EWA CZERWIENIEC*

IRON AND MANGANESE IN SURFACE WATER ENVIRONMENT – DIFFERENCES AND SIMILARITY IN PHYSICAL AND CHEMICAL CYCLES

In this paper, physical and chemical processes of iron and manganese compounds in surface water environment were studied. Special attention was paid to the boundary area (between bottom sediment and overlying water) which was the place where gradients in physical, chemical and biological properties were the greatest. The oxidation and reduction processes of these metals in the bottom sediment and in the overlaying water were presented. In the redox chemism of manganese and iron, two significant differences which – depending on environment – were responsible for the differences in transport processes and concentration in both sediment and water were described. Similarity and differences occurring as a result of seasonal oxygen stratification in lakes were taken into consideration. Transport processes of soluble and particulate compounds of these elements were considered.

1. INTRODUCTION

Iron occurs abundantly in the earth's crust (5.6%) (DOJLIDO [11]). It is washed out from rocks, soil and from sewage (mainly industrial) and mining water and enters natural water. This element in a soluble form forms bivalent compounds. Its concentration approaches several mg/dm^3. In the form of trivalent iron, it is found as chelate compounds, humic acids and polysulphides. The iron form depends on pH, redox potential, organic compound content, oxygen and carbon dioxide concentrations and microorganism activity.

Manganese also occurs abundantly in natural water. Manganese content depends on its wash out from soil, less – on the wastewater inflow. The concentration of manganese in this environment seldom exceeds 1 mg/dm^3 (DOJLIDO [11]). Soluble manganese is found as Mn^{2+}, while its oxides – as particles (insoluble) in which it is trivalent and tetravalent – are found as different crystallographic modifications.

* Department of Environmental and Chemistry Engineering, Rzeszów University of Technology, 2 Wincentego Pola Street, 35-959 Rzeszów, Poland. tel. (+48-17) 8651788, e-mail: eczer@prz.rzeszow.pl

Because iron and manganese form a great variety of forms of various oxidation number, for the sake of simplicity it can be assumed that bivalent cations are the only soluble and reduced forms. The metals occurring in higher oxidation state are the particulate forms.

2. REDOX PROCESSES

In many lakes, the content of dissolved oxygen is reduced during summer stratification, which controls redox cycles of iron and manganese. With the decrease in oxygen content the redox potential decreases which causes reduction of the oxides to soluble forms. There are two important differences in the redox processes of these metals:

1. Reduction of the manganese oxides Mn(IV) to soluble form Mn(II) occurs at a higher potential (that is at a higher oxygen concentration) than reduction of iron (Fe(III) to Fe(II)).

2. The oxidation of dissolved iron (to particulate oxide (Fe(III))) is quicker than the oxidation of dissolved manganese (to Mn(IV)).

These kinetic and thermodynamic differences have some implications. For example, the reduction of Mn^{4+} to Mn^{2+} begins at dissolved oxygen concentration approaching 2–3 mg O_2/dm^3 as found in laboratory experiment with lake sediment (SHOLKOVITZ [26]). But Fe^{3+} reduction occurs mainly in anoxic conditions. So in anoxic lake with a mobile redox interface, iron and manganese redox processes differ to some extent, depending on time and season. It can be expected that in some lakes with low oxygen concentration, the flow of Mn^{2+} from sediment and interstitial water to hypolimnion is preceded by Fe^{2+} flow. Similarly, we can predict that dissolved Fe(II) that flows from anoxic sediment to hypolimnion will be quickly precipitated on an oxic–anoxic interface, while manganese(II) would be transferred to oxic part of the lake, where it would be slowly oxidized.

During summer the increase in Fe(III) concentration in hypolimnion coincides with low oxygen concentration in water and anoxic conditions on the sediment surface. A continuous formation of a particulate suspended iron during May and June results from a fast oxidation of Fe^{2+} ions that diffuse from sediment to overlying water (WU et al. [36]). In summer, under more reducing conditions, dissolved Fe(II) compounds are accumulated in the hypolimnion because particulate iron has been reduced and dissolved. Manganese is not accumulated in the hypolimnion as suspended particles of Mn(IV) oxides because of reducing conditions. The rate of manganese oxidation is so slow that it can be transported via termocline to epilimnion without a considerable amount of precipitating oxides. This results from the fact that a reduced manganese, which comes through an oxygen layer, is not completely oxidized because abiotic manganese oxidation at pH $\leq$ 8 is exceptionally slow, while biotic oxidation occurs preferentially at the oxygen concentration ranging from 1 to 2 mg/dm^3, which takes place just above interface layer (DAVISON [7]). Complete oxidation of the manganese dissolved in overlying

water of Mendota Lake under experimental conditions and at pH = 8.5 lasted several weeks (SHOLKOWITZ [26]). It is postulated that manganese cycle occurs in hypolimnic water even if upper sediment layer is oxic. Redox cycles depend not only on climate conditions, but also on biological productivity and the type of bottom sediments.

2.1. MANGANESE AND IRON OXIDATION

There are three different mechanisms of manganese oxidation (Van VEEN et al. [32]):

1. At pH > 9 Mn^{2+} is spontaneously oxidized in water saturated with oxygen.

2. At 7.5 > pH > 9 Mn^{2+} can be catalytically oxidized by hydroxycarbonic acids.

3. At all pH values, but at optimum pH 6.5 >pH > 7.5, Mn^{2+} ions can be enzymatically oxidized by microorganisms.

In numerous aquatic environments, pH ranges from 6 to 8, therefore only the 3rd mechanism seems important. Mn(II) oxidation probably occurs on particle surfaces. DIEM [10] proved that in suspension-free lake water Mn(II) was not oxidized even after a 5-year period. Manganous ions adsorb preferentially on manganese oxides in sediments. Two mechanisms are responsible for this phenomenon: a purely inorganic adsorption mechanism and a microbiological one which can be interrupted by some antibiotics, ethanol and ultrasounds (SANTSCHI [23]). The rate of Mn(II) oxidation on particles from lakes is faster than the rate of its uptake by about an order of magnitude (CHAPNICK at al. [4]). Therefore the rate of the dissolved Mn(II) removal from lake water is controlled by the rate of its uptake, which is mostly a consequence of bacterial catalysis. The kinetics of the Mn(II) uptake and removal from water is in agreement with that observed in laboratory experiments. The uptake of Mn^{2+} ions by particles in lake, which proceeds in accordance with the Monod kinematics, is in agreement with a bacterial catalysis of manganese oxidation. The rate constant of this reaction ranging from 13 to 180 $year^{-1}$ was calculated based on the water concentration profiles for different environments obtained using laboratory models (NYFFELER et al. [22]).

For the the oxidation of Fe(II) in natural water, in contrast to oxidation of Mn(II), the presence of microorganisms is not indispensable (STUMM and MORGAN [30]). The oxidation rate, depending on pH value, rises 100-fold per each unit of pH increase. Despite the spontaneous oxidation of Fe(II), there are microorganisms which can gain energy catalyzing such a fast reaction (GHIORSE [14]). It appears, however, that in natural water spontaneous oxidation, without bacterial catalysis, is prevalent. For example, at the oxic–anoxic interface in the Gulf of Saanich the addition of antibiotics or other poisons did not affect the rate of oxidation of ferrous ions (TEBO et al. [31]).

2.2. MANGANESE AND IRON REDUCTION

It has been postulated that manganese reduction in suboxic or anoxic sediments occurs by electron transfer from organic carbon (FROEHLICH et al. [13]). However,

the exact mechanism is not well known. Certain low-molecular weight organic molecules can also reduce Mn(IV). For example, quinones and catechols, which probably are not abundant in surface sediments, can reduce manganese oxides, whereas formates, lactates, acetates or propionates cannot (STONE [29]). For example, pyruvates and oxalates, which occur in surface sediment at the concentrations of 10^{-5} M, enhance the reduction rates of MnO_2, whereas humic acids as well as Ca^{+2} and phosphate slow down this process (STONE and MORGAN [28]). Microorganisms can simultaneously reduce manganese and oxidize organic detritus, and the nature of this phenomenon has not been yet explained. Perhaps bacteria produce metabolites which can react with manganese oxides and the final products remain in the sediment (BURDIGE and NEALSON [2]). Hydrogen sulfide and iron(II) sulfide are such metabolites produced by sulphate-reducing bacteria. Another explanation is the reduction carried out by an electron donor which in an oxidized form is taken up by the bacteria and then reduced again during the respiration cycle. The reduction of manganese oxides does not lead to complete remobilization of manganese, as the concentrations of Mn^{2+} ions are also controlled by the solubility of sparingly soluble compounds: EMERSON [12] found $MnCO_3$ to be solubility limiting in anoxic sediment of Swiss Lake Greifen, and MATISOFF et al. [20] found MnS to be solubility limiting in Lake Erie. The seasonally varying fluxes of Mn^{2+} out of surface sediment from Narragansett Bay have been correlated primarily with carbon fluxes, and secondarily with temperature (HUNT 17]). This proves that there exists a close link of manganese reduction with the supply of electron donors. The maximum experimentally determined rate of manganese reduction varies between 156 and 363 $\mu mol/dm^3 \cdot day^{-1}$ (BURDIGE and NEALSON [2]). However, the values determined for field experiments are considerably lower than the values determined in a laboratory, possibly because of additional transport resistances in the field. An important question about manganese cycle concerns the sites of oxidation and reduction. The maximum concentration of subsurface Mn^{+2} ions in the ocean, which coincides with the zone of oxygen minimum and has been ascribed to the reduction of MnO_2 in water, is probably caused by diffusion of manganese from continental sediments (SANTSCHI et al. [24]).

Thermodynamically, Fe(III) compounds should be reducible in the presence of natural organic matter (STUMM and MORGAN [30]). However, if enzymatic catalysis does not take place, Fe(III) cannot be reduced by many natural organic substances which occur in surface sediment, including acetate, propionate, butyrate, methanol and ethanol (LOVLEY and PHILLIPS [19]). The presence of nitrate in sediment stabilizes the redox potential (E_h) at ~100 mV and therefore a black colour produced by iron sulphides, which is typical of anaerobic conditions in sediment, is frequently observed. There are indications, however, that at low nitrate concentrations, iron can be reduced by denitrifying bacteria (SORENSEN [27], LOVLEY and PHILLIPS [19]). Even though microorganisms as well as reducing agents are readily available in surface sediments, ferric oxides are found "buried" both in river sediments and in deep

ocean sediments (LOVLEY and PHILLIPS [19], CANFIELD [3]). LOVLEY and PHILLIPS [19] as well as CANFIELD [3] showed that amorphous hydrooxides, even if they were covered with phosphates or organic compounds, could be readily reduced in the sediment. The structure of non-reducible iron compounds is not well known. Difficulties in separating different ferric oxide phases do not allow the use of iron isotopes to measure iron reduction rates in sediment. The production rate of Fe^{2+} is no measure of the reduction rate either, as some forms of Fe(II) are sulphide, phosphate and carbonate minerals.

3. TRANSPORT MECHANISM OF IRON AND MANGANESE COMPOUNDS

As we have mentioned before, particulate and soluble iron and manganese are transported in different ways and have various concentrations in both phases, depending on environment. Insoluble forms coming from surface water and from oxidation of soluble fraction in the oxycline are sedimentary components. These particles are reduced in anoxic water, hence they can be considered a source of dissolved ions. Then they are transported due to diffusion processes. Transport within oxic and anoxic regions can be assumed to be uniform with constant diffusion coefficients (DAVISON [8]). Iron and manganese are reduced and oxidized at different rates – when seasonal oxygen deficiency occurs – manganese is reduced before iron and being released from the sediment is present in water for longer than iron (STUMM and MORGAN [30], HAMILTON-TAYLOR and MORRIS [15]). This is due to a higher manganese potential in redox process and slower kinetics of its oxidation (DAVISON [9]). The concentrations of dissolved manganese are usually maintained up to and through the oxycline, whereas dissolved iron is found at lower depths where there is no oxygen (VERDOUW and DEKKERS [34]). This element diffusing from sediment to water testifies to the abundance of reductive oxides in sediment (HAMILTON-TAYLOR et al. [16]). Conditions at the sediment–water interface are more complex. This is because of substantial differences in the rates of transport in the interstitial and overlying water. The transport within interstitial water can be approximately characterized by molecular diffusion, whereas eddy diffusion dominating in overlying water is usually 1000 times faster. Further difficulties arise if the redox boundary lays at this sediment–water interface. This is possible when the water saturated with oxygen "overlies" a reducing sediment (WEILER [35]). Due to sedimentation the particulate material from the water is transferred to the anoxic sediments, where it immediately undergoes reduction. The soluble species, which accumulate at the interface, are quickly transferred (high value of diffusion coefficient) to the overlying water, but comparatively slowly (low value of diffusion coefficient) to the sediment. For this reason the largest part of the dissolved metal returns to the water when the redox boundary coincides with the sediment–water interface. The concentration of metal may not be so high in the water, because dispersion caused by a rapid mixing of water can dominate.

As we have mentioned before, particulate manganese transferred to the sediment is usually more readily reduced than iron. Consequently, most of the manganese, which is transferred to a highly reducing sediment, is dissolved and released to water, whereas only a small fraction of iron is dissolved (DAVISON [9], ALLER [1]). Small amount of manganese is permanently retained in such a sediment, whereas most of iron reaching the sediment becomes incorporated. Because the concentration gradient in water is the highest at the surface, and the lowest near the sediment, metal ions pass from the water to the sediment, and therefore the concentration in the interstitial water also decreases with the depth of the sediment, hence the downward transport continues. The manganese reaches its maximum concentration in the water which overlies the sediment. Most of the manganese dissolved in the overlying water before it reached the sediment (DAVISON et al. [7]). Therefore iron compounds that occur in the sediment in high concentrations cannot be considered a threat to the overlying water. In the case of manganese, the above statement is not so firm because of the easy accumulation of this element in hypolimnion (WU et al. [36]).

Soluble metal ions are transferred from the redox boundary, where they originate, in an upward direction due to random transport processes. As they progress, they encounter oxygen and are oxidized to an insoluble particulate form. This oxidation is a source of particulate material. In order to obtain a simple model, we assume that as a result of random transport processes material is separated and moves in both upward and downward directions, and gravitation, which is an additional force, enhances the transport in a downward direction. When the particles pass below the redox boundary they are removed by being reduced to the soluble phase. The position of redox boundary is not permanent either in space or in time. But if it is, manganese, which is reduced more readily than iron, does tend to concentrate close to oxyciline and above it. The maximum concentration of particulate iron, however, may occur at some considerable distance from the anoxic region.

During summer stratification Mn(II) is oxidized more slowly than Fe(II), therefore the particulate material is produced in higher layers of water. Moreover, wind mixing is prevalent in shallow water, and morphometry promotes the dilution of manganese from larger volume of water in the upper layers of the lake. The removal of particles may be accelerated by coagulation processes. In the dynamic regime of small lakes, an equilibrium cannot be achieved. The rate of particle production may be faster than the rate of their removal. Hydrodynamic resuspension of material from sediment can be also considered as a source of particles.

When the redox boundary reaches an appreciable depth within the sediment the random transport processes, which influence the particulate material, are so slow that their effect is practically unimportant. Then the concentration is controlled by the "burying"of fresh material, by the upward diffusion and subsequently by the oxidation of the forms being reduced and the removal of particles due to reduction below the redox boundary. In fresh water, the redox boundary usually is established in such a way that it is at the sediment–water interface or close to it. This can result in high concentrations of particulate

iron and manganese accumulated on the sediment surface which may cause a red-brown colour (MORTIMER [21]). The layer on the sediment surface may consist of a loose association of freshly precipitated material with exceptionally high water content.

We have to proceed with all due caution in order to avoid determining the surface sediment as solid, hence different from water. The water content on the surface of rich organic sediments is high (usually exceeds 90%) and could also be regarded as a liquid of a high concentration of particles.

The particulate material is often settled reaching the bottom, where it is accumulated at the sediment–water interface. The surface of such a sediment is still riched in iron and manganese. If manganese is removed from the system, for example due to a run off, the sediment becomes richer in iron (DAVISON and WOOF [6]). The concentrations of iron and manganese in surface water are usually comparable and most of the inflowing iron and manganese are transferred to the sediment. For this reason if these elements were not be divided into redox forms, their ratio in the sediment would approach unity. In nature, an average ratio of iron to manganese in sedimentary rocks approaches 50:1, which shows that the preferential release of manganese must be ubiquitous (DAVISON [8]).

Reducing conditions in lakes cause considerable flows of many inorganic compounds through the water–sediment interface. Iron and manganese oxides are good adsorbers of these elements due to their extended surfaces. Because of the decrease in the oxygen content the oxides are dissolved, hence the elements and substances being adsorbed on their surfaces are released. Flows through the interface and migration within sediment must be controlled by the interstitial water gradients, diffusion, adsorption, sedimentation and ground water movements. This means that bioturbation during anoxic periods is insignificant. Manganese and iron undergo large seasonal circulations in an interstitial water. In reduction conditions, which occur in warmer months, the concentrations of these elements increase, which leads to large flows through interface in the direction of overlying water.

4. SUMMARY

In a fresh water environment, the greatest physical, chemical and biological gradients occur at the interface between the sediment and the overlying water. Therefore, in the study of transformation of iron and manganese compounds, our attention is focussed on the area near the boundary separating bottom sediment from overlying water. In this area, the manganese and iron undergo the most radical transformations and it also separates not only bottom sediment from water, but also oxic zone from anoxic zone.

The differences in the redox processes of manganese and iron compounds define the partial and temporal distributions of these elements not only in boundary area, but also in deeper layers of the sediment and the hypolimnion. Redox cycles depend on many factors such a climate, biological productivity and type of sediment, which characterize given ecosystem.

The transport of manganese and iron compounds, which is closely associated with redox cycles and seasonal changes, also proves that these two elements differ. Easy accumulation of manganese in hypolimnion can cause the water pollution with this element, whereas most of iron is kept in the sediment.

REFERENCES

[1] ALLER R.C., *Diagenetic process near sediment–water interface of Long Island Sound. II. Fe and Mn*, Adv. Geophys., 1980, 22, 351.

[2] BURDIGE D.J., NEALSON K.H., *Microbial manganese reduction by enrichment cultures from coastal marine sediments*, Appl. Environ. Microbiol., 1985, 50, 491–497.

[3] CANFIELD D.E., *Reactive iron in marine sediments*, Geochim. Cosmochim. Acta, 1989, 53, 619–632.

[4] CHAPNICK S.D., MOORE W.S., NEALSON K.H., *Microbially mediated manganese oxidation in a freshwater lake*, Limnol. Oceanogr., 1982, 27, 1004–1014.

[5] DAVISON W., WOOF C., RIGG E., *The dynamics of iron and manganese in a seasonally anoxic lake*, Limnol. Oceanogr., 1982, 27, 987.

[6] DAVISON W., WOOF C., *A study of the cycling of manganese and other elements in a seasonally anoxic lake*, Rostherne Mere, U.K., Water Res., 1984, 18, 727.

[7] DAVISON W., *Transport of iron and manganese in relation to the shapes of their concentration*, Hydrobiologia, 1982, 62, 463.

[8] DAVISON W., *Conceptual Models for Transport at a Redox Boundary*, [in:] W. Stumm, *Chemical Processes in Lakes*, Wiley-Interscience, 1985, New York, 31–53.

[9] DAVISON W., *Iron and manganese in lakes*, Earth Sci. Rev., 1993, 34, 119–163.

[10] DIEM D., STUMM W., *Is dissolved Mn^{+2} being oxidized by O_2 in absence of Mn-bacteria or surface catalysts?* Geochim. Cosmochim Acta, 48, 1571–1573.

[11] DOJLIDO J.R., *Chemia wód powierzchniowych*, Ekonomia i Środowisko Pub., 1995.

[12] EMERSON S., *Early diagenesis in anaerobic lake sediments: chemical equilibria in interstitial waters*, Geochim. Cosmochim. Acta, 1976, 40, 925–934.

[13] FROEHLICH P.N. et al., *Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis*, Geochim. Cosmochim. Acta, 1979, 43, 1075–1090.

[14] GHIORSE W.C., *Biology of iron- and manganese-depositing bacteria*, Annu. Rev. Microbiol., 1984, 38, 515–550.

[15] HAMILTON-TAYLOR J., MORRIS E.B., *The dynamics of iron and manganese in the surface sediments of a seasonally anoxic lake*, Arch. Hydrobiol. Suppl., 1985, 72, 135–165.

[16] HAMILTON-TAYLOR J., DAVISON W., MORFETT K., *The biogeochemical cycling of Zn, Cu, Fe, Mn, and dissolved organic C in a seasonally anoxic lake*, Limnol. Oceanogr., 1996, 41(3), 408–418.

[17] HUNT C.D., *Variability in the benthic Mn^{+2}-flux in coastal marine ecosystems resulting from temperature and primary production*, Limnol. Oceanogr., 1983, 28, 913–923.

[18] HENDERSON-SELLERS B., MARKLAND H.R., *Decaying Lakes: The Origins and Control of Cultural Eutrophication*, Wiley-Interscience, Chichester, 1987, 121–141.

[19] LOVLEY D.R., PHILLIPS E.J.P., *Availability of ferric iron for microbial reduction in bottom sediments of the freshwater tidal Potomac River*, Appl. Environ. Microbiol., 1986, 52, 751–757.

[20] MATISOFF G. et al., *Trace metals mineral equilibria in Lake Erie sediments*, J. Great Lakes Res., 1980, 6, 353–366.

[21] MORTIMER C.H., *Chemical changes between sediment and water in the Great Lakes – speculations on probably regulatory mechanism*, Limnol. Oceanogr., 1971, 10, 268.

[22] NYFFELER U.P. et al., *A kinetic approach to describe trace-element distribution between particles and solution in natural aquatic systems*, Geochim. Cosmochim. Acta, 1984, 48, 1513–1522.

[23] SANTSCHI P. et al., *Chemical processes at the sediment–water interface*, Marine Chemistry, 1990, 30, 269–315.

[24] SANTSCHI P.H. et al., *Estimates of the resistance to the chemical transport posed by the deep-sea boundary layer*, Limnol. Oceanogr., 1983, 28, 899–912.

[25] SCHINDLER D.W., *The coupling of elemental cycles by organisms: evidence from whole-lake chemical perturbations*, [in:] W. Stumm (editor), *Chemical Prosesses in Lakes*, Wiley-Interscience, 1985, New York, 225–250.

[26] SHOLKOVITZ E.R., *Redox-Related Geochemistry in Lakes: Alkali Metals, Alkaline-Earth Elements and [137]Cs*, [in:] W. Stumm, *Chemical Processes in Lakes*, Wiley-Interscience, 1985, New York, 119–142.

[27] SORENSEN J., *Reduction of ferric iron in anaerobic, marine sediment and interaction with reduction of nitrate and sulfate*, Appl. Environ. Microbiol., 1982, 43, 319–324.

[28] STONE A.T., MORGAN J.J., *Reduction and dissolution of manganese(III) and manganese(IV) oxides by organics*, Environ. Sci. Technol., 1984, 18, 450–456.

[29] STONE A.T., *Microbial metabolites and the reductive dissolution of manganese oxides: oxalate and pyruvate*, Geochim. Cosmochim. Acta, 1987, 51, 919–925.

[30] STUMM W., MORGAN J.J., *Aquatic Chemistry*, Wiley-Interscience, 1981, New York, 780 p.

[31] TEBO B.M. et al., *Microbial mediation of $Mn(II)$ and $Co(II)$ precipitation at the O_2/H_2S interfaces in two anoxic fjords*, Limnol.Oceanogr., 1985, 29, 1247–1258.

[32] Van VEEN et al., The *Sphaerotilus-Leptothrix group of bacteria*, Microbiol. Rev., 1978, 42, 329–356.

[33] VARENCOW I.M., GRASSELY G., *Geology and Geochemistry of Manganese*, Vol. I, Akad. Kiedo, 1980, Budapest.

[34] VERDOUW H., DEKKERS M.J., *Iron and manganese in Lake Vechten: dynamics and role in the cycle of reducing power*, Arch. Hydrobiol., 1980, 89, 509.

[35] WEILER R.R., *The interstitial water composition in the sediments of the Great Lakes*, Limnol. Oceanogr., 1973, 18, 918.

[36] WU F.C., WAN G.J., HUANG R.G., PU Y., CAI Y.R., *Geochemical processes of iron and manganese in a seasonally stratified lake affected by coal-mining drainage in China*, Limnology, 2001, 2, 55–62.

ŻELAZO I MANGAN W ŚRODOWISKU WÓD POWIERZCHNIOWYCH – RÓŻNICE I PODOBIEŃSTWA W CYKLACH FIZYKOCHEMICZNYCH

Opisano fizyczne i chemiczne procesy związków żelaza i manganu, jakie zachodzą w środowisku wód powierzchniowych. Szczególną uwagę zwrócono na obszar graniczny, rozdzielający osad denny od wody, który jest miejscem o największych gradientach w fizycznych, chemicznych i biologicznych właściwościach. Opisano procesy utleniania i redukcji tych metali w osadach dennych i w wodzie nadosadowej. W chemizmie redox żelaza i manganu przedstawiono dwie istotne różnice, które – w zależności od środowiska – implikują zróżnicowanie w procesach transportu oraz stężeniach zarówno w fazie osadu, jak i wody. Opisano różnice i podobieństwa, jakie wynikają z sezonowej stratyfikacji w środowisku jeziornym. Przestudiowano procesy przenoszenia związków żelaza i manganu zarówno rozpuszczonych, jak i zawieszonych (cząsteczkowych).

Reviewed by Jerzy Chmielowski