ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 13, pp. 2194–2206. © Pleiades Publishing, Ltd., 2012.
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Manganese Forms and Their Content and Transformations in Freshwater Sediments (Analytical Review)

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Received December 23, 2011

Abstract—The concentrations of different manganese forms in the solid phase and pore water of freshwater sediments are discussed. Mechanisms of redox processes with participation of manganese are examined. Data on the concentration of manganese in freshwater nodules are summarized.

DOI: 10.1134/S107036321213004X

INTRODUCTION

Manganese plays an important role in the biotic turnover of matter and energy in water reservoirs. The lack of Mn(II) in plants makes photosynthesis impossible. Manganese(II) is capable of replacing magnesium(II) in DNA complexes, so that matrix syntheses continue but lead to different products. Manganese(III) and manganese(IV) oxides and soluble Mn(III) complexes are the strongest (after oxygen) oxidants. At pH 7 they catalyze polymerization of organic compounds thus affecting generation of humus and oxidize humic and fulvic acids to bioavailable low-molecular-weight organic compounds. Manganese oxides firmly bind some heavy metals and microelements (Co, Ni, Ba, etc.) in the crystal lattice and determine their fate in a water body.

The primary source of Mn is volcanic rocks and glacial clastic deposits. Manganese compounds accumulate in the solid phase of bottom sediments and undergo transformations with partial transfer to pore solution. They are distributed along the sediment profile, enter into near-bottom water, and precipitate as authigenic minerals both inside sediments and on their surface. The mechanisms of transformation and distribution of Mn in the upper layers of sediments are related to physical, chemical, and biological processes and are extensively studied. Numerous publications that provide versatile representation of Mn fate in freshwater and seawater sediments and the absence of generalized data on this topic in Russian literature over the past decade have stimulated me to write a small analytical review.

CHEMICAL PROPERTIES AND MAJOR FORMS OF MANGANESE IN THE SOLID PHASE OF SEDIMENTS

Manganese is the 25th element in the Periodic Table. It forms chemical bonds with participation of both 4*s* and 3*d* orbitals. It may exist in several oxidation states from 0 to +7. Acid medium favors formation of Mn(II) cations, while strongly alkaline medium, anionic Mn(VI) complexes. Manganese(IV) derivatives (most frequently MnO_2) are formed in neutral, weakly acidic, and weakly basic media under aerobic conditions. The chemical behavior of Mn is characterized mainly by redox reactions. Increase in the degree of oxidation is accompanied by enhancement of the ability of manganese to form anionic complexes and binary compounds [1].

Manganese occurs in nature in three oxidation states, Mn(II), Mn(III), and Mn(IV). Biological systems contain only Mn(II) and Mn(III) compounds. Bivalent manganese exists only in solution, tervalent manganese occurs both in dissolved state and in solid phase, and quatervalent manganese, only in solid phase.

Uncomplexed Mn(III) ion is unstable in aqueous solution. It oxidizes water to produce Mn(II) and oxygen. Many Mn(III) complexes are quite stable; an example is the oxalate complex $[Mn(C_2O_4)_3]_3$ [2]. The major part of Mn(III) oxides in solid phase may be formed initially (over a period of several hours or days) as a result of abiotic autocatalytic oxidation of Mn(II) on the Mn(IV) oxide surface. Fast bacterial oxidation of Mn(II) to Mn(IV) is responsible for the prevalence of Mn(IV) in aqueous medium. Manganese(II) in solution is a weak reducing agent, whereas MnO_2 and MnOOH are strong oxidants.

Manganese makes up about 0.098% of the Earth's crust, and its concentration in soils is about 0.085%. Unlike iron, manganese in soil does not form associates with aluminosilicates but accumulates in the sand and silt fraction as oxide particles. Precipitation of Mn from solution at $pH < 8$ is very slow even at high concentration, and it occurs only in the presence of Mn-oxidizing microorganisms [3].

The following forms of occurrence of Mn in nature are distinguished: primary and secondary minerals, oxides and hydroxides, carbonates, organic substances, poorly soluble salts, and readily soluble and adsorbed forms. Abundant Mn compounds are its oxides occurring as the following minerals: manganosite (MnO) and pyrochroite [$MnO\cdot H_2O$ or $Mn(OH)_2$] which contain Mn(II), braunite (Mn_2O_3) and manganite ($Mn_2O_3\cdot H_2O$ or MnOOH) which contain Mn(III), pyrolusite (MnO_2), and hausmannite [Mn_3O_4, a mixture of Mn(II) and Mn(III)] [4].

Manganese(IV) oxide MnO_2 is the final product of Mn(II) oxidation; it is also formed via disproportionation[1] of dissolved Mn(III) complexes [5]. Manganese dioxide in aqueous solution indispensably forms relatively stable needle-shaped colloidal hydroxide. Like most metal hydroxides, MnO_2 is characterized by a large specific surface which ranges from 150 $m^2\,g^{-1}$ for γ-MnO_2 to 300 $m^2\,g^{-1}$ for δ-MnO_2 [6].

Surface-bound protons and hydroxide ions may exchange on the MnO_2 surface as a result of variation of the relative activities of these ions in solution. Insofar as H^+ and OH^- are potential-determining ions, the surface charge of MnO_2 depends on pH. Within pH 5–11 colloidal aqueous manganese dioxide (sol) possesses a net negative surface charge and is the most stable at pH 7. Organic colloids do not affect its stability. Silica precipitates Mn sol only in the presence of Ca^{2+} [7].

The other MnO_2-containing minerals found in sediments and soils are todorokite $(Mn^{2+}, Ca)Mn_3^{4+}O_7\cdot nH_2O$, birnessite $(Na, Ca, K)_{0.6}\cdot(Mn^{4+}Mn^{3+})_2O_4\cdot 15H_2O$, vernadite $(Mn^{4+}, Fe^{3+}, Ca, Na)\cdot(O,OH)_2\cdot nH_2O$, and hollandite $Ba(Mn^{2+}Mn^{4+})_8O_{16}$ [7, 8].

Apart from oxides, seawater and freshwater sediments often contain rhodochrosite (manganese carbonate $MnCO_3$), usually as isomorphous mixtures with Fe, Ca, and Mg. It constitutes the major Mn-containing mineral in anoxic medium with pH values from neutral to weakly alkaline. The rate of its formation increases in parallel with CO_2 partial pressure and decreases as the concentration of fulvic acids increases at constant levels of supersaturation [9]. Calcium-rich rhodochrosite was found in sediments of the central part of Baltic Sea [10]. The pore water of sediments from Long Island Sound was also supersaturated with respect to $MnCO_3$ [11]. Rhodochrosite precipitates from water in Lake Baldegg (Switzerland) [12]; it is generated in sediments of Lake Michigan [13]. Rhodochrosite is the major Mn mineral in soils in an industrially polluted wetland in France [14]. Manganese carbonate also dominates in soils and sediments in mangrove systems of Brazil [15].

The occurrence of alabandite (manganese sulfide MnS) in anoxic freshwater sediments is discussed in the literature. Oversaturation of sediment pore water with MnS was found in the deep-water area of Lake Geneva, where the total sulfur content of sediments attained 2% but the mineral itself was not detected [16]. Despite supersaturation with respect to MnS, there are no proofs for its precipitation from sediment pore water from Lake Baldegg and Lake Greifen (Switzerland) [17]. Sediments with a high Mn(II)/Fe(II) ratio in mackinawite (FeS) formation areas contained mackinawite particles with a MnS content of several mole percent. Presumably, MnS was formed via adsorption of Mn(II) on mackinawite, and the adsorption efficiency decreased as the salinity of pore solution increased [18]. In sediments of meromictic Lake Suigetsu (Japan) Mn is incorporated into iron sulfides, e.g., into pyrite (FeS_2) [19]. All marine pore waters are supersaturated with respect to MnS_2 [11]. Thus some amount of manganese sulfides occurring in freshwater sediments is unlikely to appear as a result of precipitation from pore solution even though the latter is supersaturated with respect to these compounds. It is more probable that this is the result of manganese adsorption by iron sulfides and subsequent co-precipitation.

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[1] Disproportionation is simultaneous oxidation and reduction of a chemical element in a single process: $2Mn^{III} + 2\,H_2O \rightarrow Mn^{II} + MnO_{2(t)} + 4H^+$.

Apart from minerals, manganese forms isolable by sequential chemical extractions may be distinguished in sediment solid phase. The most widely used sequential extraction procedure was developed by Tessier to study forms of occurrence of heavy metals (HM). This procedure has a number of drawbacks, including incomplete dissolution of carrier phases, dissolution of secondary geochemical phases, and incomplete removal of dissolved metals due to re-adsorption, reprecipitation, or change of the oxidation state. Comparison of three sequential extraction procedures for heavy metals in marine sediments showed that the Tessier procedure gives the lowest concentration values for the acid-soluble and oxidable fractions [20]. Therefore, in keeping with the requirements of particular studies, many authors make use of modified Tessier's procedures which often give hardly comparable fractions. Several major HM-bearing components (including Mn-containing) are generally determined, namely iron and manganese carbonates, oxides, and hydroxides, clay minerals, and humic substances (organic matter) [21].

Sequential extractions also separate exchange and adsorbed fractions. Exchange fraction is represented by Mn cations bound to sediment solid phase (clays, organic substances, and Al, Fe, and Mn oxides and hydroxides) via electrostatic forces. In adsorbed fraction manganese is retained on the surface of amorphous films formed by Fe, Al, and Mn oxides, silica, and aluminosilicates and poorly crystallized oxide, carbonate, and phosphate films.

Table 1 contains some data characterizing manganese forms according to Tesseir or modified procedures. Despite the diversity of these data, the items in Table 1 can be grouped. Manganese compounds associated with sulfides, carbonates, and organic substances dominate in sediments of Rybnic reservoir used for cooling of water and marine lagoon sediments. Sediments of Góreckie Lake and Lake Geneva contain mainly manganese compounds with carbonates. The carbonate fraction of sediments from Geneva Lake contain 50–80% of total Mn. Sediments in Australian estuary and in the Rhine are enriched in adsorbed manganese, and those in Kainji Lake of Nigeria and wetland in France, in exchange Mn. Finally, manganese associated with iron and manganese oxides and hydroxides dominated in sediments from Dnepr water reservoirs, as well as from the US wetland.

High concentration of sulfide-bound manganese in sludge from Rybnic (Table 1) was not discussed in [22]. However, it may be presumed that water therein contain a lot of sulfates (taking into account that the reservoir is used as cooling agent for heat power plant) which are reduced to hydrogen sulfide under anoxic conditions, and hydrogen sulfide reacts with iron oxides: $3H_2S + 2FeOOH \rightarrow FeS + FeS_2 + 4H_2O$. Anaerobic oxidation of hydrogen sulfide with MnO_2 according to the equation $H_2S + 4MnO_2 + 2H_2O \rightarrow SO_4^{2-} + 4Mn^{2+} + 6OH^-$ produces pore-water manganese which is adsorbed by iron sulfides. Analogous processes may occur in sediments of marine lagoon (Italy), leading to increased concentration of manganese sulfides. This assumption is consistent with the trend of variation of Mn content of water in Rybnic reservoir during aeration (Table 1). Aeration of water involves oxidation of iron sulfides in the upper layers of sludge (the depth of oxygen penetration into sludge is 0.7 cm [31] and more). A part of iron sulfide-bound manganese is released to pore water, so that its concentration decreases. Aeration is also accompanied by appreciable reduction of the manganese carbonate content (Mn_{carb}) and the total Mn content of sludge. Presumably, enhanced degradation of organic matter in the upper layer of sediments leads to decrease of pH, and manganese carbonate partly dissolves. As a result, Mn(II) enters into pore solution and then into water.

The occurrence of manganese in sediments in the carbonate form (rhodochrosite) is typical primarily of carbonate lakes where $CaCO_3$ precipitates from water. Geneva Lake is not an exception, as well as Góreckie Lake in Poland. According to the X-ray absorption spectroscopy data, the major form of manganese in soils of wetland in France is also rhodochrosite throughout a year. The authors believe that Mn carbonates develop on oxide and silicate soil films [14].

The total concentration of Mn in fine-grain sand of Kainji Lake of Nigeria is considerably lower than in other sediments. A high relative concentratin of exchange Mn in sediments indicates high reactivity of manganese compounds [30]. Increase in the relative concentration of the most mobile fraction was noted for samples with lower clay particle content. This is consistent with the concept implying accumulation of Mn in the sand and silt fraction of soils [3, 8].

In Dnepr reservoirs, the major form of manganese is its compounds associated with Fe and Mn oxides, which is typical of low-carbonate water bodies in

Table 1. Manganese content of the sediment solid phase determined by Tessier's sequential extraction procedure and its modifications

Water reservoir	Mn_{tot}	Mn_{exch}		Mn_{adsorb}		Mn_{org}		Mn_{carb}		$Mn_{sulfide}$		OS, %	Reference
	mg kg $^{-1}$	mg kg $^{-1}$	%[a]	mg kg $^{-1}$	%	mg kg^{-1}	%	mg kg $^{-1}$	%	mg kg $^{-1}$	%		
	Rybnic reservoir, Poland												[22]
Before aeration	2336.4	173.6	7.3	11.4	0.5	548.3	26.9	681.0	28.7	922.5	38.9	26.9	
During aeration	1906.4	141.9	6.0	16.1	0.7	458.0	26.9	585.9	24.3	704.5	29.7	–	
Dnepr reservoirs, Ukraine	Mn_{tot}	Mn_{exch}		Mn_{oxide}		Mn_{org}		Mn_{carb}		Mn_{res}		OS, %	
	mg kg $^{-1}$	mg kg $^{-1}$	%	mg kg $^{-1}$	%	mg kg $^{-1}$	%	mg kg $^{-1}$	%	mg kg $^{-1}$	%		
Kiev	3450[b]	–	2.0	–	76.0	–	10.0	–	8.0	–	4.0	6.5	[23, 24]
Kanev	–	–	1.0	–	88.0	–	9.0	–	2.0	–	<1	11.3	
Kremenchug	2575[b]	–	<1	–	90.0	–	10.0	–	<1	–	<1	9.7	
Zaporozh'e	2920[b]	–	<1	–	93.0	–	6.0	–	<1	–	<1	9.5	
Kakhovka	1905	–	2.0	–	94.0	–	3.0	–	<1	–	<1	11.1	
Góreckie Lake, Poland	–	–	11	–	31	–	6.1	–	41	–	9.9	–	[25]
Lake Geneva, Switzerland	–	–	–	–	30	–	<10	–	50–80	–	60	–	[16]
Rhine, Germany	5830	–	–	–	32.4	–	3.8	–	–	–	–	–	[26]
Estuary, Australia	–	100	–	300	–	15	–	–	–	110			[27]
Wetland, France	1400–1700	53–1150	–	24–175	–	8.4–60	–	46–542	–	0.8–10	–	13.0	[14]
Marine lagoon, Italy	656	7.9±7.8	7.2	136±3.1	20.7	159±0.36	24.2	178±2.9	27.1	175±0.81	26.7	–	[28]
Kaindji Lake, Nigeria	55–116	–	27–50	–	23–30	–	15–29	–	–	–	–	–	[29]
Wetland, USA	600	130	22	200	33	100	17	120	20	50	8	60	[30]

[a] In percent of Mn_{total}, except for OS (organic substances).
[b] Dash denotes no data available.

moderate climate zone with low organic matter content. Manganese oxides are poorly adsorbed by negatively charged layered silicates, for they possess a negative charge over a wide pH range (see above). Therefore, manganese in sediments is not associated with alumosilicates. In aqueous systems clays exist as substrates covered by metal oxides or organic substances [28]. Exceptions are mixed-layered illite–smectite minerals that are capable of fixing a large amount of Mn [3].

It is believed that the concentration of organic manganese (i.e., bound to organic substances), as well as of silicate Mn (bound to clays) in sediments is generally low. This may be interpreted in terms of predominant formation of Mn^{2+} complexes with HSO_3^-, SO_4^{2-}, and phosphate ions rather than with organic compounds. The organic and exchange fractions in Geneva Lake constitute overall less than 10% of total Mn. Analogous values were found for Dnepr reservoirs (Table 1). However, the concentration of organic manganese in sediments of Rybnic reservoir, marine lagoon (Italy), and Kainji Lake of Nigeria was higher by a factor of 2–3 (27–29% of total Mn; Table 1). Similar values (24–27%) were given by other authors who estimated the fraction of organic manganese complexes in total Mn^{2+} content [32, 33]. It was recognized in 1990s that complexation of dissolved manganese by organic compounds may strongly affect manganese cycle at the oxic–anoxic boundary [5].

The concentrations of organic matter in Dnepr reservoirs (clayey silts) given in Table 1 correspond to earlier studies; analogous data for most other sediments are unavailable. This fact is even more surprising, taking into account that authors usually note almost exceptional role of microorganisms on the transformation of chemical compounds. The efficiency of microbiotic activity directly depends on the concentration and composition of organic matter.

Sediments in US wetland contain mostly manganese bound to Fe and Mn oxides and very little residual manganese, while the concentration of organic substances is high (60%). However, the relative Mn_{org} content is fairly low. A question arises so as to whether forms of occurrence and mechanisms of formation of manganese bound to organic substances in sediments of different water bodies and wetlands are identical.

The sequential extraction procedure for isolation of manganese from sediments is very laborious. Therefore, many authors believe to be sufficient to estimate the concentration of two or three manganese forms in sediments, namely total, acid-soluble (0.1 N H_2SO_4 or 10% HCl), and pore-water soluble. It is presumed that acid-soluble Mn content corresponds to the concentration of all mobile (i.e., bioavailable) Mn forms in sediment solid phase. The ratio of extractable and dissolved Mn in sediments characterizes variation of its mobility both inside a single water reservoir and ingoing from one reservoir to another.

If determination of inorganic manganese compounds is believed to be sufficient for some purposes, parallel (or sequential) oxalate and dithionite or citrate–dithionite–bicarbonate extractions are performed. By analogy with soils, oxalate extraction is presumed to isolate mainly amorphous manganese compounds from sediments, and dithionite extraction, the sum of amorphous and crystalline compounds. Addition to oxalate and dithionite extracts of pyrophosphate extract (before two preceding) makes it possible to quantify organic manganese in sediments. The selectivity of the above extractions is also fairly arbitrary, but in many cases good results are obtained.

Redshaw et al. [34] analyzed by the extraction method sediments collected from seven reservoirs in the Anglian Water region. The relative amorphous Mn contents were found to be similar and were 22–26% of the overall Mn content. However, the absolute concentrations of amorphous Mn in sediments of the seven reservoirs ranged from 0.09 to 0.27 mg g^{-1}. The relative content of organic Mn was 9–35% of total Mn (0.03–0.37 mg g^{-1}), which differs only slightly from the data given in Table 1. Significant (≥95%) correlations were observed between different Mn forms: $Mn_{org} \overset{0.97}{\text{—}} Mn_{amorph} \overset{0.77}{\text{—}} Mn_{cryst} \overset{0.90}{\text{—}} OS \overset{0.82}{\text{—}} Mn_{tot}$ (the underscored numbers are correlation coefficients). The concentration of Mn_{cryst} in silts is directly related to the concentration of organic substances (OS), which cannot be interpreted as a consequence of input of both these with runoff, for there is no significant correlation between the OS and Fe_{cryst} contents of sediments in the same reservoirs [35]. It may be presumed that increased organic matter content of sediments favors authigenic formation of Mn-containing minerals. There is no significant relationship between the OS and Mn_{org} contents of sediments, though it was found for Fe_{org} [35]. This means that the mechanisms of formation of Fe_{org} and Mn_{org} are different. The existence of a significant correlation between amorphous and crystalline forms of Mn and the absence of such correlation for analogous Fe forms indicates higher availability of Mn_{cryst} for bacterial transformation as compared to Fe_{cryst}. Probably, this conclusion is not new, but it points out that the procedures used for fractionation of Mn in sediments provide real and comparable results.

PORE SOLUTION

Manganese appears in pore solution as a result of bacterial transformation of Mn in sediment solid phase (primary of most mobile manganese forms). The concentration of Mn in pore solution of silty sediments in different reservoirs ranges from 0.04 to 74.5 mg l^{-1}, the concentration of Mn in the solid phase being 0.01 to 5.6% (Table 2). The Mn content of sediments from lake Nordbytjernet in Southeast Norway corresponds to that found for ferromanganese crusts and nodules (see below), although Mn occurs therein in scattered state. The concentration of Mn in pore water of sediments in the above lake was not determined. It reached 50–70 mg l^{-1} in anoxic water layers in the stagnation period [39]. Taking into account that organic substances are strong reducing agents toward Mn(IV) [33] (in the case of bacterial reduction) and that their concentration in lake sediments is fairly high (24%), equally high concentration of Mn in pore solution might be expected.

High Mn content (60 mg l^{-1}) was detected 6 cm up and down water–sediment boundary in wetland of France (Table 2), which indicated supersaturation with respect to rhodochrosite [14].

The ratio between the concentrations of Mn in pore water (Mn_{pw}) and sediment solid phase ($Mn_{s.ph}$) varies over approximately the same range as the concentration of Mn_{pw} and is 0.03–60.0 (Table 2). However, high (or low) concentration of Mn_{pw} not always matches that of $Mn_{s.ph}$.

There are a few data on the relation between Mn contents of pore water and solid phase of sediments. A reverse relation was found in 12 of 30 core samples of sediments from Green Bay (Lake Michigan), 5 core samples displayed direct relation, and 13 core samples showed no relation [47]. Presumably, the presence or absence of a relation between Mn_{pw} and $Mn_{s,ph}$ is determined by specificity of nodule formation (iron manganese nodules containing up to 22% of Mn were found in sediments from Green Bay).

An intra-annual relation between Mn_{pw} and $Mn_{s,ph}$ contents of silts from the Mozhaisk water reservoir was found for the 0–2- and 10–15-cm layer, whereas the 2–10-cm layer lacked such relation [45]. This pattern was rationalized by properties of structures formed in different silt layers in the course of transformation and redistribution of substances. The relations between Mn_{pw} and $Mn_{s,ph}$ during the under-ice period and in the remaining part of a year are different: the reverse relation for the 0–2-cm layer turns direct; by contrast, for the 10–15-cm layer, the direct relation in the under-ice period changes to reverse in the remaining part of a year. The reasons were considered in detail in [45].

Pore solution of sediments from Kiev reservoir contains dissolved Mn mainly as uncoordinated ions whose fraction is no less than 75–95% of Mn_{tot}. Complexed Mn (to organic compounds) is represented by 80–90% by complexes with molecular weights of 60–70 and more than 70 kDa. About 40% of dissolved Mn in the anoxic hypolimnion of eutrophic lake Fukami-ike (Japan) occurs as organic substances with a molecular weight of 1000 to 50000 Da [49]. The major part of Mn in organomineral compounds in soils is also bound to relatively high-molecular fractions [50]. Low stability of organic manganese complexes was noted in [48].

Until recently pore-water manganese was considered to be exclusively Mn(II). Trouwborst et. al. [51] showed that soluble Mn(III) was produced at the top of the suboxic zone by oxidation of Mn(II) and at the bottom of the suboxic zone by reduction of MnO_2 reduction. In each case, Mn(III) was stabilized by unknown natural ligands. The concentrations of soluble Mn(III) in the Black Sea constituted up to 100% of the total dissolved Mn pool (0.28 mg l^{-1}). Micromolar concentrations of dissolved Mn(III) were found in the Chesapeake Bay (USA). The authors concluded that Mn(III) should be ubiquitous at all water column and sediment oxic–anoxic interfaces in the environment [51]. The formation of Mn(III) via oxidation of Mn(II) and reduction of Mn(IV) inside marine and freshwater sediments cannot be ruled out.

Dissolved Mn(III) is a strong oxidant which may be important in natural biogeochemical processes. At a concentration of 0.28–550 mg l^{-1} in neutral medium manganese(III) forms a strong complex with pyrophosphate anion. Manganese(III) pyrophosphate is capable of acting as terminal electron acceptor in microbiological systems. *Schewanella putrefaciens* strain MR-1 catalyzed the reduction of Mn(III)-

Table 2. Manganese content of the solid phase and pore water in top-layer sediments

Water reservoir	Solid phase, Mn, mg g^{-1}		Pore water, Mn, mg l^{-1}	Reference	Mn$_{pw}$[a]/Mn$_{s.ph}$
	total Mn	Fe/Mn			
Lakes					
Punnus-Yarvi (Krasnoe), Russia	1.8	3.2	12–32	[36]	≥6.7
Geneva	2.0		20.0	[16]	10
Zugersee, Switzerland	0.73		≤7.0	[37]	~0.09
Baldeggersee, Switzerland	–		≤18.2	The same	
Lilla Ullevifjärden, Sweden	>10		3.3–40.0	[38]	–
Nordbytjernet, Norway	56.0	3.3	–	[39]	–
Rostherne Mere, England	8.1		22.5	[40]	2.8
Mullett, USA	~1.4	14.3	0.04	[41]	0.03
Mendota, USA	1.3	0.06	–	[42]	–
Feldsee, Germany	1.5–1.8		3.0–7.7	[43]	~6.5
Ursee, Germany	0.13		0.4	The same	3.1
Charlotte, Nova Scotia	17.0		0.66	[44]	0.04
Khadzhibey Estuary, Ukraine	0.88		6.6	[24]	7.5
Water reservoirs					
Mozhaisk, Russia	0.1–9.5[b]	–	30.0–74.5	[45]	4.9[c]
Kiev, Ukraine	2.1	–	5.1	[24]	2.4
Dubăsari, Moldova	0.6	–	0.11–0.18	[46]	~2.4
Wetland, France	1.4–1.6	–	60.0	[14]	40

[a] The subscript "pw" stands for pore water, and "s.ph," for sediment solid phase.
[b] Mn$_{tot}$ is manganese extractable with 0.1 N H_2SO_4.
[c] Average annual data.

pyrophosphate with formate or lactate as electron donors. The MR-1-catalyzed reduction of Mn(III) was inhibited under aerobic conditions but only slightly under anaerobic conditions upon addition of an alternate electron acceptor, nitrate. The reduction of Mn(III) can be coupled to the cycling of Fe, S, and C [5].

Manganese(III) readily disproportionates into Mn(II) and MnO_2. The rate of its disproportionation decreases at low pH, high concentration of Mn(II), and low concentration of Mn(III). Spontaneous disproportionation occurs at a Mn(III) concentration exceeding 100 μM (5.5 mg l^{-1}) [52].

MECHANISMS OF TRANSFORMATION OF MANGANESE COMPOUNDS

Manganese forms in sediments are determined by processes of its transformation. The main processes are adsorption, oxidation/reduction, ligand binding, mineral precipitation/dissolution, and assimilation by living organisms. In the present review redox processes with participation of manganese are considered, taking into account that they are most important in its turnover and studied in most detail.

Manganese(II) ion is energetically very stable; its anoxic oxidation is slower by four to five orders of magnitude than the oxidation of Fe [53]. The rate of oxidation of Mn(II) depends on pH, concentration of O_2, and temperature, and it increases with increase of these parameters. Oxidation of Mn(II) can be biotic and abiotic. Abiotic oxidation is possible in two ways: (1) fast autooxidation in solution at pH > ~8.5, and (2) slow oxidation catalyzed by hydroxy carboxylic acids at pH > 7.5.

At pH ~8.5 and higher intermediate cationic oxide complexes are formed which mediate sorption of Mn^{2+} on Mn oxides. The sorption process is faster than initial oxidation of Mn^{2+}. Further oxidation of Mn^{2+} in the sorbed complex may occur at a different rate than the initial oxidation. As a result, thermodynamically predictable redox equilibrium is attained in several hours or days [54]. Oxides formed via abiotic oxidation are characterized by lower specific surface areas than those obtained by biooxidation [55].

Microbial oxidation of Mn(II) is faster by five orders of magnitude than abiotic oxidation of Mn in natural water [56]. The major oxidants are bacteria, their spores, and fungi. The main path of bacterial oxidation of Mn(II) is enzymatic. Although bacteria that are capable of oxidizing Mn(II) are phylogenetically different, they all need multicopper oxidase-like enzyme to oxidize Mn. The oxidation of Mn(II) to Mn(IV) occurs via soluble or enzyme-complexed Mn(III) as intermediate oxidation product. The primary Mn(IV) biooxide formed is a phyllomanganate most similar to δ-MnO_2 or acid birnessite ($Na_{0.3}Ca_{0.1}K_{0.1}Mn^{4+}Mn^{3+}O_4\cdot 1.5H_2O$) [57].

Mature dormant spores of *Bacillus* sp., strain SG-1, are capable of oxidizing Mn; on the other hand, vegetative cells of the same strain can reduce MnO_2 under low-oxygen conditions. Presumably, manganese was oxidized by a spore component, possibly an exosporium or spore coat protein. The oxidative activity decreased when spores were completely incrusted, i.e., their active sites were blocked. The oxidation is of Mn(II) is possible over a wide range of its concentration, from 1 nM to 25 mM ($\sim 0.06\times 10^{-6}$ to 1.4 g l^{-1}) [56].

Apart from bacteria, some fungi oxidize Mn(II) under oxic conditions. A large amount of manganese oxide accumulates in soils around fungal hyphae[2] (Fig. 1). Although fungi are believed to be active only in oxic environment, recent studies have shown that fungi may adapt to anoxic respiration via reduction of nitrates to NO and N_2O (Fisher et al., 2009, cited by [59]).

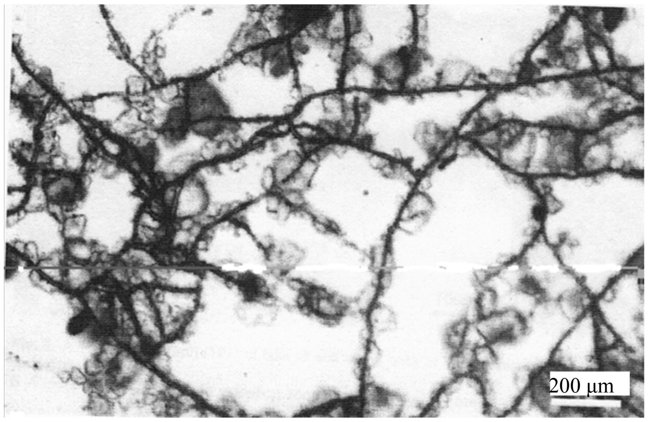

Fig. 1. Manganese oxides on the fungal hypha surface [58].

Three mechanisms of Mn(II) oxidation are generally considered:

(1) By the action of $OH^{\cdot\cdot}$ and $H_2O^{\cdot}$ radicals generated as a result of aerobic/anaerobic respiration of microorganisms in low-oxygen environment; the oxidation of Mn^{2+} produces Mn(III) and Mn(IV) oxides [60];

(2) By the action of multicopper oxidases which catalyze most microbiological (induced by bacteria and fungi) Mn(II) oxidation processes [57]; multicopper oxidases mediate electron transfer from Mn^{2+} to O_2, i.e., the concentration of oxygen should be sufficient for their functioning [61];

(3) With heme-containing manganese peroxidases which oxidize Mn(II) to Mn(III):

$$2Mn^{2+} + 2H^+ + H_2O_2 \rightarrow 2Mn^{3+} + 2H_2O.$$

Manganese(III) thus formed oxidizes lignin or other complex organic substances, being reduced again to Mn(II) [62].

The reduction of manganese oxides with anaerobic microorganisms is a facultative process; enterobacteria and bacilli are the most active species [63]. Microorganisms are capable of reducing manganese oxides both in solution and in the solid phase, and the process can occur under both oxic and anoxic conditions. The reduction of Mn(IV) to Mn(II) starts when the oxygen concentration in water is 2–3 mg l^{-1} (1/3 to 1/4 of the saturation level) [64]. Obligate anaerobes have been

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[2] Hypha is a long, branching filamentous structure of a fungus, which consists of numerous cells or contains numerous nuclei.

unknown until 1993 when they were classified as *Geobacter metallireducens* [65].

Manganese oxides can be reduced directly with Mn reductase, or the reduction can be purely chemical. In the chemical process, the reducing agents can be Fe(II) and sulfides generated by microbiologically mediated reactions [66] which provide energy for bacterial growth [67]. Most readily degradable organic matter is incapable of reducing Mn(IV) otherwise than enzymatically [68].

Bacterial reduction of Mn(IV) in the upper 1–2.5-cm layer of sediments in the Black Sea contributes 13 to 73% to the oxidation of C_{org} [69]. In the Kandalaksha Gulf of the White Sea Mn(IV) plays the key role (almost 100%) in anoxic oxidation of organic substances in a few top centimeters of sediments [70]. Mesocosm experiments showed that the contribution of Mn reduction to the overall mineralization of organic substances in the presence of polychaetes is equal to zero (polychaetes aerate sediments). However, the control value was also as small as 0.1% [71]. A probable reason is low Mn content in the environment. Estimations of the role of Mn(IV) in oxidation of freshwater sediments are not familiar to the author.

Thus the reduction of Mn oxides can occur under both anoxic and oxic conditions, while the oxidation of Mn occurs mainly under oxic or suboxic conditions. Both processes can follow both biotic and abiotic pathways. This raises the question on the mechanism ensuring intra-annual fluctuations of mobile Mn content of the solid phase of sediments from the Mozhaisk reservoir in the Eh range from –130 to +40 mV and pH range from 6.80 to 7.45 [45].

The review would be incomplete without considering issues related to the formation and occurrence of ferromanganese nodules. The overwhelming number of recent publications deal with marine and oceanic concretions, and relevant monographs are available. While briefly summarizing the results of studies on freshwater sediments I thought it necessary to discuss this problem as well.

FERROMANGANESE NODULES (FMN)

Ferromanganese nodules (concretions) are authigenic mineral concretions consisting of iron and manganese hydroxides (with inclusion of other elements) and terrigenous material, which are formed on the bottom of lakes, seas, and oceans, as well as in soils and swamps.

Ferromanganese nodules in most lakes (Baikal, Onezhskoe, Michigan, Punnus-Yarvi, Imandra, etc.) occur as crusts (plane concretions) and nodules (spherical concretions) [47, 72–75]. Tubular concretions were recently found for the first time in Lake Baikal [76]. Three types of FMN in lake George (USA) were recognized: spherical, discoidal, and lumps [77]. Four distinct morphotypes of FMN from Second Connecticut Lake were described (Fig. 2): irregular laminated convex plates that form concentric rings around a nucleating center (A), continuous pustular pavements that extend >10 m^2 (B), nonlaminated and nonnucleated masses with pebbles scattered throughout the matrix (C), and small nonnucleated laminated structures >2 cm (D, E, F). Their growth rate was estimated at 26 mm/100 years [78]. The growth rate of concretions in three Canadian lakes was considerably higher, 0.1–0.5 mm $year^{-1}$ [79]. For comparison, the growth rate of oceanic concretions is 1–3 mm/1000 years [80].

The origin of nodules may be both diagenetic and microbiological [74]. Nodules often occur on the sediment surface but may also be found at some depth, being completely buried in silt.

The size of IMC varies from a few millimeters to more than 10 cm. Ferromanganese nodules in Second Connecticut Lake reach 46 cm in diameter. Nodule abundance depends strongly on sedimentation rates, with the most abundant deposits occurring where sedimentation is lowest [81]. The concentration of Mn in FMN (Table 3) varies over a wide range, from 0.15 to 35.9%, the Mn/Fe ratio being 0.01 [82] to 4.0, depending on the location.

In Oneida Lake (NY, USA) precipitants from the lake water and the surfaces of nodules at the sediment–water interface are enriched in Mn, whereas nodules buried in lake sediments have surface layers enriched in Fe [83]. The absolute and relative Mn contents of nodules from Onezhskoe Lake (occurring in the littoral zone) are higher than in ore crusts (occurring mainly in the profundal zone). The Mn/Fe ratio is 0.9 and 0.03, respectively [73]. Nodules in podzolic soils contain 1.6 to 13.1% of Mn, and its concentration increases reversely to the nodule size [84].

In all cases, a tendency to separate accumulation of Mn and Fe is observed, which is determined by different stabilization fields of their compounds. Even insignificant variation of Eh and pH induce strong changes in the Mn/Fe ratio [73].

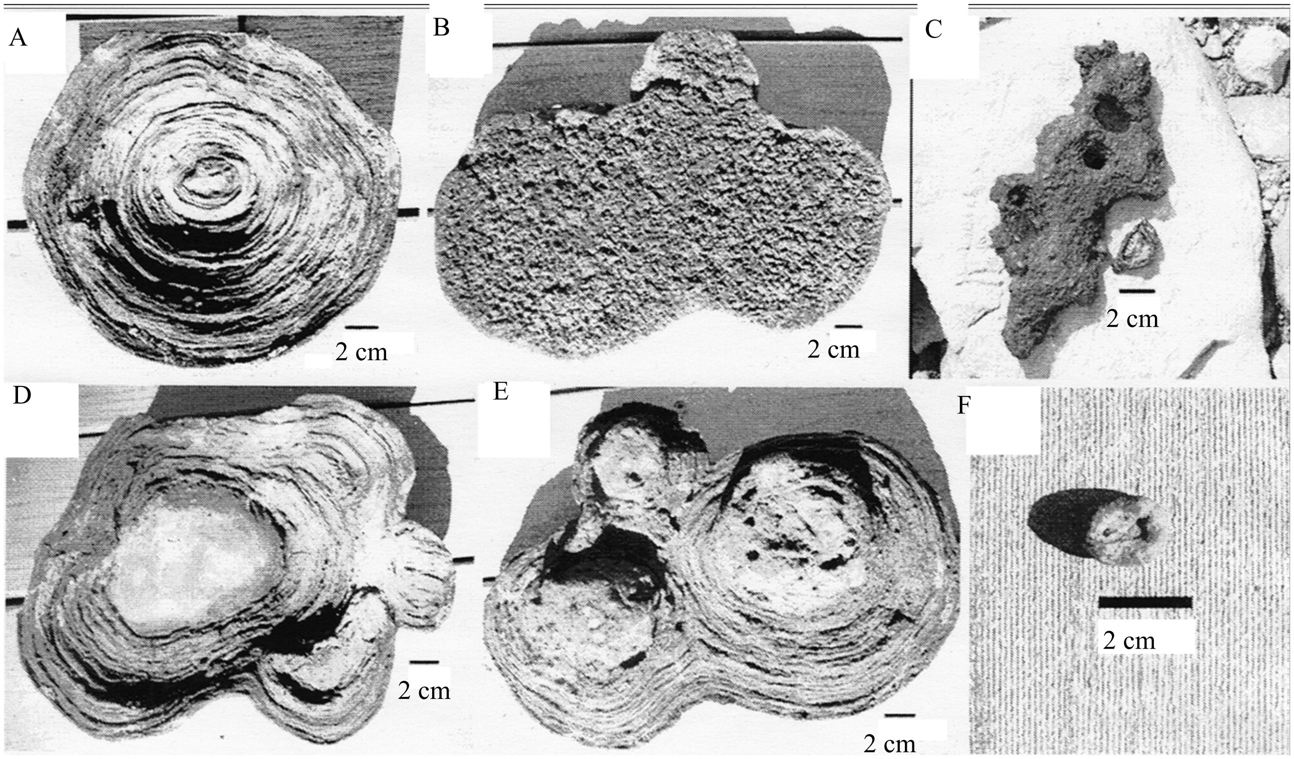

Fig. 2. Ferromanganese nodules from Second Connecticut Lake (USA) [77]; for comments, see text.

Ferromanganese nodules are natural collectors of a number of microelements (Co, Ni, Zn, etc.). Diagenetic formation of ores is accompanied by accumulation of organic matter in nodules. The average organic matter content of ore crusts from Onezhskoe Lake (10.2%) is twice as high as that of sediments (5.7%) [73]. Soil concretions (hardpans) displayed a direct relation between Fe/Mn ratio and C_{org} [74]. Analogous relation was found for oceanic nodules. This relation is likely to be determined by effective participation of organic ligands in the formation of iron hydroxides and their weak contribution to the formation of manganese oxides in the initial stage of generation of nodules [85].

Ferromanganese nodules have porous structure and a large specific surface (200–400 $m^2\ g^{-1}$) which is not typical of natural minerals. However, their specific surface area is a minor factor responsible for their sorption capacity; a more important factor is the degree

Table 3. Manganese content of freshwater ferromanganese nodules

Lake	Appearance of FMN	Depth, m	Mn content, %	Mn/Fe	Reference
Baikal, Russia	Crusts Nodules	– –	0.61–4.9 0.15–3.8	0.74 to 4.0 0.68 to 1.3	[72]
Michigan, USA	Nodules	–	≤22	0.15–2.13	[47]
Punnus-Yarvi, Russia	Nodules	2.5–3.0	≤26	0.2–3.1	[74]
Imandra, Russia	Crusts	-	8.17	0.27	[75]
George, USA	Nodules	21–36	3.6	0.22	[76]
Grand, USA	Nodules	–	33.0	–	
Three Canadian lakes	Nodules	0.5–2.0	15.7–35.9	0.43–2.56	[78]

of oxidation of nodules which increases as a result of ion-exchange sorption on non-stoichiometric manganese oxide constituting the base material of nodules [86]. Additional precipitation of Mn onto nodules is favored by catalytic effect of already precipitated MnO_2 [73].

In ferromanganese nodules from Lake Baikal Mn is represented by psilomelane and vernadite [87], in nodules from Punnus-Yarvi Lake, by psilomelane and more rarely rhodochrosite [36], and in nodules from Lake Georg, by birnessite and amorphous compounds [77].

CONCLUSIONS

(1) The major manganese compounds in freshwater sediments are its oxides and carbonates.

(2) The oxidation and reduction of manganese compounds is generally catalyzed by microorganisms (bacteria, bacterial spores, and fungi).

(3) Manganese oxides can be reduced under both anoxic and oxic conditions, whereas the oxidation of Mn occurs mainly under oxic conditions.

(4) A direct relation exists between the concentrations of crystalline Mn and organic matter in sediments of seven lakes in England. The concentration of Mn bound to organic substances does not depend on the concentration of the latter.

(5) The concentration ratio of Mn in the solid phase and pore water of sediments ranges from 10^{-2} to 10^{2}. The maximal (minimal) concentrations of soluble and solid-phase Mn do not always match each other.

ACKNOWLEDGMENTS

The author thanks the staff of the Institute of Water Problems, Russian Academy of Sciences, for help in obtaining scientific literature.

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