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Elements of the Iron and Manganese Cycles in Lake Baikal

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Abstract—Using data obtained in recent years, we considered the external mass balance and characteristics of internal iron and manganese cycles in Lake Baikal (biological uptake, remineralization, sedimentary and diffusive fluxes, accumulation in sediments, time of renewal, etc.). Some previous results and common concepts were critically reevaluated.

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INTRODUCTION

The limnic system of Baikal is different from other deep lakes of the world in that its water column is persistently enriched in oxygen down to the bottom. This is related to the low bioproductivity of the lake resulting in a low production of destructible organic matter [1] and the regular sink of oxygen-rich surface waters into the deep zone [2, 3]. The relative content of oxygen in the surface waters ranges from 94 to 104% saturation [1, 3]. The concentration of oxygen is 10–12 mg/l in the water at 20–50 m above the bottom [4] and does not fall below 6 mg/l even at 2–5 mm above the bottom [5]. Oxygen penetrates into the bottom sediments, which results in that the surface sediments are oxidized over most of the Baikal bottom, which is among the most important features of the lake. The intense diagenetic accumulation of iron and manganese takes place in the present-day oxidized zone, the thickness of which in the deep-water part of the lake is 2–5 cm and, occasionally, up to 10–15 cm or even more. The chemical differentiation of these elements produces secondary forms of their concentration as Fe–Mn enriched layers, crusts, and nodules.

However, in addition to bottom sediments, iron and manganese are concentrated in living organisms. It is known that the availability of dissolved iron limits the growth of plankton over considerable areas of the ocean, and it may influence the intensity of the biological carbon pump (e.g., [6]). Diatom algae intensely extract both iron and manganese from the water column [7]. Diatoms dominate the plankton community of Baikal, and biological uptake may therefore play an important role in the internal cycle of these elements. The enrichment factors in phytoplankton are 4 for Fe and 8 for Mn [8]. The extensive data that have been accumulated over many years and new data on the fluxes of chemical elements and the chemistry of pore waters and riverine and lake suspended particles provided a basis for estimating the main characteristics of the internal Fe and Mn cycles in the lake, reassessing the external mass balance, and revising some previous results, which are the goals of this study.

METHODS OF CALCULATION AND RESULTS

Since Fe and Mn enter the lake in particulate and dissolved states, mass balance estimates are based on the water budget of the lake and the budget of suspended particles. The extensive published data summarized in [9] suggest that the riverine input plays the main role in the supply of chemical elements to the lake, whereas the atmospheric input is minor, and the contribution of underground sources can be ignored. Thus, the mass balance can be characterized by estimating Fe and Mn fluxes in dissolved and suspended forms with riverine input, as well as their dry and wet deposition from the atmosphere. The output of chemical elements is realized with the water of the Angara River, the only outlet of the lake. The difference between the input and output corresponds to the accumulation of elements, which may occur in bottom sediments and aquatic organisms.

The dissolved and colloidal forms of Fe and Mn in the water column are in part consumed by biota, the death of which results in the formation of a biogenic particulate flux to the bottom. The level of remineralization of biological particles can be estimated from the difference between the biological uptake and biogenic flux. The settling of particles on the bottom (sedimentation) occurs in the forms of biogenic and lithogenic fluxes. The lithogenic flux consists mainly of particles formed in the water column as a result of hydroxide coagulation and smaller particles of lithogenic origin.

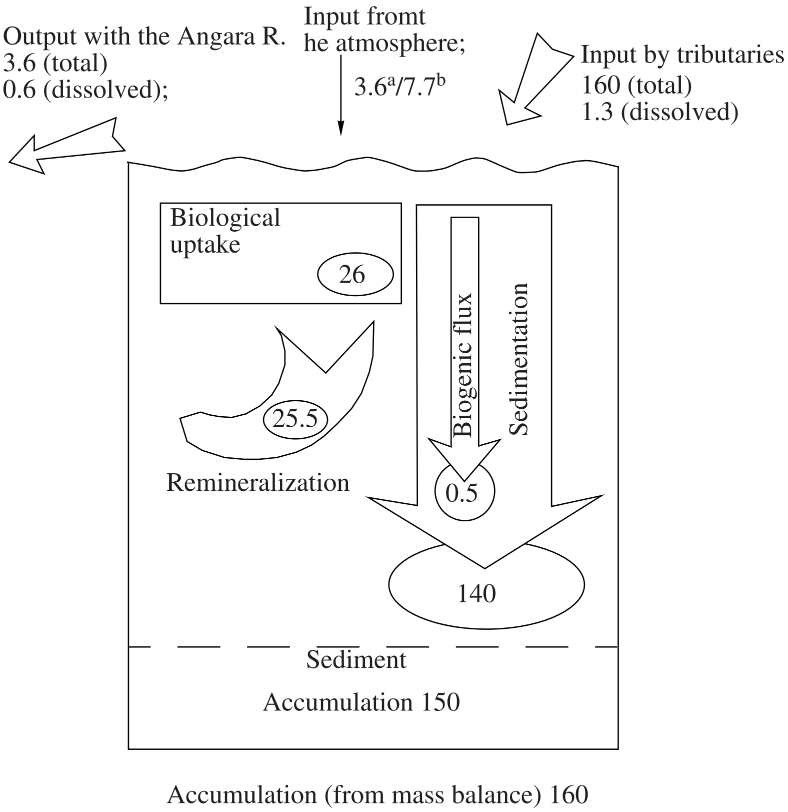

Fig. 1. Box diagram showing the mass balance of iron and elements of its internal cycle. All values are in thousand tons per year, except for the inventory in the water column, which is given in thousand tons. The input from the atmosphere was calculated as the sum of dry and wet deposition using the data from (a) [8] and (b) [17].

For instance, the total suspended Mn includes up to 24% amorphous hydroxides in the Indian Ocean and up to 28% of adsorbed forms and amorphous Mn in the Pacific Ocean [10]. The sedimentary flux is opposed by the diffusive flux of dissolved Fe and Mn species from the bottom sediments. Although the sediments of Baikal are oxidized, the concentrations of Fe^{2+} and Mn^{2+} in the pore waters of surface sediments are higher than those in the bottom water owing to the small thickness of the oxidized zone and the intense dissolution of its lower part at the redox boundary [11, 12]. A concentration gradient is formed at the water–sediment interface and can, under favorable conditions, promote a diffusive flux to the water column.

These are the components of the external mass balance and internal cycles of iron and manganese in Baikal, which are estimated in this paper. Data on the area of the lake and its particular regions and the volume of the water column were taken from [13]. Given the approximate nature of our calculations, the raw data and obtained results were usually rounded to the second decimal place.

I. The external mass balance for the two elements (Figs. 1, 2) was calculated and discussed in detail previously [14]. These calculations were based on the data on the input of Fe and Mn with dissolved and suspended materials transported by fluvial waters into Baikal and published estimates of the atmospheric flux of these elements. The total input of particulate and dissolved iron by riverine input is 160 kt/yr, including 1.3 kt/yr of dissolved iron. The calculations made by other authors on the basis of averaged data yielded a similar value of dissolved flux of 2.7 kt Fe per year [8]. (Much higher estimates of about 28 kt/yr were reported in some previous studies [15, 16].) The output of iron by the Angara River is 3.6 kt/yr [14], including 0.6 kt/yr of dissolved iron [16]. The total riverine input of manganese is 5.0 kt/yr [14], including 0.3 [8] to 0.4 kt/yr [16] of dissolved Mn. The annual manganese removal by Angara water was estimated as 0.4 kt [14], and dissolved manganese accounts for only 0.02 [8] or 0.04 kt/yr [16].

The data of Vetrov and Kuznetsova [8] indicate that 0.1 kt Mn and 3.6 kt Fe enter every year the lake from the atmosphere. An attempt to account for the precipitation of the elements on the water surface of the lake, both with atmospheric precipitation and as aerosols, yielded two times higher values: 0.2 kt Mn and 7.7 kt Fe [17]. These authors believed that the dry deposition is approximately equal to the wet one.

Thus, the total input of Fe and Mn into Baikal both by the riverine input and atmospheric flux is about

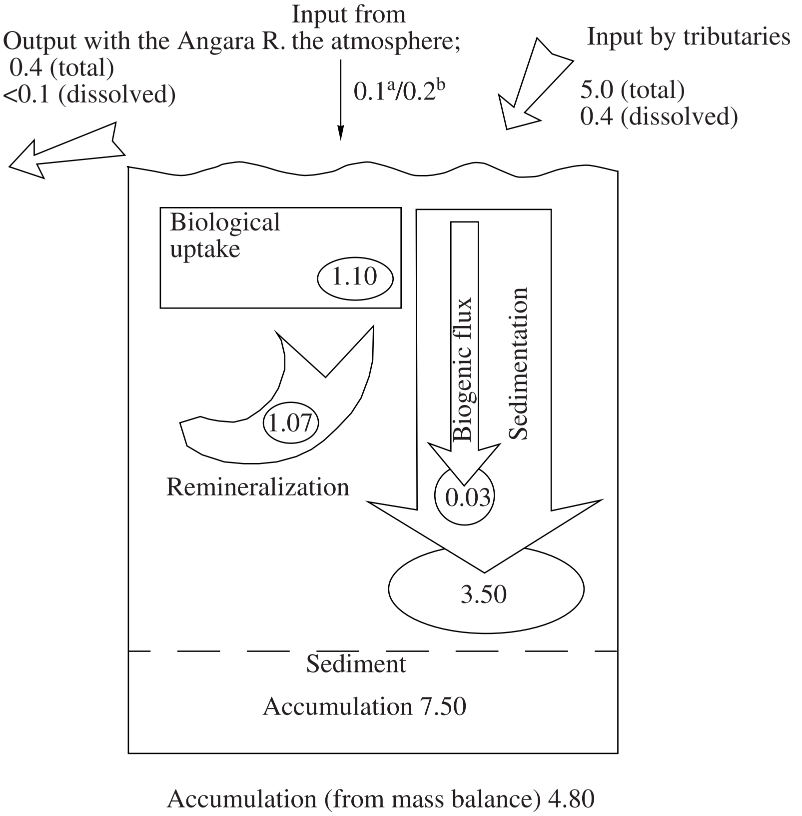

Fig. 2. Box diagram showing the mass balance of manganese and elements of its internal cycle. All values are in thousand tons per year, except for the inventory in the water column, which is given in thousand tons. The input from the atmosphere was calculated as the sum of dry and wet deposition using the data from (a) [8] and (b) [17].

170 kt/yr and 5.2 kt/yr, respectively. After subtracting the output of elements from the lake with the Angara River, the accumulation rate of Fe and Mn in Baikal can be estimated as about 160 and 4.8 kt/yr, respectively. These values are presented in Figs. 1 and 2 as "accumulation (from mass balance)."

II. **The internal cycle of the elements** was characterized in the following way.

(1) *Biological uptake of the elements.* It is known that the major portion of Fe and Mn in Baikal is biologically accumulated by the plankton, and only a small fraction is fixed by the higher members of the trophic chain [8, 16]. The concentration of Fe in the phytoplankton of Baikal is 950–1400 µg/g dry weight [8] averaging about 1200 µg/g dry weight; the latter value was used in our calculations. According to Levina et al. [18], the concentrations may reach 3000–6000 µg/g. All of these values are comparable with data for seas and oceans: the average concentration of Fe is 900 µg/g in oceanic phytoplankton [19] and up to 1000–6000 µg/g in marine diatom algae. The concentration of Mn in Baikal plankton ranges from 40 to 100 µg/g [18] and averages 80 µg/g according to [8]. These values are also in agreement with those reported for the plankton of seas and oceans: the concentrations of Mn in the bulk phytoplankton of oceans and seas are 10–30 and up to 220 µg/g, respectively [10].

The suspended particulate material at the surface of Baikal water contains 12 [20] to 15% [21] of organic carbon (C_{org}). The suspended particles of surface waters are dominated by biological materials [22], and we assumed therefore that C/Fe = 15 : 0.12 = 125. The average C/Mn ratio of oceanic phytoplankton is 2000 (Lisitsyn, 1964; cited after [10]). According to [7], the level of biological accumulation in freshwater basins must be somewhat lower, and we assumed therefore that C/Mn = 3000 in Baikal.

The calculation of the biologic uptake of elements relies heavily on the magnitude of primary production, which was most thoroughly estimated for Baikal by K.K. Votintsev. However, the values reported by this author and his colleagues vary from 33.2×10^6 to 6.9×10^6 t C_{org} per year [1, 15, 23, 24]. The analysis of these estimates based on calculations of the production–destruction characteristics of the lake [25] shows that the most reliable value of primary production is 3.2×10^6 t C_{org} per year. This value is consistent with the later estimates of other authors (Goldman et al., 1992;

cited after [26]) and was used in our calculations. Given the primary production of Baikal of 33.2×10^6 t C_{org} per year [23], C/Fe = 125, and C/Mn = 3000, the biological uptake of iron and magnesium must be about 26 and 1.1 kt/yr, respectively.

(2) Sedimentation consists of biogenic and lithogenic fluxes. They can be calculated on the basis of recent results obtained by sediment traps, which were deployed for several years in the southern and northern parts of the lake [27]. Particles precipitating near the bottom at a depth of 1305 m in Southern Baikal and 885 m in Northern Baikal were collected in lower traps. The total particulate flux measured using these traps showed considerable seasonal and interannual variability ranging from milligrams to a few grams per square meter per day. The average total particulate flux is 117 g/(m^2 yr) in Southern Baikal and 94 g/(m^2 yr) in Northern Baikal [27]. An average value of 105 g/(m^2 yr) was used in calculations for the whole lake.

(a) Biogenic flux. The "pure" flux of organic carbon estimated from the C_{org} content in the material of the lower traps (remaining after the remineralization of organic particles during their settling in the water column) is 220 mmol C/(m^2 yr) in Southern Baikal and 125 mmol C/(m^2 yr) in Northern Baikal [27]. The average value is 172.5 mmol C/(m^2 yr) or 2.07 g C/(m^2 yr). Recalculation to the whole lake floor, which has an area of 31432 km^2, yields a total C_{org} flux of 67 kt/yr. The plausibility of this value can be checked by simple calculations. Given an average particulate flux of 105 g/(m^2 yr) and a near-bottom C_{org} flux of 2.07 g C/(m^2 yr), the concentration of C_{org} in the sedimentary material reaching the bottom must be 1.97%. This estimate is practically identical to the average content of C_{org} in the surface sediments of the lake (1.9% [28]).

Although the concentrations of Fe and Mn in the materials of the traps were not measured, it is possible to estimate their possible C/Fe and C/Mn values. Only about 13% of the C_{org} produced in the epilimnion is buried in the bottom sediments [29]. In biological suspended particles, Fe and Mn are mainly incorporated in the siliceous valves of planktonic diatoms. According to preliminary data, no more than 9% of diatom valves formed in the water column reach the bottom [28]. Thus, it can be roughly estimated that only about one tenth of both C_{org} and Fe and Mn incorporated in the valves of near-surface planktonic diatoms is deposited on the bottom. Therefore, despite the strong alteration of organic matter near the bottom, the C/Fe and C/Mn ratios of materials from the lower traps are approximately the same as in the surface plankton. Given the total flux of C_{org} for the whole lake (67 kt/yr) and C/Fe = 125, the biogenic flux of Fe is 0.54 kt/yr. Similar calculations for the biogenic flux of Mn yielded a value of about 0.03 kt/yr.

(b) Total (biogenic and lithogenic) flux. The transparent waters of Baikal contain a negligible amount of suspended particles, which are difficult to collect and analyze. Therefore, few data exist on the concentration of Fe and Mn in the suspended material. Data reported in [30] showed considerable variations in concentrations: by a factor of 15 for Fe and 2 for Mn. Our results [31, 32] revealed an even higher variability in Mn concentration in the lake suspended particles: from a few hundredths to a few tenths of a percent (by a factor of 10–20); these values are similar to those reported for the suspended particles of seas and oceans [10]. It can be assumed that the concentrations of Fe and Mn in the suspended particles of the lake are approximately equal to those in riverine suspended particles [32]: 4% Fe and 0.1% Mn. Multiplying these values by the average value of particulate flux, the annual Fe and Mn sedimentation in the lake is estimated as about 140 and 3.5 kt, respectively.

(3) Remineralization in the water column was determined as the difference between the biological uptake of an element and its biogenic flux. Using the above estimates, the annual values were estimated as about 25.5 kt Fe and 1.58 kt Mn.

(4) The diffusive flux from the pore waters of bottom sediments cannot be experimentally measured because of the great depth of the lake. Only a conventional value of possible flux can be calculated by multiplying the average concentration gradient of Fe and Mn near the water–sediment interface by their diffusion coefficients. Such estimates were carried out more than 20 years ago [16] and yielded extremely high values for diffusive fluxes. New measurements of Fe and Mn concentrations in the pore and near-bottom waters were performed during joint Russian–American expeditions. Pore waters were collected using a modern method of water squeezing from a core into a syringe [33]. The collected pore water passes without any contact with air through a system of filters, the last of which has a nominal pore diameter of 0.2 μ. The filtered bottom and poor waters were analyzed by direct current plasma atomic emission spectrometry (DCP–AES) at the United States Geological Survey. The error of determination was from 1 to 7%. The obtained data were used to calculate average concentration gradients at each of the 33 stations investigated. The gradients were subsequently averaged over the four main regions of the lake (table), and diffusive flux densities were estimated from these data. The total possible diffusive flux from the bottom sediments of the whole lake is about 3.7 kt Fe and 4.6 kt Mn per year.

(5) The intensity of element accumulation in the bottom sediments was calculated as a product of the average rate of sedimentary material accumulation in the lake and the concentrations of Fe and Mn in the surface sedimentary layer (table). The former value was obtained in the following manner. The input of suspended particles by riverine waters into the lake was estimated by several authors [15, 35–37] between 2×10^6 to 4.2×10^6 t/yr, with an average of 3.4×10^6 t/yr. On the other hand, various indirect estimates suggested

Estimation of the rate of Fe and Mn accumulation in the surface sediments of Baikal

Parameter	Southern Baikal	Central Baikal	Northern Baikal	Selenga Avandelta	Whole lake
Rate of sediment accumulation, t/yr (after [35])	0.15×10^6	0.18×10^6	0.45×10^6	2.2×10^6	3×10^6
Average Fe concentration in the surface sedimentary layer, %*	5.1	6.0	4.5	5.1	–
Average Mn concentration in the surface sedimentary layer, %*	0.25	1.00	0.63	0.11	–
Rate of Fe accumulation in the surface sedimentary layer, kt/yr	7.7	11.0	20	110	150
Rate of Mn accumulation in the surface sedimentary layer, kt/yr	0.4	1.8	2.8	2.4	7.5

* Calculated after [34].

an average sedimentation rate of 1.8×10^6 t/yr for Baikal [15, 38–41]. Combining these two values, the average rate of sediment accumulation in the lake is estimated as 2.6×10^6 t/yr. This result is similar to the value calculated from the most comprehensive dataset on the input of suspended particles with Baikal rivers, 2.95×10^6 t/yr [35], and this value (3×10^6 t/yr) was therefore used in further calculations. Their results showed that the surface sediments accumulate annually 150 kt Fe and 7.5 kt Mn on average (table). These estimates are shown in Figs. 1 and 2 as "accumulation."

(6) The inventory of elements in a water column is usually estimated in order to determine the time of element renewal in the lake. This parameter is calculated by dividing the inventory by the rate of dissolved output. The inventory was estimated by multiplying the average concentration in water by the volume of water, which equals 23600 km^3. It is known that the measurable concentrations of trace element in seawater significantly decreased during the past decades owing to the improvement of sampling and analysis methods. We believe that this is also true of low-mineralized (sum of ions is 96–98 mg/l [1]) Baikal water. The lowest concentrations measured in Baikal water were therefore used in our calculations: 5 μg/l Fe and 0.3 μg/l Mn [42, 43]. However, it cannot be excluded that the real concentrations can be lower than the published minimum values. On the other hand, our recent measurements of Fe concentration in particular samples of riverine water are comparable with the previously reported ones [42]. The calculated inventory of Fe in the water column is 120 kt, and the time of Fe renewal is 92 yr. The respective parameters for Mn are 7.1 kt and 18 yr. Thus, the conventional time of renewal of these elements is approximately 20–90 yr.

DISCUSSION

More than 95% of iron and manganese are supplied to Baikal by riverine input, whereas the atmospheric flux accounts for no more than 4–5% of the total input, even accounting for element precipitation on the water surface with aerosols (Figs. 1, 2). The river load is definitely dominated by suspended particles, whereas the contribution of dissolved species is only 1% for Fe and 8% for Mn. The major portion of Fe and Mn entering Baikal (92–95% by weight) remains in the lake accumulating in its bottom sediments. Coarse suspended particles settle near the mouths of tributaries, whereas fine particles are transported by the system of permanent circulation currents existing in Baikal and deposited along the shores and along the lateral limbs of these currents intersecting the lake [44]. Only the finest fraction of riverine suspended particles can be transported into the open lake contributing to the sedimentary flux. The grain size of this fraction in the ocean is less than 0.01 mm [10], which is probably also true of Baikal. A minor fraction of the sedimentary flux, 1% for Mn and 5% for Fe, can be related to dry deposition from the atmosphere.

The biological uptake of metal ions by phytoplankton in the limnological cycle includes both their consumption by living cells and interaction with the cell surface [45]. The biota of Baikal actively consumes iron and manganese: the biological accumulation of the elements is about 16–22% of the mass of Fe and Mn entering Baikal with the riverine input. The biological assimilation is higher (by a factor of two for Mn and five for Fe) than the input of dissolved elements to the lake. On the one hand, this indirectly supports the suggestion of [7] on the possibility of iron assimilation by aquatic organisms not only from solutions but also from insoluble colloids. This can occur owing to the photo- and enzymatic reduction of Fe(III) on the surface of cells by various phytoplankton species [46]. On the other hand, it is known that the availability of dissolved iron controls the development of phytoplankton in the ocean (e.g., [6]). It is possible that an iron deficit occurs periodically in Baikal and impedes the development of diatoms. This is supported by the pattern of vertical distribution of iron in a water column under ice [42], which showed that the concentration of Fe in the photic zone may decrease to zero at negative temperature stratification.

Taking into account the intense Fe and Mn uptake by plankton, the question arises whether the process of biological assimilation in Baikal is favorable for the transportation of these elements to bottom sediments. There is an opinion [19] that the chemical composition of bottom sediments from the halistatic regions of the ocean is inherited from the composition of living matter (plankton). According to Vinogradov [7], the different levels of biological accumulation of chemical elements can explain the difference in their contents between freshwater and oceanic sediments.

The biota of Lake Baikal (plankton) consumes 26 kt Fe and 1.1 kt Mn every year (Figs. 1, 2), but the biogenic flux of these elements is small: 0.5 kt Fe and 0.03 kt Mn. Thus, the biological material is extensively mineralized in the water column. Owing to this process, 97–98% of the mass of Fe and Mn assimilated by plankton are mineralized during the settling of biological particles in the deep waters of Baikal. In other words, only 2–3% of the mass of these elements reach the bottom after plankton death, i.e., biological assimilation does not play a significant role in the transportation of Fe and Mn to the bottom sediments of Baikal.

The deposited particles are accumulated on the floor. Since the bottom sediments of deep Baikal zones are oxidized, the contents of Fe and Mn in the surface sedimentary layer are significantly affected by the diagenetic redistribution of these elements. For instance, diagenetically enriched sedimentary layers may contain up to 100 times more manganese than the ambient sediments, whereas the enrichment factor of iron is rarely higher than ten (e.g., [12]). Owing to the diagenetic mobilization and redistribution of elements, the rate of manganese accumulation in surface sediments (7.5 kt/yr) is twice that of the sedimentary flux (3.5 kt/yr) (Fig. 2). Iron shows a lower geochemical mobility, and these two parameters are similar to each other, 140 and 150 kt/yr, respectively (Fig. 1). For the same reason, the rate of manganese accumulation (7.5 kt/yr) is 1.5 times higher than the value calculated from mass balance (4.8 kt/yr) (Fig. 2).

The newly calculated values of possible diffusive fluxes from the bottom sediments to the water column are an order of magnitude lower than previous estimates [16]. However, although in this study we used the best available techniques for the sampling of sediments, bottom water, and pore water and analyzed the samples with high accuracy, the obtained flux values (3.7 kt Fe and 4.6 kt Mn per year) are too high to be plausible. It is possible that part of fine colloids, which are amply produced during manganese oxidation, passes into pore water samples through ultrafine filters, and the measured Mn^{2+} concentrations are therefore overestimated. Another possible source of errors can be related to the calculation procedure, which is based on average rather than true concentration gradients, and the rough averaging of obtained fluxes in each region of the lake. Thus, it must be admitted that our efforts to calculate in such a way the possible diffusive fluxes of Fe and Mn between the bottom sediments and water proved to be futile.

The calculated time of renewal of these elements (20–90 yr) is much lower than the time of water renewal in Baikal (more than 300 yr [38]), which is in agreement with their rapid removal from the internal cycle owing to oxidation in oxygen-enriched water. If the real concentrations of Fe and Mn in the lake water are significantly lower, the inventory of these elements is lower and their cycling is even faster. Unfortunately, the lack of modern data on the concentrations of Fe and Mn in river and lake waters does not allow us to obtain more reliable estimates for the time of element renewal in Baikal.

All the presented calculations are approximate and depend on the quality of the data used. Nonetheless, they give some insight into the modern level of our knowledge on the functioning of the ecosystem and the role of various internal processes in it. Such estimates are a convenient way of summarizing data accumulated at a certain stage of studies and provide a means of controlling the reliability of the data.

CONCLUSIONS

The mass balance and internal cycle of Fe and Mn in Lake Baikal were estimated for the first time taking into account the dissolved and particulate input of these elements from the atmosphere and with fluvial waters, the composition of suspended particles in the lake, data on the particulate flux in the water column, and diffusive flux from the pore water of sediments. The following inferences can be drawn. Most of the elements (more than 95%) are delivered to Baikal with fluvial waters, mainly as particulate element flux, and 92–98% of the delivered elements remain in the lake accumulating in bottom sediments. Biota consumes a significant portion of Fe (16%) and Mn (22%) introduced by fluvial waters, but it is mainly remineralized during the settling of biological particles in the deep waters of the lake. As a result, biological assimilation plays a minor role in the transportation of Fe and Mn to bottom sediments. It is possible that iron may limit the development of planktonic diatoms, which is indicated by the fact that the level of its biological assimilation is higher than the input of dissolved iron into the lake. The intense diagenetic mobilization and redistribution of manganese result in that its accumulation rate in the surface sediments is twice the sedimentary flux and 1.5 times higher than the accumulation calculated from mass balance. Since iron and manganese are rapidly eliminated from the internal cycle, the calculated conditional time of their renewal in the water column is several tens of years, which is much shorter than the time of water renewal in Baikal (more than 300 years).

The obtained results suggest that the diffusive fluxes of elements from bottom sediments cannot be estimated from average concentration gradients near the water–sediment interface. They also indicate a need to obtain new reliable data on the concentrations of Fe and Mn in the water of Baikal and its tributaries.

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