2</sup>, maximum depth 15.5 m, mean depth 6.4 m, volume  $6.44 \times 10^6$  m<sup>3</sup> [36] and a mean retention time of 13 weeks. It is divided into two main basins, labelled A and B (fig. 1), separated by a ridge at a depth of ca. 9 m. The main inflow, Black Beck, enters at a shallow northern bay; as all other inflows are small streams, Black Beck probably accounts for ca. 50% of the total water supply to the lake. The summer stratification extends from April or May to October, during which an anoxic hypolimnion develops. Periods of inverse stratification and partial ice cover occur in most winters but rarely last longer than a few weeks.

## 2. Methods

All water samples, and measurements *in situ*, were taken at a buoyed station (close to that used by Mortimer [28]) in the deepest part of the larger north basin, A, of the lake (fig. 1).

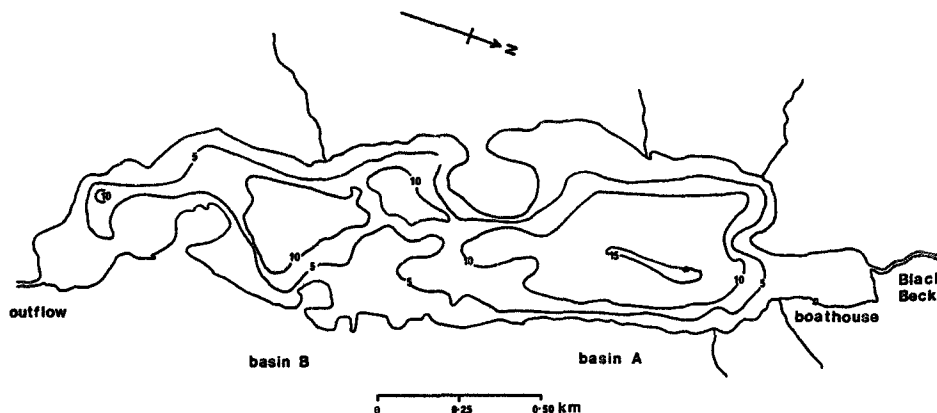


Figure 1. Map of Esthwaite Water with sampling position (●) and basins A and B indicated.

Water temperature and dissolved oxygen were measured in situ using an oxygen electrode with incorporated thermistor [26]. The day to day repeatability was respectively  $\pm 0.05^\circ\text{C}$  and  $\pm 5\%$ . Continuous temperature-depth profiles were also obtained using a lowered thermistor with suitable bridge circuit, potential source, depth sensor and x-y (Servoscribe M) recorder.

Wind speed and direction were recorded continuously; wind speeds were obtained from an anemometer at the lake boathouse (fig.1) and direction from another system situated about 100 m from the eastern shore, as described by Heaney and Talling [15]. Rainfall was measured daily at the same site, using a standard U.K. Meteorological Office gauge. Solar radiation was measured as daily totals at the Windermere Laboratory, about 4 km from the lake, by a Kipp CM6 thermopile solarimeter with integrator.

Vertical profiles of horizontal beam attenuation were obtained from a Schenk transparency meter or 'transmissometer' of the Sauberer [37] pattern, with output taken through a logarithmic converter and recorded in units of attenuation increment,  $\Delta \log(I_0/I)$ , relative to air on a small potentiometric, Servoscribe M, x-y recorder. The instrument effectively measured the attenuation of a collimated light beam by a fixed path length (0.5 m) of water. To it was attached a pressure transducer (Bell & Howell, Type 4-366) and the twin outputs indicating attenuation and depth were continuously plotted as the assembly was slowly lowered (ca.  $5\text{--}10\text{ m min}^{-1}$ ) through the water column. Fuller details will be given by Talling (in prep.).

Water samples were collected at 1-m intervals by a peristaltic pump coupled to tubing lowered to the appropriate depth [5, 7]. All samples were collected into ca. 130 ml borosilicate stoppered bottles. Filtered samples were obtained directly in the field by pumping water through a 47 mm 'Swin Lok' filterholder (Nuclepore) bearing a Whatman GF/F glass-fibre filter, placed in a side-tube close to the main pump outlet. Since the water had come directly from the measured depth without contact with air, anoxic samples were filtered before appreciable change in their chemical composition could occur. The GF/F filter removes 98% of particles of

nominal 0.7  $\mu\text{m}$  size. Kennedy et al. [22], Byrne and Kester [2] and the present results have shown that the 'soluble' fraction so obtained can have a significant proportion of colloidal iron particles.

The digestion method described by Davison and Rigg [9] was used to measure the total iron in water samples and in the filtered samples. These measurements will be described hereafter as 'total iron' and 'filtered iron' respectively. Ferrous iron was measured by polarography, as described by Davison [4]. This provides unambiguous measurements of ferrous iron, and for these waters has been shown to be a measure of the aquated ferrous ion [6, 8].

Integrated water samples were taken from the 0–5 m layer by use of a vertical plastic tube of the type described by Lund [24]. Only determinations of total iron were performed on these samples.

### 3. Results

#### 3.1 *Stratification cycle*

The distinctive features of thermal stratification during 1977 and 1978 (fig.2) are as follows. From late June to late August a more stable stratification developed in 1977 than in 1978 and the hypolimnion was more effectively isolated from the waters above. This is illustrated by the near-horizontal isotherms for that time, whereas for 1978 the downward progression of the isotherms indicates a steady influx of warmer water into the lower layers. For the same period the surface temperatures were significantly higher in 1977. The breakdown of thermal stability in 1978 was a progressive process as the upper mixed layer successively penetrated to deeper waters; in 1977, however, it centred upon two major mixing events, one in late August and the other, after a period of relative stability, in late September.

These events are influenced by variations in wind velocity and solar radiation income which are shown as weekly means of daily integrals in figure 3. From June to mid-August the solar radiation was consistently higher in 1977 than in 1978, especially in early August, and probably accounts for the higher surface temperatures in 1977. Over the same period the wind data shows no consistent trend, even when wind direction and maximal velocities (not illustrated) are also considered. Thus the greater isolation of the hypolimnion in 1977 (fig.2) is probably due to greater epilimnetic heating (and density differentials) rather than differences in wind stress. After mid-August the solar radiation was similar in both years, but for the three successive weeks in 1977 the lake was subjected to a higher wind stress. This produced the pronounced mixing at that time. Then, after a period of calm, very strong winds in late September resulted in complete vertical mixing. By contrast, in 1978 there were consistent moderate winds from early September onwards, which contributed to the progressive increase in the wind-mixed layer and a more gradual approach to isothermal conditions by the end of October. The processes governing energy income and energy redistribution are not independent, but for a given period of time one is likely to be the dominant factor determining hypolimnetic stability. Later in the season heat loss by back-radiation and convec-

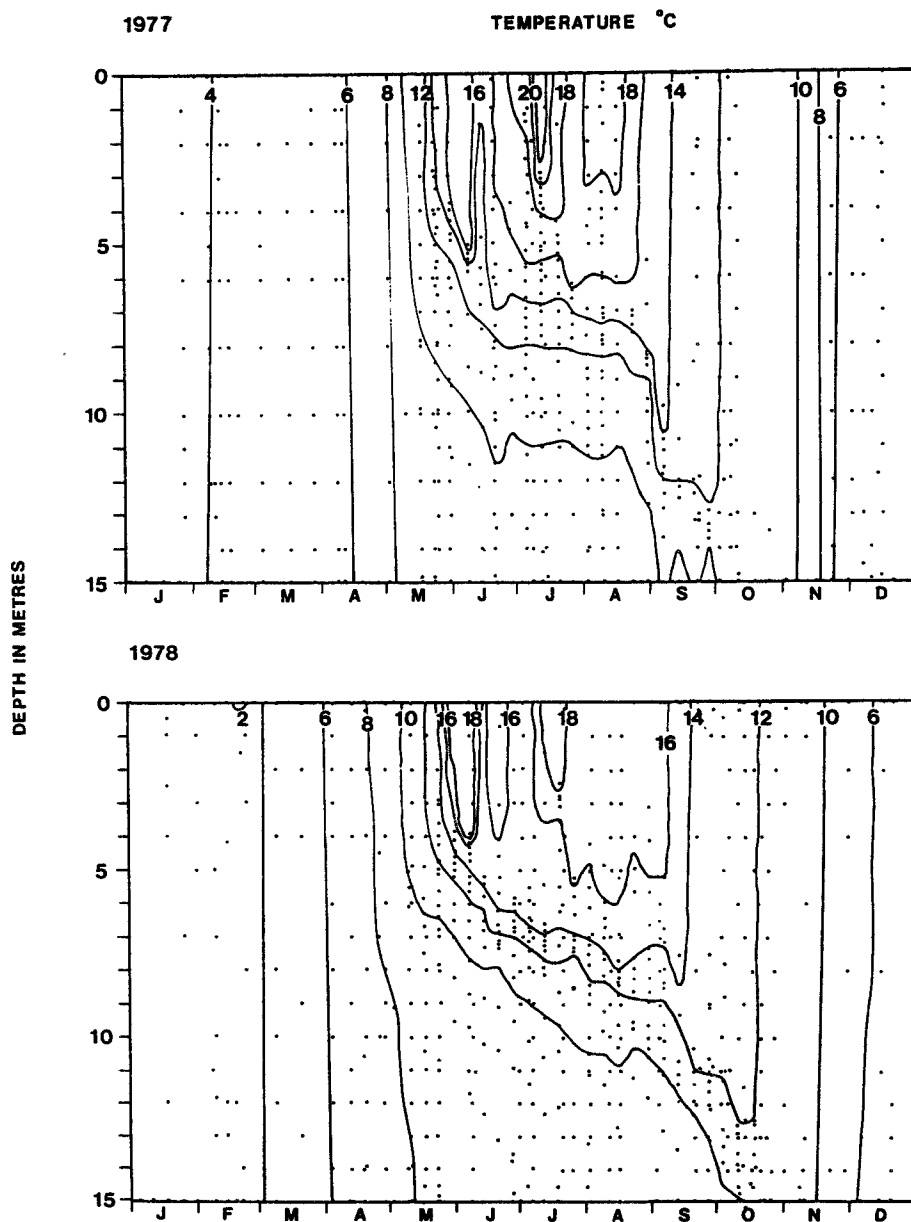


Figure 2. The depth-time distribution of temperature (isotherms in °C) during 1977 and 1978.

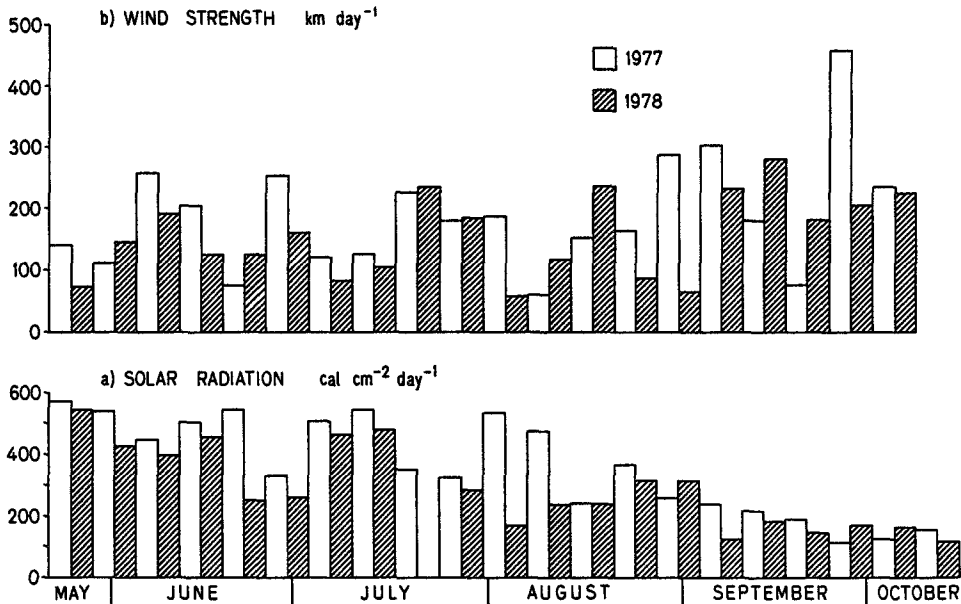


Figure 3. Weekly means, expressed as paired histograms for 1977 (open) and 1978 (solid), of (a) solar radiation ( $\text{cal cm}^{-2} \text{ day}^{-1}$ ) and (b) wind strength ( $\text{km day}^{-1}$ ).

tive cooling may enhance, or possibly even replace, the destabilizing effects of wind. However this effect was not pronounced for the two years considered here.

The depth-time distribution of dissolved oxygen (fig. 4) further reflects the stability of the lake. In 1977 complete deoxygenation ( $<10 \mu\text{moles l}^{-1}$ ) was found at the bottom of the lake by late June, and in early August the lake was deoxygenated to within 7 m of the surface. At the end of August appreciable oxygen extended to 12 m depth, and after temporary restabilization the lake became completely oxygenated by the end of September. In 1978 anoxic conditions were detected in late July. The lake then rapidly deoxygenated up to 7 m depth, and thereafter the anoxic zone gradually decreased until the end of October, by which time oxygen had penetrated to all depths. Although other factors exist, the limited upward extension of anoxia in 1978 is probably related to the less isolated nature of the hypolimnion in that year.

### 3.2 Depth-time distribution of iron

Depth profiles of total and filtered iron for the period 24 July 1978 to 27 October 1978 are shown in figure 5. Some polarographic measurements of ferrous iron are also included. The limit of the upper mixed layer was taken as the depth at which the temperature was  $0.5^\circ\text{C}$  lower than at 1 m depth. Near-surface (e.g. diurnal) heating during periods of complete calm does not greatly influence this measurement. This measure of mixed depth, and the depth zone in which oxygen is

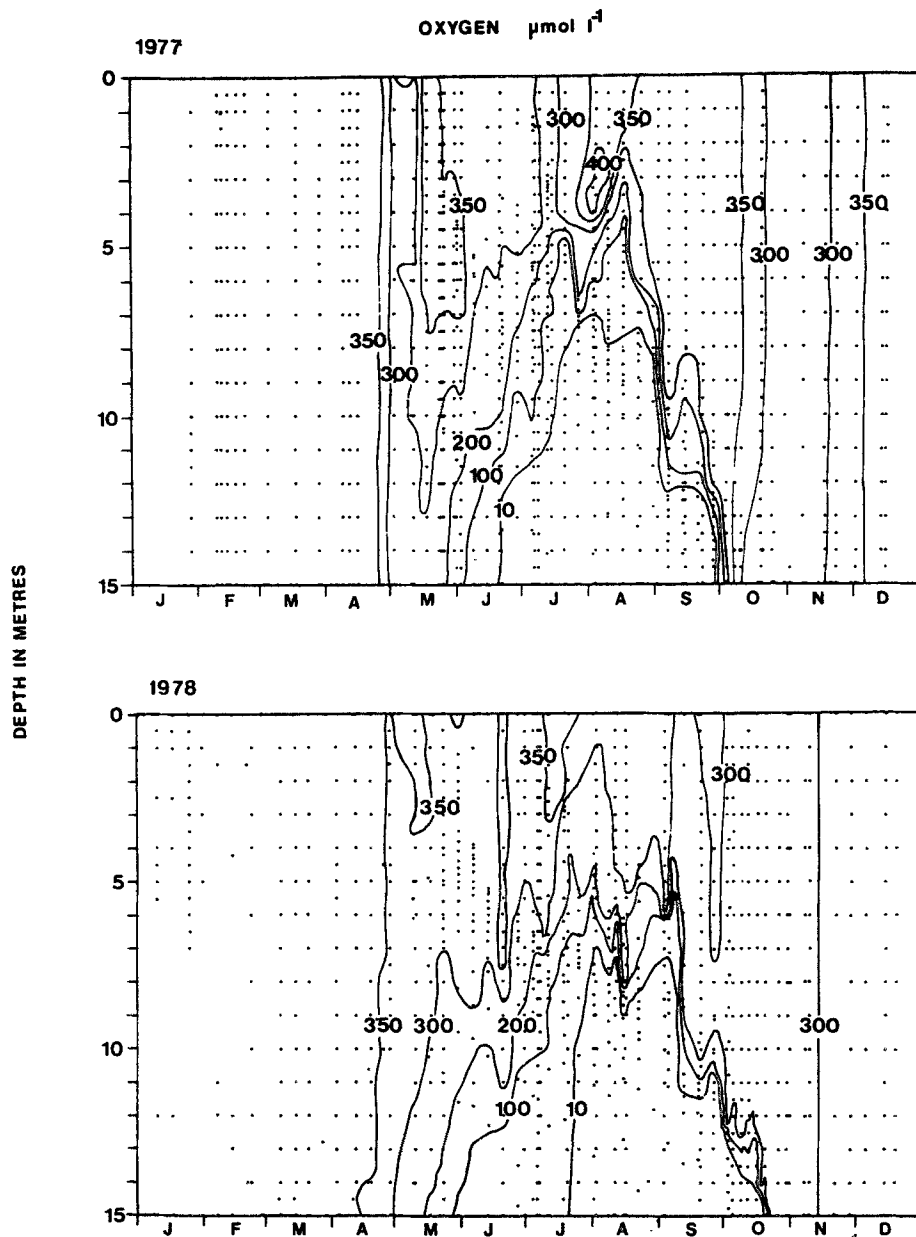


Figure 4. The depth-time distribution of dissolved oxygen (isopleths in  $\mu\text{moles l}^{-1}$ ) during 1977 and 1978.

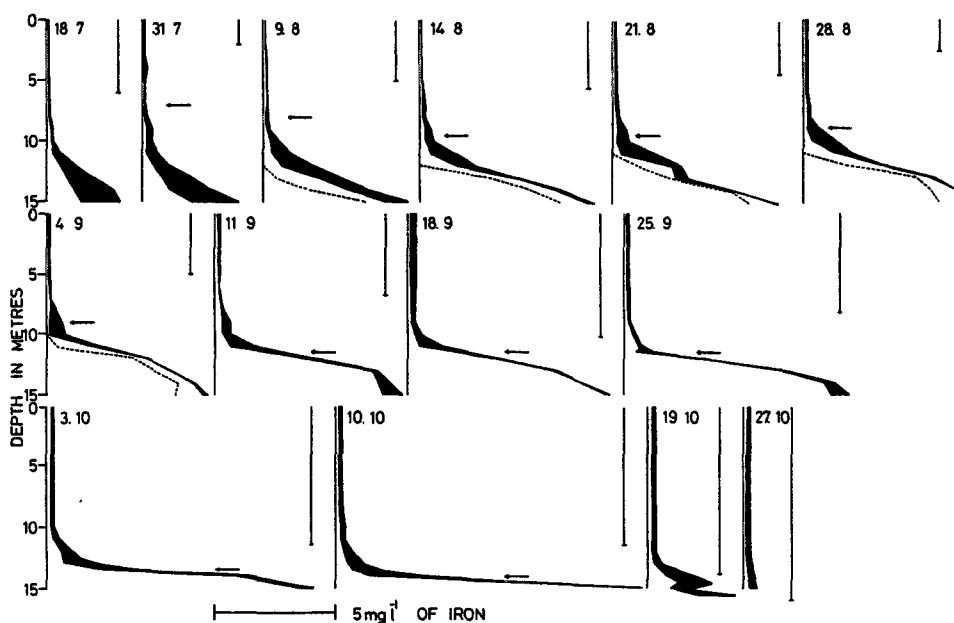


Figure 5. Concentration-depth profiles of iron fractions measured throughout the summer of 1978. Total iron is shown as the upper line of the solid region and filtered iron as the lower line; particulate iron, as the difference between these two measurements, is indicated by the solid area and ---- indicates polarographically determined iron. The wind-mixed depth,  $\perp$ , and the oxic/anoxic boundary,  $\leftarrow$ , are shown.

$<10 \mu\text{moles l}^{-1}$ , are indicated in figure 5. The earlier profiles show a considerable particulate component of iron in the deepest water. Although this is later gradually reduced, a particulate component is observed throughout the summer near the oxic/anoxic boundary.

The formation of such iron profiles has been explained by Mortimer [28], as outlined in the introduction. He attributed the increased ferric component which appears prior to complete deoxygenation of the bottom waters to an increased rate of diffusion of ferrous iron from the sediment and its oxidation to ferric hydroxide at higher levels in the water. Our explanation puts greater emphasis on the position of the oxic/anoxic boundary. This, during the summer, effectively moves from the sediment, into the water column and then back into the sediment in the autumn. The highly organic sediment of the lake is strongly reduced except, during ice-free winter months, for the uppermost cm layer which is in contact with the oxygenated waters above and which may also reflect mechanical disturbance [11]. Early in the year, as the lake warms up and begins to stratify, the rate of transport of oxygen to the sediment decreases and so the oxidized layer of sediment becomes thinner as oxygen consumption in the sediment continues. Eventually the oxic/anoxic boundary extends to the overlying water and the whole of the sediment becomes reduced. Once a microlayer of anoxic water, overlain by oxic water, exists above the



sediment, ferrous iron diffuses through the anoxic layer and becomes oxidized when it reaches the oxic boundary. The particles of ferric iron so formed are then subject to lake transport processes and may either be mixed upwards by eddy diffusion or sink to the sediment. Therefore there is likely to be a considerable flux of particulate iron into the bottom water before such water becomes anoxic and contains measurable ferrous iron. When anoxic conditions develop in the bottom waters, ferrous iron is transported through this water and is precipitated as a particulate ferric oxy/hydroxide at the oxygen boundary. Hence a particulate ferric layer always exists in the lake, although it is in the sediment during winter and in the water column during summer.

The polarographic measurements of ferrous iron (fig.5) support this interpretation. On 24 July no measurable concentration was found in the water column, and on 31 July ferrous iron appeared only over the sediments at 15 m. Therefore the appreciable concentrations of filtered iron above 15 m were probably due to freshly oxidized colloidal iron which was being rapidly recycled. As the season progressed

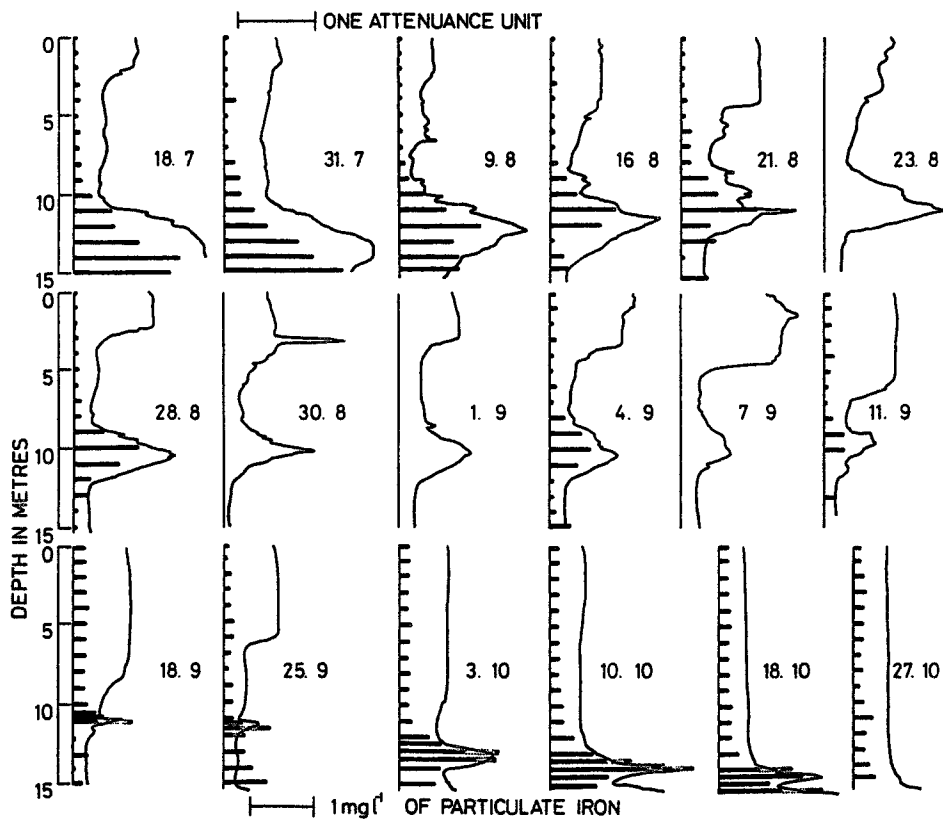


Figure 6. Attenuance-depth profiles measured in situ and particulate iron concentrations, during 1978. The indicated unit of attenuance,  $\log I_0/I$ , is convertible to a beam attenuance coefficient in  $\text{m}^{-1}$  (as used by Heaney and Talling [15]) by multiplication by the factor 4.6.

the difference between the measurements of filtered iron and ferrous iron decreased, because ferrous iron then dominated in the anoxic waters and the particulate component became less important, except near the oxic/anoxic boundary.

In 1939, Mortimer [28] found the first measurable ferrous iron on 27 July. This agrees well with the timing in 1978 and indicates that at least some hypolimnetic processes have changed little after 39 years.

The layer of particulate iron has been followed in more detail by measurements in situ of turbidity. Continuous records of beam attenuation versus depth were obtained during 1978 (fig. 6) in parallel with iron analyses. The differences between total and filtered iron concentrations, measured on the same days and at the same depths, correspond to the particulate iron component; it correlates well with the attenuation peak which develops in the hypolimnion. The increased attenuation near the surface of the lake has been shown to be due to phytoplankton [15]. No appreciable algal population exists in the hypolimnion and a minimum of attenuation, which moves with the position of the thermocline, is always observed between that due to the phytoplankton and particulate iron. Figure 7 shows an excellent relationship between the deep attenuation and the differences between total iron and polarographic iron when measurements were made at finer intervals of 0.25 m. Because the distribution of iron particle size cannot be assumed to be constant, no attempt was made to calibrate attenuation increment against concentration of particulate iron.

During 1977 a longer series of attenuation profiles was obtained (fig. 8), recorded at various sensitivities to show maximum detail. They indicate how particulate iron accumulates in deep water before anoxic conditions are established there. Soon after the oxic/anoxic boundary has moved into the bottom waters some reduction in the near-bottom attenuation occurs. The overlying peak of attenuation progresses up the

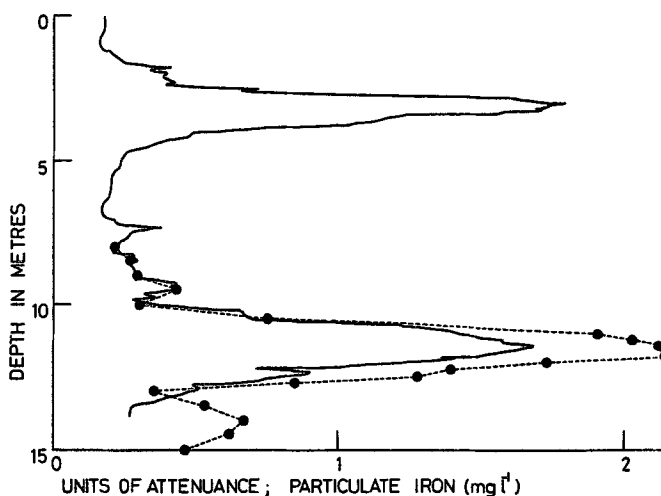


Figure 7. Attenuance-depth profile (—) measured in situ for 11 August 1977 and the difference between total iron and polarographically measured iron (●).

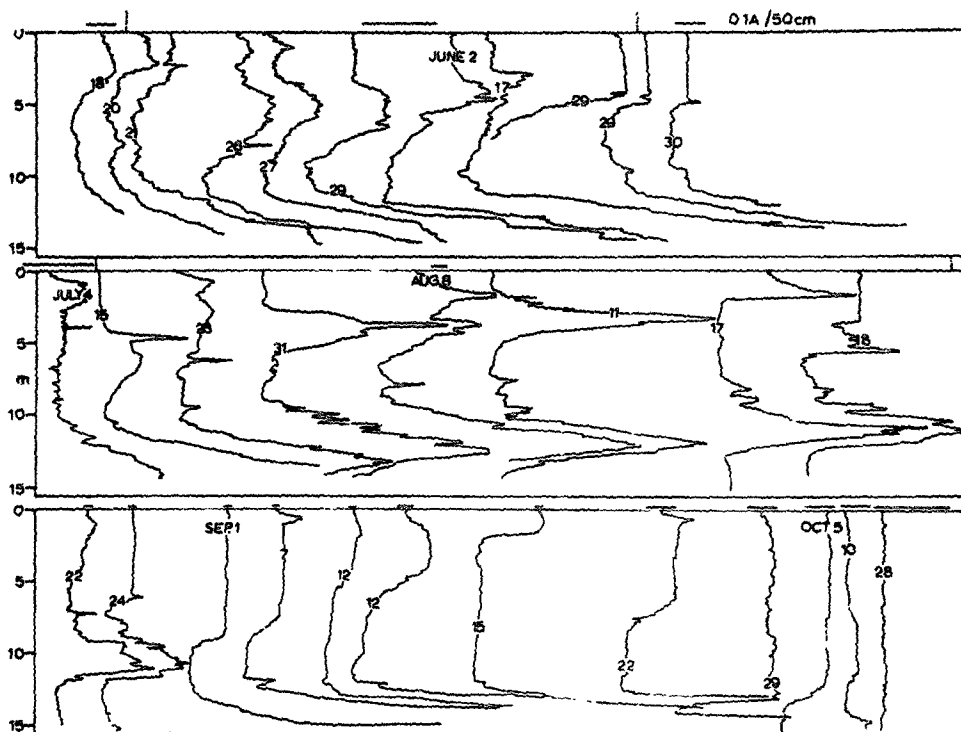


Figure 8. Attenuance-depth profiles measured in situ during 1977. Use of different sensitivities is indicated by scale bars of 0.1 attenuation unit (A) per 50 cm light path. Successive profiles are displaced, by arbitrary intervals, to the right.

water column and is at first fairly symmetrical. However, during the period of high thermal stability through July and August (fig.2 and 4) the bottom of the peak becomes more sharply defined, and a sharp boundary between the particulate and reduced phase develops.

One factor here is the presence of sulphide. When Davison and Heaney [8] assessed the solubility of ferrous sulphide in the lake during 1977, they calculated that on 24 August the lake water was saturated with respect to ferrous sulphide at depths below 13 m. It is possible that the ferrous sulphide and ferric hydroxide particles interact and increase their mutual rates of sinking. More probably, under these extreme reducing conditions - enhanced by the presence of sulphide - ferric hydroxide is rapidly reduced, and so any particles sinking into the bottom layer are consumed by the reaction  $\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$ . Moreover, Jones (unpublished results) has shown that there is an abundant bacterial population, immediately below the peak of particulate iron, and that these bacteria may be involved in iron transformations [21]. In general terms, the shape of the upper half of the attenuation maximum is determined by mixing processes, and that of the lower half by sinking of particulates prone to reduction and solubilization.

In 1978 anoxic conditions never developed to the same extent and the evidence for rapid reduction of sedimenting particles was not found. When more strongly reducing hypolimnetic conditions – indicated by presence of ferrous sulphide – have been prevalent in other years (e.g. 1975, 1976), a similar asymmetric peak with a very sharp lower edge has been observed.

Profiles measured in 1977 after 22 August (fig. 8) show an additional increase in attenuation below the peak due to particulate iron. This increased turbidity was caused by the precipitation of ferrous sulphide [8]. In 1978 such precipitation was not evident until much later in the year and then only near the sediment. It appears that the lesser stability of stratification due to reduced solar heating, compared with 1977, resulted in a fundamental difference of chemical events in the ostensibly isolated hypolimnion. The annual pattern of chemical changes in the hypolimnion of such a lake cannot be regarded as constant.

The simultaneous presence of particulate ferric hydroxide and ferrous sulphide in the lake water can be observed directly. When equal volumes of water collected from 1-m depth intervals were filtered (anoxically where appropriate) a striking gradation of filter colour was produced. As an example consider the attenuation profile for 24 August 1977 (fig. 8). The filter deposits from 0 to 4 m depth were distinctly brown due to the abundant dinoflagellate *Ceratium hirundinella* O.F. Müller which has dominated the late summer plankton in recent years [15]. The filters for 5–8 m were almost colourless, and then for 9–12 m a gradation in red to brown colours was observed with maximal intensity at 12 m. At 13 m the filter was again faintly coloured, but the filters then increased in blackness with depth. Thus the measured profiles of attenuation are in agreement with a qualitative assessment of colour.

### 3.3 Budgets of iron within the lake

In figure 9 the volumes of successive strata of water (0–0.5, 0.5–1.5, 1.5–2.5 ... 14.5–15.5 m) have been used to calculate the quantity of iron in kg in each layer of the lake. Although the lake has two distinct basins, they are linked at depths less than 10 m and, because the movement of iron throughout the whole lake was being considered, volumes for the combined basins were used. The resultant quantities of iron are plotted against time. Thus the high concentrations observed in the relatively small hypolimnetic volumes are realistically weighted in comparison with the low concentrations in the much larger epilimnetic volumes.

From July to August the iron content increases in the lowest strata as ferrous iron is released from the sediment and mixed into the overlying waters. The 9.5–13.5-m region of the lake experiences the largest increase in iron by weight, favoured by the balance between the concentration-depth profile and lake morphometry. At the end of August, when the upper mixed layer extends to greater depths, there is a consequent removal of iron from the 9.5–10.5-m stratum. Therefore the iron content for this stratum then reaches a maximum, followed by a progressive reduction due to the predominance of losses by mixing and sedimentation. The contents of lower strata also develop maxima, but at successively later times in the year, as the upper mixed layer (fig. 9) gradually enlarges. Coincident with the removal of iron from

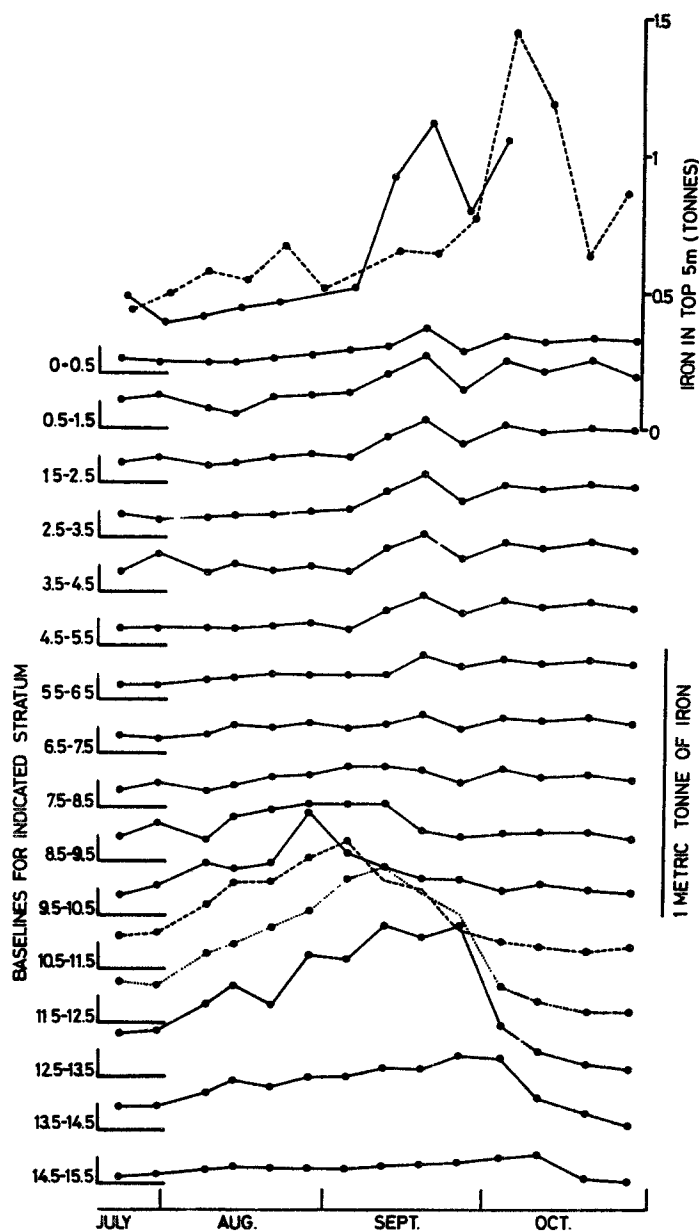


Figure 9. The seasonal dependence for 1978 of the total iron (tons) in each 1-m stratum of the lake; note each stratum has a different baseline. The 0-5-m data for 1977 (----) and 1978 (—) are also plotted above.

the lower strata, there is an increase in the upper strata. As the concentration is homogeneous from wind mixing, a similar increase is observed at all depths less than 5 m. Two distinct peaks appear in the upper strata, on 18 September and 3 October, and these correspond to the most rapid removal of iron from the 9.5–11.5- and 11.5–13.5-m layers respectively. Thus iron is transported from the hypolimnion into the epilimnion by mixing processes.

Samples from the integrating 0–5-m tube (fig. 9) clearly reflect the same changes. The analogous 0–5-m tube values for 1977, also shown, demonstrate that only one large transfer of iron from hypolimnion to epilimnion occurred in that year, during the vigorous mixing which immediately preceded overturn (fig. 2).

The 'nodal point' of the lake for iron transportation is at or near a depth of 8 m, because the iron content of the 7.5–8.5-m layer shows least seasonal change (fig. 9). Therefore a simplified assessment of the iron movements can be obtained from seasonal changes in the total quantities of iron in the 0–8.5- and 8.5–15.5-m layers, shown in figure 10, together with the complete year-long plot of values from the 0–5-m tube. The maximum content of hypolimnetic iron in mid-August is very clear, and its decline is well matched by a commensurate rise in epilimnetic iron. Directly measured values from the 0–5-m tube are parallel to the calculated 0–8.5-m values in periods when they overlap, and demonstrate that the 1978 starting point of 24 July represents a time when the total iron in the lake was near to the annual 'background' level. After the mid-October overturn the iron content in the water column decreased at a fairly uniform rate to reach a background value by late December. The cause of this loss is discussed in the next section, which deals with sources and sinks of iron.

Figures 9 and 10 are based on the total iron measured at each layer of the lake. Figure 11 shows a seasonal plot of the total iron, soluble iron and their difference computed for the whole lake. It shows that the particulate component remains fairly constant, and that almost all the change in iron content is attributable to the soluble component. This suggests that there is a mechanism for continual removal of particulate iron, so that a near steady-state concentration is maintained.

### 3.4 Budgets of iron to and from the lake

In all budget calculations it is assumed that on average the inflow of water to the lake equals the outflow, which was the measured quantity. The quantity of iron discharged from the lake per week throughout 1978 was estimated from the lake level, measured daily, and its relation to outflow rate. The latter was measured in a turbulent stretch of the outflow near the lake by a dilution gauging technique (further details in Heller [16]). It was assumed that the concentration of iron in the outflow was the same as that measured each week in the epilimnion with the 0–5-m tube sampler. The cumulative loss of iron from the lake is plotted against time, from a starting point on 8 January 1978 (fig. 10).

The estimate of annual discharge ( $3.4 \times 10^7$  m<sup>3</sup> in 1978) was checked by rainfall measurements. The rainfall recorded at a site 50 m above lake level some 200 m from the lake shore was 177 cm, which (if representative) corresponds to a volume on the catchment, area 17.1 km<sup>2</sup>, of  $3.0 \times 10^7$  m<sup>3</sup>. The agreement with the discharge

data is reasonable. Evapo-transpiration is likely to account for about 20% of the rainfall, but conversely the measured rainfall is probably exceeded on higher parts of the catchment.

The slope of the plot of cumulative loss in figure 10 indicates the rate of discharge of iron from the lake. This rate was high in the wet months of September to March and almost negligible for the relatively dry months of April to August. Therefore changes in the mass of iron within epilimnion and hypolimnion during July and August could not have been appreciably affected by lake inflow and outflow. Moreover it is unlikely that the sharp increase in epilimnetic iron during September could be due to external sources, and so the previous evidence for transfer of iron from hypolimnion to epilimnion by mixing is supported.

However, since the rate of decrease of lake iron content from mid-October to mid-December is much faster than the rate of removal as indicated by iron concentra-

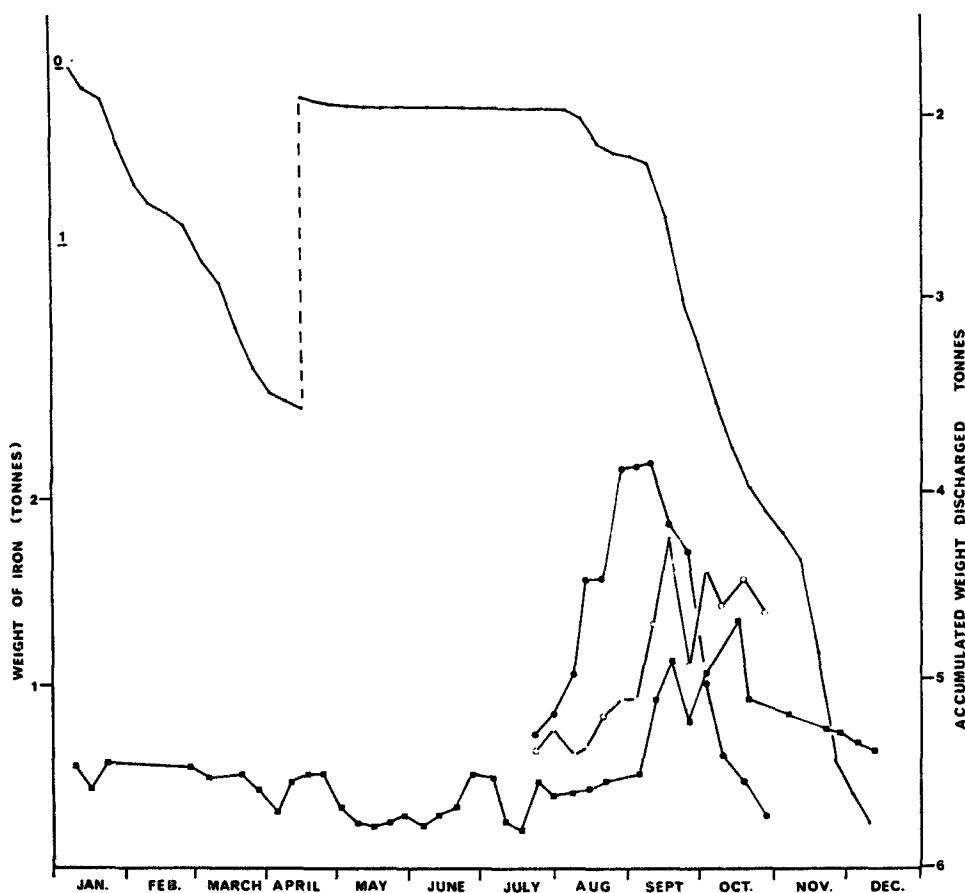


Figure 10. The seasonal dependence of the total iron in the 8.5–15.5-m layer (●), the 0–8.5-m layer (○) and the integrated 0–5-m tube layer (■) for 1978. The accumulated quantity of iron discharged from the lake, assuming a zero value for 8 January, is also plotted (with one scale offset).

tions in the epilimnion (fig. 10), the elevated concentration of epilimnetic iron during this time cannot be exclusively attributed to a single large pulsed input from the hypolimnion. Mortimer [28] observed a similar elevated iron concentration which was maintained for several months. He suggested that wind circulation was probably maintaining the iron in suspension, and attributed a sharp fall in iron concentration on ice cover to rapid settling of the material. His explanation cannot account for the results of 1978 because the high rate of discharge during this period implies an additional input of iron to maintain the elevated concentration. Two factors could explain the higher concentration. The concentration of total iron in the major inflow is always higher than that of the epilimnetic lake water. For 1975, 37 separate analyses showed that the concentration was on average a factor of 3.2 higher. If iron particles entering the lake are slowly removed from suspension over a period of weeks, then during long residence times the iron concentration in the lake will drop to low values due to the long time available for settling, and during short residence times the concentration will be higher because the iron will have had insufficient time to settle out. In addition, the evidence of Pennington [33] from seston traps and rates of sediment accumulation shows that considerable resuspension of material occurs in this lake during the autumn overturn. Therefore there is a strong possibility that additional iron to sustain an elevated concentration is supplied from resuspension of sediment by vigorous wind mixing and water circulation.

Other features described by Mortimer [28] for the 1939 season apparently conflict with slow loss of iron from the epilimnion. He plotted iron content as  $\text{g m}^{-2}$  in a 0–13-m water column, and showed a rapid rise in mid-August and a rapid fall (within one week) in early October. He concluded that most of the iron was deposited at the mud surface within a very short time of overturn. The abrupt rise and fall

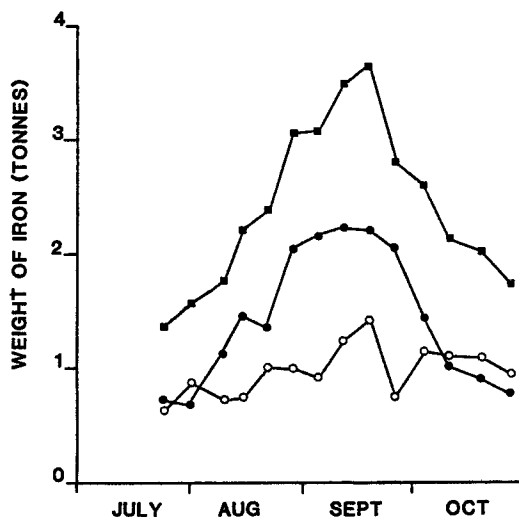


Figure 11. Total iron (■), filtered iron (●) and the difference, i.e. particulate iron (○), in tons in the whole lake for 1978.



in the quantity of iron is actually an artifact because he did not take lake morphometry into account, and so his graph really reflected the rapid changes in hypolimnetic concentrations. The real changes of total iron in the lake occur quite slowly as is shown for 1978 in figure 11. There is no evidence for the initially dissolved iron of the hypolimnion being rapidly transferred to the mud surface when oxidation occurs at overturn. On the contrary, because these freshly formed oxide particles will be small they will probably have lower mean sinking rates than much iron associated with the larger mineral particles of the inflow.

Table 1. Estimates of yearly sources and sinks of iron, in metric tons per annum.

Annual outflow from lake	6.4
Annual dissolution from sediments	1.8–3.6
Annual accumulation in sediments	15–60
Minimum annual input (from inflow concentrations)	20
Minimum net loss from water column	14

Table 1 attempts to quantify the major sources and sinks of iron for the whole of 1978. The annual outflow of iron of 6.4 metric tons was obtained by summing all the outflow values shown in figure 10. From figure 10, about 1.8 metric tons had dissolved from the sediment between mid-July and early September to appear as ferrous iron in the hypolimnion. Further accumulation of soluble iron was obscured by wind-mixed transfer to the epilimnion, but as the deepest sediments remained anoxic for a further 1½ months possibly 3.6 metric tons could dissolve in total. However the rate of dissolution from the sediment is likely to be most rapid early in the season, because the concentration gradient of dissolved iron in the sediment will then be greatest and more area of sediment is exposed to deoxygenated water. The value of 3.6 metric tons is therefore probably a maximum estimate. Pennington [33] has used distributions of  $^{137}\text{Cs}$  to determine the average rate of accumulation of sediments at the deepest sites in Esthwaite Water in recent years. From an analysis of the total iron at 1-cm intervals in a dated sediment core (Lishman, unpublished work) the quantity of iron deposited in a given area of sediment in 9 years – 1963–72 – was calculated, and used to estimate an average rate of accumulation of iron in the sediments of 60 metric tons per annum. Pennington [33] provides evidence for a much increased annual rate of accumulation during recent years in Esthwaite Water, and shows that resuspension of sediment takes place in autumn. Therefore rates of accumulation at the deepest part may be greater than at littoral locations, and the estimate of 60 metric tons – based on the total lake area – could be an overestimate of the iron flux to the sediment. As 55% of the lake area is enclosed by the 5-m depth contour, above which scouring by wind mixing may be prevalent, the error due to wind scouring is probably about a factor of 2. Moreover, Pennington et al. [34] have shown that for another small lake of similar productivity, deposition below the wind-scoured depth can be concentrated in the deeper sites by up to a factor of 2. Therefore the lower limit for annual accumulation is probably 15 metric tons. The difficulty in replicating cores from the same site [34] and the possibilities, mentioned above, of nonhomogeneous accumulation of sediment, leads to the

conclusion that analysis of the dated core results in an estimated accumulation rate of 15–60 metric tons per annum.

As already mentioned, in 1975 the iron concentration in the major inflow, Black Beck, was enhanced on average by a factor of 3.2 over the epilimnion value. Similar enhancement factors applied in 1974 and 1976 and for other small inflowing streams. Assuming that this same factor would apply in 1978, the volume of water discharged was used to calculate a minimum inflow of iron of 20 metric tons ( $\sim$ outflow loss of 6.4 metric tons  $\times$  enhancement factor of 3.2) and hence a minimum net loss from the lake water column of 14 metric tons ( $\approx 20 - 6.4$ ) per annum. The values are minimal because the concentration of iron in the inflows includes some very high but isolated values. With such an erratic distribution a mean will tend to underestimate the cumulative amount of iron flowing into the lake.

Measurements during 1978 for direct deposition of air-borne iron near Esthwaite Water yield, when calculated for the lake area, the negligible quantity of 0.1 metric tons per annum [3]. Similarly, determination of the iron content of plankton of the largest annual crop, dominated by the dinoflagellate *Ceratium hirundinella* [15], gave an estimate of 0.14 metric tons lost to the sediment during the rapid sedimentation of *Ceratium* cysts near overturn. From a knowledge of seasonal plankton production annual sedimentation of iron associated with plankton is unlikely to be greater than three times this quantity.

The minimum net loss from the water column and annual accumulation in the sediment (table 1) should agree if the lake iron budget is to balance. When the possible range for the sediment accumulation rate and the possibility of underestimating the net loss are considered the agreement is reasonable. The gross budget in table 1, although approximate, is probably sufficiently accurate to permit two major conclusions. Using the range of iron loading provided by the accumulation in the sediments and the annual discharge of iron, some 70–90% of the annual iron load can be estimated to accumulate in the sediment. Again using the extremes of the calculated ranges, the iron which dissolves from the sediments each year represents 30–60% of the annual discharge, but only 3–18% of the total annual iron loading to the lake. Most of the iron which dissolves from the sediment is probably washed out of the lake; if so, it is freshly deposited iron which is dissolved each year.

### 3.5 Calculation of fluxes

The shape of the profiles in figure 5 can be used to calculate fluxes of iron if rates of vertical transport are known. Since temperature profiles were measured weekly the flux gradient method [20] could be used to calculate the eddy diffusion coefficient,  $K_z$ , at weekly intervals and 1-m intervals of depth,  $z$ . From the lake morphometry and temperature profiles the total heat content of the waters below each horizon in the lake was calculated for successive weeks to provide the heat flow per unit time. The slope of the temperature profile at the same depth provided the thermal gradient and so allowed calculation of  $K_z$ . Because only deep waters were considered and large phytoplankton populations provided surface shading [13], direct solar heating at depth could be ignored.

Values of  $K_z$  were calculated for 1977 and 1978. Unfortunately the week to week

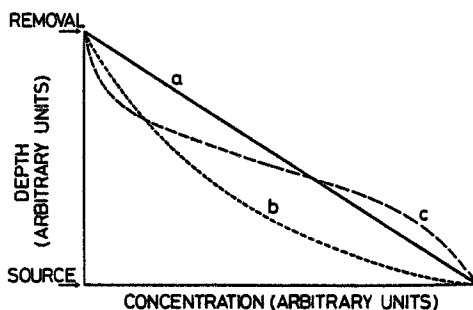


Figure 12. Schematic concentration-depth profiles for a simple cylindrical Fickian diffusion model (a); for a point source at the bottom of a concave basin (b); and the measured shape for Esthwaite Water (c).

precision of temperature measurement was no better than  $0.05^{\circ}\text{C}$ ; this, and a slightly fluctuating lake level, limited the accuracy for  $K_z$ . However,  $K_z$  was obviously very variable in the hypolimnion, being as high as  $0.05\text{ cm}^2\text{ s}^{-1}$  during periods of severe wind stress in the epilimnion, whereas in very stable conditions, as in early August 1977, it was well below the probable detection limit of  $0.01\text{ cm}^2\text{ s}^{-1}$ . An average of all calculated values, which sometimes were negative, was  $0.01\text{ cm}^2\text{ s}^{-1}$  with a range of  $\pm 0.005\text{ cm}^2\text{ s}^{-1}$ , for all depths below 9 m. This value is in reasonable agreement with Mortimer's [28] estimate of  $0.02\text{ cm}^2\text{ s}^{-1}$  for 1939. In all flux calculations  $K_z$  was assumed to be constant with respect to time and depth at  $0.01\text{ cm}^2\text{ s}^{-1}$ .

Assume that the lake can be represented by a cylinder of water with a constant iron input from the base which represents the sediment, and a constant rate of removal by oxidation at some point,  $z$ , from it, which represents the oxic/anoxic boundary. Then, at steady state, Fickian diffusion will produce a linear profile (fig. 12a) [1]. If the cylinder was saucer-shaped like the lake basin, input from a point source at the bottom of the basin would result in a concave profile (fig. 12b). However, comparison with figure 5 shows that the more usual shape for Esthwaite Water is that of figure 12c. Since the rate of change of concentration with depth reaches a maximum at a few metres from the bottom of the lake, the flux must be maximal at this depth. This implies another source of input other than that from the deepest part of the lake basin.

The horizontal rate of transport of water in the hypolimnion is several orders of magnitude more rapid than the vertical rate [30]. Therefore each basin may be assumed to be horizontally uniform. That is, each stratum of water may be regarded as completely mixed and no lateral concentration gradient exists at the adjoining sediment. This assumption only applies to an individual basin; results for 1971 show that there can be small differences in concentrations at comparable depths in the two basins. The upper strata of water in the hypolimnion contact a larger surface area of sediment than do the lower strata, and sediment-derived iron may be laterally supplied to each stratum. This model of a horizontally uniform lake provides a mechanism for additional iron input to the mid-water region of the hypolimnion. To calculate this extra input it is necessary to have a knowledge of lake morphometry and to assume that the flux of iron from the sediment is constant

for all anoxic hypolimnetic sediment. Hesslein [17] has used a similar model and given a detailed appraisal of the assumptions necessary to calculate the distribution of chemical species in lakes.

A sample calculation is provided in table 2. From the slope of the concentration profile at 14 m depth,  $(dc/dz)_{z=14}$ , the flux of iron,  $F$ , through  $1 \text{ cm}^2$  of the 14-m horizon may be calculated. Knowing the area of the lake bounded by the 14-m contour, the flux,  $F_A$ , through the whole 14-m horizon may be calculated. If it is assumed that all this iron has originated from the sediment,  $F$  may be equated to the rate of iron release per unit surface area of sediment. From a knowledge of the cross-sectional area of the lake,  $A_z$ , at 1-m intervals of depth, the extra area of sediment,  $\Delta A_z$ , contacted in moving from a lower to higher stratum may be evaluated, and, assuming uniform release of iron from all anoxic sediments, the lateral flux of iron,  $F_L$ , may be calculated for each layer. The slope of the concentration-depth profile at a given depth in the lake provides the net iron flux,  $F_A$ . If the lateral sediment contribution,  $F_L$ , is subtracted, the residue will be the flux which originates only from within the water mass,  $F_w$ . In the calculation as illustrated in table 2, the lake areas used were for basin A only, because below 10 m the two major basins of the lake are isolated when stratification is established. Use was made of the more complete measurements for filtered iron which, when reducing conditions are well developed, agree well with the polarographically measured ferrous iron (fig. 5).

The above calculation has not taken the change in profile shape with time into account, implying that the concentrations of iron approach steady state over short periods of time. This condition is almost although not completely met, because the change in concentrations between two consecutive dates is relatively small (fig. 5).

Table 2. Sample calculation for 28 August 1978 of iron fluxes within the hypolimnion of basin A, estimated sinking rate for iron and residence time of iron in each 1-m stratum.

Specified quantity	Units							
Depth, $z$	m	9	10	11	12	13	14	15
Area of 1-m stratum, $A_z$	$\text{cm}^2 \times 10^{-8}$		20.84	14.88	8.91	5.88	2.86	0.80
Filtered iron concentration, $C_z$	$\mu\text{g l}^{-1}$	162	329	1245	3053	5170	6298	6599
Flux per unit area, $F_z = (C_{z+1} - C_z)/2$	$\text{g cm}^{-2}\text{s}^{-1} \times 10^{11}$		5.42	13.6	19.6	16.2	7.2	
Flux through each 1-m stratum, $F_A = F_z \cdot A_z$	$\text{g s}^{-1} \times 10^3$		113	203	175	95.4	20.4	
Incremental sediment area, $\Delta A_z = A_z - A_{z+1}$	$\text{cm}^2 \times 10^{-8}$		5.96	5.97	3.03	3.02		
Lateral flux, $F_L = \Delta A_z \cdot F_{(z=14)}$	$\text{g s}^{-1} \times 10^3$		42.6	42.7	21.7	21.6		
Water-associated flux, $F_w = F_A - F_L$	$\text{g s}^{-1} \times 10^3$		70.4	160	153	73.8		
Flux from redissolution, $F_d = F_{w(z)} - F_{w(z+1)}$	$\text{g s}^{-1} \times 10^3$			7.0	79.2	53.4		
$F_d$ per unit area, $F_d/A_z$	$\text{g cm}^{-2}\text{s}^{-1} \times 10^{11}$				8.9	9.08		
Minimum sinking flux	$\mu\text{g cm}^{-2}\text{day}^{-1}$				7.7	7.85		
Quantity of iron in stratum, $W_z = C_z \cdot A_z$	kg		69	185	272	304		
Residence time of iron, $W_z/F_{A(z)}$	days		7.07	10.5	18	36.9		

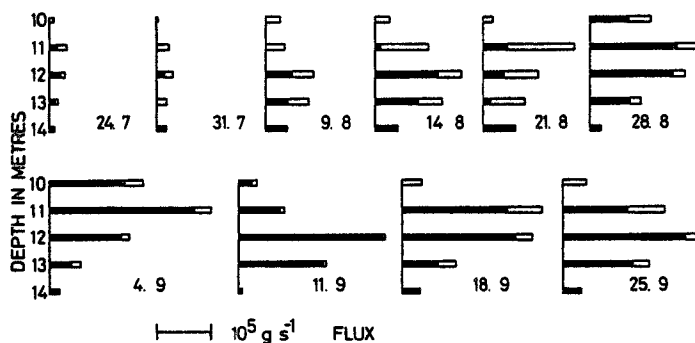


Figure 13. The measured flux of filtered iron,  $F_A$ , shown by complete histograms, and the calculated flux of iron within the water body,  $F_w$ , as solid histograms, for different depths of basin A during the summer of 1978.

Moreover, from a knowledge of the net flux into each 1-m stratum and the total iron contained therein, the corresponding residence time of iron may be calculated (table 2). This is typically 10–30 days.

The net flux,  $F_A$ , calculated directly from the slope of the profile, and the water-derived flux,  $F_w = F_A - F_L$ , through each 1-m stratum from 10 to 14 m, are plotted as histograms at weekly intervals in figure 13. If no other factor mediates in the transport of iron, the water-derived flux  $F_w$  should be the same for each layer of the lake. From 24 July to possibly 21 August this might indeed be so. Later, however, the flux was greatest at either 11 or 12 m, possibly because the oxidized particulate iron formed at the oxic/anoxic boundary settles by gravity and is then reduced on reaching the lower very reducing waters.

Table 2 illustrates a means of estimating the downward or sedimenting flux of particulate iron. For a given 1-m stratum, which from figure 5 can be assumed to be free from particulate iron, the difference between the water-derived flux of the layer and the flux of iron,  $F_w$ , from the layer below can be attributed to settling and redissolving iron. The same calculation may not be performed in the particulate layer itself (e.g. 10 and 11 m, table 2) because a continuous cycling between oxidized and reduced iron might be occurring with little net sedimentation. For the period of 28 August to 25 September 1978, values for the flux of sedimenting iron ranged from 3 to 22  $\mu\text{g cm}^{-2} \text{ day}^{-1}$ . Values measured directly from sediment traps situated at 11 m over the deepest area ranged from 7 to 34  $\mu\text{g cm}^{-2} \text{ day}^{-1}$  for the corresponding period in 1979 (Davison et al., in preparation). This close agreement lends support for the various assumptions made, which are:

1.  $K_z$  is constant with depth and equal to  $0.01 \text{ cm}^2 \text{ s}^{-1}$ .
2. The lake basin is horizontally uniform.
3. The flux of ferrous iron from sediment to water is the same for all anoxic sediments irrespective of lake depth.
4. The flux of ferrous iron through the 14-m horizon is exclusively derived from the sediment.

5. For periods of weeks near-steady state conditions apply to the iron profiles.
6. Reduction of all sinking ferric iron takes place in the water column.

Assumptions 1, 2, 3 and 5 have independent supporting evidence but 4 and 6 are supported largely by the calculation itself. Although the shape of the attenuation profiles, as explained in section 3.2, supports assumption 6, the main evidence lies in the shape of the profiles of soluble iron and the independent check on sedimentation rates.

The chief error is likely to be due to the estimate of flux from the sediment. It was calculated from the difference in iron concentrations at 15 and 13 m which will only approximate to the true flux at the deepest point of the lake. The error is likely to be within a factor of 2. This would affect the numerical result but not the general conclusion regarding iron recycling within the water column, which is primarily dictated by the convex shape of the iron profiles.  $K_z$  does not remain constant with time, but is subject to sudden changes brought about by severe wind stress. However, the calculated fluxes are based on profile shapes which remain relatively constant for periods of weeks and so it is appropriate to use an average value for  $K_z$ .

#### 4. Discussion

The results enable a scheme for transport of iron in Esthwaite Water to be constructed (fig. 14). It is dominated by the iron supplied via the inflow entering the lake and sinking to accumulate in the sediment, although during summer stratification an

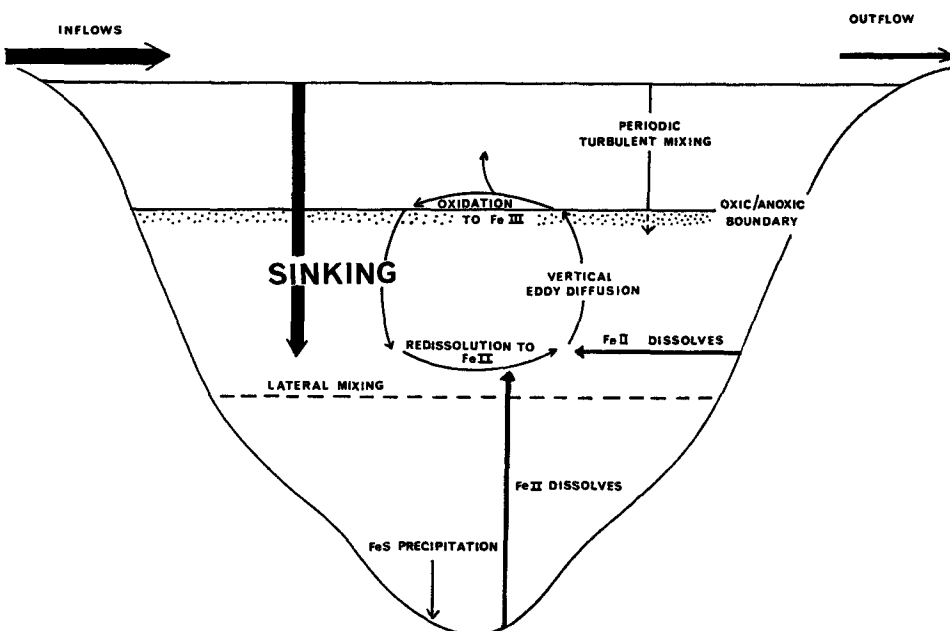


Figure 14. Model for the movement of iron in a lake with an anoxic hypolimnion, indicating the relative importance of various transport processes.

internal cycling of iron occurs. The hypolimnion may be considered as a series of laterally uniform horizontal layers. Fe II is supplied by dissolution from the sediments at all hypolimnetic depths, but the concentration gradients between layers ensure an upward transport of Fe II by eddy diffusion. On reaching the oxic/anoxic boundary Fe II is oxidized to particulate ferric oxy/hydroxides, which may be mixed into the higher waters of the lake or sink to become reduced and recycled. In addition if the solubility of ferrous sulphide is exceeded, iron may sediment in an insoluble ferrous form.

The vertical transport of iron is controlled by three major processes. Although hypolimnetic eddy diffusion is subject to changes with respect to depth and time it may be regarded as a relatively constant mechanism for transport when time intervals of several weeks are considered. This is not so for the episodic turbulent mixing processes of the epilimnion which are very dependent on changes in wind strength. Gravitational sinking forces persist throughout the water column but their effect depends on particle size.

This work extends that of Mortimer [28, 29] in considering the transfer of water to and from the lake and the importance of sediment-derived iron in the overall budget. Although ferrous dissolution dominates the movement of iron for a short summer period, it does not play a major role in the annual transport of iron. For 1978 it could have accounted for 30–60% of the annual discharge from the lake, but only 3–18% of the total iron loading to the lake. The calculations also indicated that most (70–90%) of the iron that entered the lake was retained in the sediments, which is similar to a value of 84–88% estimated in a complete lake budget for a dimictic lake on the Canadian Shield [38]. The arguments which are necessary to balance the net loss from the water mass with the accumulation in the sediment (table 1) suggest that iron may be preferentially accumulating in the deep sediments rather than at littoral sites.

Mackereth [27] analyzed the iron and manganese content of the postglacial sediments of Esthwaite Water and two less productive lakes, Windermere and Ennerdale Water. He provided arguments to show that for Esthwaite Water changes in the ratio of Fe to Mn in the sediments are due to events within the lake rather than to a changing ratio of elements in the inflow. To account for the cycles in the percentage composition of iron and manganese he suggested that the solubilization of iron and its subsequent removal from the lake could alter the iron content of the sediment. But if the fraction solubilized each year only represents 3–18% of the total iron supplied to the sediment, the sediment composition should not be appreciably affected in the current climate regime. Furthermore a simple increase in reducing intensity in the lake would not lead to increased loss of iron from the lake, because its movement is primarily determined by the extent of deoxygenation and wind mixing. A reduced flow of material to the lake, caused by a sustained period of low rainfall, could bring about a situation where an appreciable proportion of iron could be lost from the lake due to its solubilization from the sediments. This postulation of a cyclic variation in rainfall in postglacial times agrees with unpublished work of Pennington.

In view of the general similarities between events in 1939–40 [28, 29] and in 1977–78, the differences apparent between adjacent years are worth comment. In

response to meteorological differences a more stable and isolated hypolimnion developed in 1977 than in 1978; considerable ferrous sulphide was formed in 1977 and very little in 1978. Since the presence or absence of sulphide has been used to differentiate between two classes of lake eutrophication [19], Esthwaite Water is apparently capable of changing its class because of differences in weather in successive years. Mortimer's results [28, 29] illustrate that the marked differences between 1977 and 1978 are not exceptional. Like that for 1977, the depth-time diagram for temperature in 1939 shows near-horizontal isotherms during midsummer whereas in 1940 they were steeply sloping. The exceptionally warm and sunny summer of 1976 has already been characterized [13] by very stable hypolimnetic temperatures and pronounced secondary thermoclines in the epilimnion, and a similar pattern has been reported for the warm summer of 1975 [14]. These results tend to reinforce the view of an effectively isolated hypolimnion. Yet the results of this work demonstrate that for iron distribution this is not so because iron is continually transferred between the two compartments of the lake. This transport of iron only becomes apparent when the morphometry of the basin is considered. If dependence is placed solely on concentrations, the extremely high concentrations in the low-volume hypolimnetic waters mask the movement of the mass of iron. The introduction of morphometric factors also illustrates that iron is not immediately reprecipitated at the sediment after overturn. On the contrary the maintenance of high iron levels for several months supports Pennington's [33] contention, based on seston trapping, that resuspension of sedimenting material occurs during this period, because simple wind mixing of the water cannot maintain the concentration at such high levels.

The movements of iron according to the model of figure 14 depend on a variety of rates: of dissolution from the sediment, of horizontal water movement, of vertical water movement, of oxidation, of sinking, and of redissolution. It is the relative expression of these rates which determines the observed behaviour of iron in a particular lake. For Esthwaite Water the fluxes associated with rates of vertical transport, oxidation and sinking are balanced in such a way that a considerable concentration of particulate iron accumulates in a discrete water layer. A similar phenomenon has been observed in Beppu Bay, Japan [18]. This particulate component, intermediate in the recycling process, will be critically dependent on these rate processes for its existence as a measurable concentration, and in other lake systems it may not be observed. Figures 6 and 8 show that meteorological effects may greatly modify its formation in Esthwaite Water. This is probably due to changes over depth and time in the vertical mixing coefficient,  $K_z$ , although rates of oxidation and reduction may also vary with time and position in the lake.

There have been few studies which have quantified fluxes of iron in freshwater systems. Verdouw and Dekkers [42] have studied the dynamics of iron in an excavated sand pit. They used sediment traps to estimate the sinking flux of iron as  $1\text{--}3.5 \mu\text{g cm}^{-2} \text{ day}^{-1}$  which is of similar magnitude to the  $3\text{--}22 \mu\text{g cm}^{-2} \text{ day}^{-1}$  calculated in this work. Redissolution of iron probably did not affect their trapping results because the iron profiles were concave in shape. Fillos and Swanson [10] used laboratory tank experiments to measure the rate of release of iron from lake sediment under anaerobic conditions at  $30^\circ\text{C}$ . In view of the high temperature their



value of ca.  $10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$  is consistent with the values used in this study (table 2 and fig.3) which ranged from 2 to  $22 \times 10^{-11} \text{ g cm}^{-2} \text{ s}^{-1}$  (the fluxes measured at 14 m). Murray and Gill's [32] estimate for the release from a saline sediment was  $4.7 \times 10^{-11} \text{ g cm}^{-2} \text{ s}^{-1}$ , which again agrees well. Their value was obtained by considering gross iron budgets; estimates from concentration gradients in interstitial water are not reliable.

The present work can ascribe some importance to the various pathways indicated in figure 14. The flux calculations show that contributions from sinking and redissolution processes are of comparable magnitude to those from dissolution from the sediment and vertical transport. Therefore, excluding the overriding dominance of lateral mixing, all the hypolimnetic processes indicated in figure 14 may make appreciable contributions to the recycling of iron. Although the redox cycling of iron is small compared to the iron loading of the lake, there is no implication that its effect is small because associated transport of nutrients and trace metals to and from the sediments and within the lake could profoundly affect the whole lake ecosystem.

## 5. Summary

The seasonal and depth distributions of the concentrations of total and filtered iron in a seasonally anoxic lake basin of Esthwaite Water, English Lake District, are described for two years.

A variable combination of solar radiation and wind stress affects the hydrodynamic stability of the lake including the hypolimnion, and possibly its chemical processes, for example by controlling the presence or absence of ferrous sulphide. The stability of the particulate ferric oxy/hydroxide layer depends on a delicate balance between turbulence and reducing conditions, as these factors control the rates of vertical mixing and ferrous oxidation.

The attenuation of a horizontal light beam in the hypolimnion correlates well with the concentration of particulate iron. Systematic measurements in situ of such attenuation, recorded continuously against depth, were used to follow the particulate iron components in the lake, making it possible to resolve the fine details of distribution.

In late summer, as epilimnetic mixing processes depress the oxic/anoxic boundary, the reduced iron of the hypolimnion is progressively oxidized and transferred to the epilimnetic waters in which it is uniformly mixed. The concentration of epilimnetic iron reaches a maximum near overturn and then progressively decreases. The slow decline is due to iron being retained in the water column by resuspension of sedimented material.

The mass of particulate iron in the lake changes little throughout the year. The large summer increase in the mass of total iron is almost exclusively attributable to the soluble fraction. Sediment-derived ferrous iron accounts for only 3–18% of the annual iron loading to the lake; probably most of this sediment-derived fraction is washed out of the lake rather than returned to the sediment. However, most (70–90%) of the iron which annually flows into the lake is accumulated in the sediment.

The shape of the concentration-depth profile was used to estimate fluxes of iron to

or from various strata of the lake. Redissolution of sinking ferric particles appears to be a significant component of iron movement within the hypolimnion and causes substantial recycling of iron between the ferrous and ferric states in the water column. Minimal sinking fluxes of  $3\text{--}22\ \mu\text{g cm}^{-2}\text{ day}^{-1}$  were calculated using the concentration-depth profiles.

A schematic model for the movement of iron within and to and from an anoxic basin is given; it is critically dependent upon the many rate processes involved.

## ZUSAMMENFASSUNG

Es wird die vertikale und zeitliche (2 Jahre) Verteilung des Eisens (Gesamteisen und Eisen im Filtrat) in einem saisonal anaeroben See (Esthwaite Water, English Lake District) beschrieben.

Die hydrodynamische Stabilität des Sees einschliesslich des Hypolimnions wird durch die Sonnenstrahlung und den Wind, beide mit variablen Anteilen, beeinflusst. Möglicherweise unterliegen auch die chemischen Prozesse diesem Einfluss, z.B. indem das Vorhandensein oder Fehlen von Eisensulfid dadurch bestimmt wird. Ob die partikuläre Eisenoxidhydrat-Schicht stabil ist oder nicht, hängt davon ab, ob das empfindliche Gleichgewicht zwischen Turbulenz und Reduktionsbedingungen erfüllt ist, indem diese Faktoren die Geschwindigkeiten der vertikalen Mischung und der Fe(II)-Oxidation bestimmen.

Die horizontale Lichtextinktion im Hypolimnion korreliert gut mit der Konzentration des partikulären Eisens. Systematische Messungen dieser Extinktion (Trübung) in situ, mit einem x-y-Schreiber kontinuierlich gegen die Tiefe aufgetragen, werden dazu verwendet, das partikuläre Eisen im See zu verfolgen. Dadurch wurde es möglich, die Verteilung im Detail sichtbar zu machen.

Im Spätsommer, wenn die fortschreitende Mischung im Epilimnion die Grenze zwischen der sauerstoffhaltigen und sauerstofffreien Schicht absenkt, wird reduziertes Eisen aus dem Hypolimnion zunehmend oxidiert und ins epilimnische Wasser transferiert, wo es homogen eingemischt wird. Die Eisenkonzentration erreicht im Epilimnion bzw. in der zirkulierenden Schicht ungefähr bei Vollzirkulation ihr Maximum und nimmt sodann allmählich wieder ab. Dass dieser Rückgang langsam vor sich geht, ist auf Resuspension von sedimentiertem Material in den Wasserkörper zurückzuführen.

Das Seetotal des partikulären Eisens ändert sich im Laufe des Jahres wenig. Der starke Anstieg des Gesamteisens im Sommer ist fast ausschliesslich durch den gelösten Anteil bedingt. Das sedimentbürtige Eisen-II trägt nur 3–18% zur jährlichen Eisenbelastung des Sees bei. Wahrscheinlich wird der Hauptteil dieser Fraktion aus dem See ausgewaschen und nicht mehr ins Sediment eingebaut. Trotzdem werden 70–90% der allochthonen Eisenfracht im Sediment akkumuliert.

Aus dem Verlauf der Konzentrations-Tiefen-Profile wurden Eisenfluxe zwischen verschiedenen Schichten des Sees berechnet. Die Auflösung absinkender Fe(III)-Partikeln scheint dabei eine wichtige Komponente der Eisenbewegung innerhalb des Hypolimnions zu sein; sie verursacht einen beträchtlichen Kreislauf zwischen den Fe(II)- und Fe(III)-Formen im Wasserkörper. Aus den Konzentrations-Tiefen-Profilen wurden minimale Sedimentationsraten von 3 bis  $22\ \mu\text{g cm}^{-2}\text{ Tag}^{-1}$  berechnet.

Für die Bewegung des Eisens zu und aus einem anoxischen Seebecken sowie innerhalb desselben wird ein chemisches Modell entwickelt: Dieses hängt entscheidend von den vielen beteiligten Umsatzvorgängen ab.

## RÉSUMÉ

*Transformations et mouvements saisonniers du fer dans un lac anglais productif dans l'eau profonde et anaérobie*

Cet exposé décrit, sur une période de deux ans, les distributions (d'après la saison et la profondeur) des concentrations de fer entier et filtré dans un bassin lacustre saisonnièrement anaérobie: Esthwaite Water dans la région des lacs anglais.

Une combinaison variable de la radiation solaire et de la force du vent influe sur la stabilité hydrodynamique du lac, y compris l'hypolimnion, et peut-être sur ses réactions chimiques, par exemple en réglant la présence ou l'absence de pyrite de fer. La stabilité de la couche particulière d'oxy/hydroxide ferrique

dépend d'un équilibre délicat entre la turbulence et les conditions réductrices, puisque ces facteurs régissent les taux de mélange vertical et d'oxydation ferreuse.

L'extinction d'un rayon de lumière horizontal dans l'hypolimnion est en bonne corrélation avec la concentration de fer particulaire. Des mesures systématiques de cette extinction in situ, enregistrées d'une façon continue d'après la profondeur, ont été utilisées pour suivre les composants de fer particulaire du lac, permettant de déterminer des détails précis de distribution.

Ver la fin de l'été, à mesure que les processus de mélange dans l'épilimnion abaissent le seuil de la couche oxygénée/désoxygénée, le fer réduit de l'hypolimnion est progressivement oxydé, puis est transféré aux eaux de l'épilimnion où il est uniformément mélangé. La concentration de fer épilimnique atteint son maximum lors de la pleine circulation, puis elle diminue progressivement. Cette lente diminution est due à la conservation du fer dans la masse d'eau par la resuspension de substances sédimentaires.

La masse de fer particulaire dans le lac change peu au cours de l'année. La grande augmentation estivale de la masse de fer entier est presque exclusivement attribuable à la fraction soluble. Le fer ferreux qui provient du sédiment ne représente que 3-18% de la charge annuelle de fer dans le lac; il est probable que la plupart de cette fraction sédimentaire soit éliminée par l'eau courante du lac, plutôt que réintégrée dans le sédiment. Cependant, la plupart (70-90%) du fer qui entre annuellement dans le lac s'accumule dans le sédiment.

On a utilisé la forme du profil de concentration d'après la profondeur pour évaluer les flux du fer qui vont vers les diverses couches du lac ou en proviennent. La redissolution de particules ferriques en cours de sédimentation semble être un élément significatif du mouvement du fer dans l'hypolimnion et provoque un recyclage considérable du fer entre les états ferreux et ferrique dans la masse d'eau. Des taux de sédimentation minimums de 3 à 22  $\mu\text{g cm}^{-2} \text{ jour}^{-1}$  ont été calculés en utilisant des profils de concentration d'après la profondeur.

L'exposé comprend un modèle schématique du mouvement du fer qui entre et qui sort d'un bassin anaérobie; ce modèle dépend de façon décisive des nombreux processus impliqués.

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