

## Influence of Sedimentary Fe and Mn on the Oxygenation of Overlying Waters in Dam Reservoirs

Piotr Koszelnik<sup>1\*</sup>, Lilianna Bartoszek<sup>1</sup>

<sup>1</sup> Department of Environmental Engineering and Chemistry Rzeszów University of Technology, al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

\* Corresponding author's e-mail: pkoszel@prz.edu.pl

### ABSTRACT

This paper reports the work to determine the impact that concentrations of manganese (Mn) and iron (Fe) in the bottom sediments of shallow dam reservoirs exert upon the dissolved oxygen concentrations of overlying waters. Specifically, the work was conducted in the period of 2013–2014 in six shallow artificial reservoirs located in SE Poland. The waters of all the reservoirs studied are relatively well oxygenated, though both supersaturation and anoxic conditions are observed seasonally across the 50–150% range. The reported reactions of bottom sediments were between pH 7.7 and 8.2, while the mean concentrations of Mn and Fe were found to vary widely from site to site (Mn from 0.068 to 1.48 g/kg d.w. and Fe from 2.48 to 24.0 g/kg d.w.). It was not possible to demonstrate any direct relationship between sediment Fe and Mn concentrations, the Mn/Fe ratio or pH on the one hand and the oxygenation of reservoir waters on the other. However, multiple regression analysis did allow for the identification of a significant influence of both Mn content and sediment pH on the oxygen concentration in reservoir waters. In simple terms, both an increase in Mn and a decrease in pH can be said to result in more fully aerobic conditions in waters.

**Keywords:** manganese, iron, dissolved oxygen, dam reservoir

### INTRODUCTION

Iron (Fe) and manganese (Mn) are elements commonly present in the aquatic environment [Kaleta et al. 2007, Czaplicka et al. 2017]. While mainly natural in origin, they can also derive from anthropogenic sources, especially in surface waters [Grochowska and Tandyrak 2009, Molenda 2013]. Equally, the concentrations in bottom sediments are typically many times higher than those in waters as such, given occurrence of these elements in the form of salts that are only sparingly soluble. Both elements act to render phosphate inactive, in this way limiting processes of eutrophication [Bartoszek and Tomaszek 2011]. The effect is highly dependent on the oxidation and reduction of the coupled pairs Fe(II)/Fe(III) and Mn(II)/Mn(IV), which result either in precipitation or dissolution – commonly with phosphate [Gantzer et al. 2009, Naeher et al. 2013, Dunalska

et al. 2015]. A further connected result may be intensification of the processes by which autochthonous organic matter is first produced and then decomposes, and the latter process may in turn give rise to oxygen deficits in the near-bottom zone.

Equally, as internal loading with phosphates is the cause of progressive degradation in many ecosystems of both natural and artificial bodies of water [Kowalczywska-Madura et al. 2010, Zelenáková et al. 2013], the dynamics to the oxidation and reduction of Fe and Mn can be assumed to exert an indirect influence on the process, presumably in line with the concentrations of the latter that are actually present in bottom sediments [Bartoszek and Tomaszek 2008]. In fact, the process may have yet-further consequences, not least impairment of the quality of water for use and/or the emission of greenhouse gases and odours to the atmosphere [Grabas et al. 2011, Gruca-Rokosz et al. 2011, Gruca-Rokosz and Tomaszek 2015].

The work described in this paper has concerned the impact the Mn and Fe concentrations in the bottom sediments of shallow dam reservoirs are able to exert on the dissolved oxygen concentrations in overlying waters. Given that the elements under study increase the retention potential of bottom sediments against phosphates, they may serve as an intermediate indicator of ecosystem resistance. The knowledge on this will therefore prove useful, given the interest in trying to safeguard such aquatic ecosystems against eutrophication.

## STUDIED SITES AND METHODS USED

The samples of bottom sediment were taken at 15 sampling sites in 6 artificial reservoirs located in SE Poland. The characteristics of the reservoirs and sites studied are as shown in Table 1. The sediment was collected nine times through the 2013–2014 period, using a gravity sediment corer (KC Kajak of Denmark). The top (0–5 cm) layer was used in chemical analysis following drying. Microwave mineralization ( $\text{HNO}_3$ , 2–4.5 MPa) was applied to allow for Mn and Fe determinations using an ICP spectrometer (Integra, GBC). The results were calculated as g of element vs. kg dry weight of sediment. The pH of deionized water extracts was also measured in the laboratory, while dissolved oxygen ( $\text{O}_2$ ) and temperature were recorded *in situ* using a portable multimeter (MultiLine WTW). All statistical analysis was performed in *Statistica* software package.

## RESULTS

The waters under study were found to be relatively well-oxygenated, with the average  $\text{O}_2$  concentration in the range 7.38 mg/L (BL12) to 10.20 mg/L (OZ6). The analysis of seasonal variation in water saturation with oxygen ( $\text{XO}_2$ ) indicates that for most of the sites tested, values were in the 75–100% range (Fig. 1). Equally, some of the sites at Brzóza Królewska, Ożanna and Rzeszów reservoirs were characterized by supersaturation, mainly during summer periods. In turn, Cierpiz and Blizne reservoirs reported a high degree of hypoxia, given the figures for saturation below 60% (Fig. 1). The supersaturation of water with oxygen can be observed in eutrophic, shallow ecosystems, in the summer, when the processes

of photosynthesis can outpace the oxygen consumption. The deficiencies may in turn indicate high oxygen consumption within bottom sediments, in the absence of any possibility for these shortages to be made good from sources other than the atmosphere [Stańczykowska-Piotrowska 1990, Wójcik 2016].

Table 2 compiles statistics that present the results obtained. The Fe content was found to vary across a wide range. In Rzeszów and Blizne reservoirs, as well as some sites in Kamionka reservoir, the values were in the range of 13.38–24.00 g/kg. The other reservoirs were in turn characterized by the values in the 2.48–7.35 g/kg range. In Blizne reservoir, a Mn concentration over 1.2 g/kg was measured, while the corresponding figure for Rzeszów reservoir was of about 0.5 g/kg d.m. Elsewhere, the values were below 0.2 g/kg. The concentrations of the two elements studied were correlated ( $r^2 = 0.5517$ ,  $p = 0.0015$ ). The sediments were of alkaline reaction, with me-

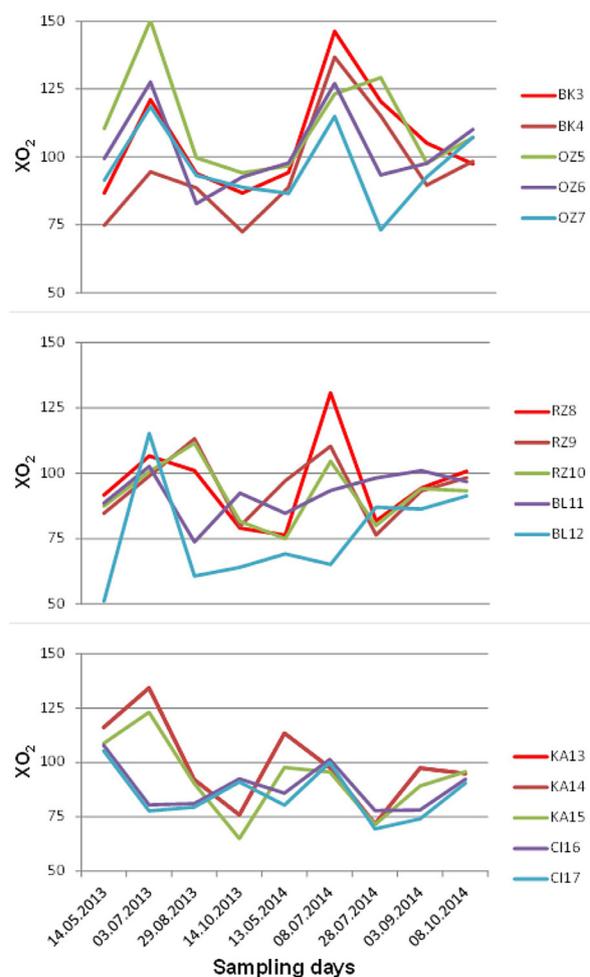


Fig. 1. Seasonal variability of percent oxygen saturation

**Table 1.** Characteristics of studied reservoirs (own data)

Reservoir	Coordinate	River (Stream)	Volume	Depth mean (max.)	Res. area	Hydraulic retention time	Catchment area	Urban	Forestry	Agriculture	Pasture, meadows	Studied site	Site depth
			10 <sup>3</sup> m <sup>3</sup>	m									ha
Brzóza Królewska	50°14'N 22°19' E	Tarlaka	50	0.7(1.5)	7.05	2.5	30.4	10	30	40	20	BK3	1.2
												BK4	1.2
Ozanna	50°17'N 22°31' E	Złota Rzeka	275	1.4(3.7)	20	3.5	136.3	8	36	28	28	OZ5	1.2
												OZ6	1.3
												OZ7	1.5
Rzeszów	50°00'N 21°59' E	Wisłok	1800	0.6(4.9)	68.2	0.8	2025	10	20	55	15	RZ8	1.0
												RZ9	1.0
												RZ10	1.0
Blizne	49°44'N 22°00' E	Łądzierz	137	1.6(3.9)	8.66	18.0	12.0	2	27	53	18	BL11	1.2
												BL12	1.3
Kamionka	50°08'N 21°40' E	Tuszymka Duża	105	1.5(3)	7	4.8	84.8	12	35	30	23	KA13	1.3
												KA14	1.6
												KA15	1.7
Cierpisz	50°09'N 21°43' E	Tuszymka Duża	22	0.9(1.5)	2.3	1.2	54.5	8	43	35	14	CI16	1.2
												CI17	1.2

**Table 2.** Variability of studied bottom sediment parameters

Site		Fe	Mn	pH	O <sub>2</sub>	100·Mn/Fe	Site		Fe	Mn	pH	O <sub>2</sub>	100·Mn/Fe	Site		Fe	Mn	pH	O <sub>2</sub>	100·Mn/Fe
BK3	Mean	2.48	0.09	8.38	9.83	3.63	RZ8	Mean	21.0	0.541	8.37	9.02	2.58	KA13	Mean	13.38	0.18	8.00	9.40	1.35
	Min.	1.73	0.05	7.79	8.83	2.89		Min.	18.0	0.436	8.08	7.17	2.42		Min.	3.47	0.05	7.54	7.15	1.44
	Max.	4.78	0.14	8.97	10.91	2.93		Max.	23.8	0.665	8.89	10.8	2.79		Max.	27.36	0.46	8.38	10.67	1.68
	SD	0.90	0.02	0.4	0.7	2.22		SD	1.8	0.08	0.2	1.2	4.44		SD	7.5	0.1	0.2	1.3	1.33
BK4	Mean	7.44	0.26	8.21	8.92	3.49	RZ9	Mean	24.0	0.652	8.52	8.95	2.72	KA14	Mean	4.24	0.068	8.01	9.27	1.60
	Min.	3.05	0.08	7.47	7.94	2.62		Min.	19.1	0.487	8.31	6.93	2.55		Min.	2.36	0.036	7.20	6.05	1.53
	Max.	15.22	0.48	8.75	10.77	3.15		Max.	27.0	0.851	8.96	10.58	3.15		Max.	9.53	0.155	8.56	11.53	1.63
	SD	4.14	0.15	0.4	0.8	3.62		SD	2.5	0.13	0.2	1.1	5.20		SD	2.3	0.04	0.5	1.7	1.74
OZ5	Mean	3.16	0.092	8.62	10.2	2.91	RZ10	Mean	22.2	0.598	8.55	8.71	2.69	KA15	Mean	6.74	0.117	7.93	8.67	1.74
	Min.	1.31	0.034	8.01	9.2	2.60		Min.	19.1	0.466	8.27	7.33	2.44		Min.	1.72	0.035	7.48	5.96	2.03
	Max.	8.04	0.283	9.18	12.0	3.52		Max.	29.6	0.697	9.00	10.49	2.35		Max.	14.19	0.246	8.53	10.14	1.73
	SD	2.0	0.08	0.4	1.0	4.00		SD	3.2	0.07	0.3	1.0	2.19		SD	4.0	0.08	0.3	1.5	2.00
OZ6	Mean	7.21	0.146	8.55	9.52	2.02	BL11	Mean	19.86	1.24	8.43	8.90	6.24	CI16	Mean	2.49	0.071	7.77	8.31	2.85
	Min.	2.74	0.080	7.75	7.59	2.92		Min.	16.77	0.47	8.11	7.40	2.80		Min.	1.41	0.035	6.98	6.31	2.48
	Max.	12.54	0.263	9.53	11.95	2.10		Max.	23.02	3.41	8.55	10.09	14.81		Max.	4.22	0.130	8.22	9.81	3.08
	SD	3.8	0.07	0.6	1.3	1.84		SD	2.21	0.96	0.1	0.9	43.44		SD	0.9	0.03	0.4	1.3	3.33
OZ7	Mean	7.35	0.153	8.40	9.00	2.08	BL12	Mean	17.50	1.48	8.33	7.38	8.46	CI17	Mean	3.12	0.080	7.91	8.05	2.56
	Min.	1.25	0.066	7.50	5.97	5.28		Min.	13.46	1.02	7.98	4.78	7.58		Min.	2.42	0.043	7.38	5.76	1.78
	Max.	14.66	0.382	9.40	11.73	2.61		Max.	19.61	2.45	8.83	10.14	12.49		Max.	4.09	0.122	8.53	9.70	2.98
	SD	4.8	0.10	0.5	1.5	2.08		SD	1.79	0.48	0.3	1.8	26.82		SD	0.7	0.03	0.3	1.4	4.29

dian pH values in the 7.77–8.62 range. The calculated values for the 100·Mn/Fe ratio varied from 1.35–1 (KA13) to 8.46–1 (BL12) and depended slightly on the Mn concentration in sediments ( $r^2 = 0.3296$ ,  $p = 0.0252$ ). However, no dependence on Fe was observed.

The analysis of the influence of the independent variables (Fe, Mn, pH and Mn/Fe) on the dependent variable (O<sub>2</sub>) is reported in Table 3. In practice, no significant relationships were found that would describe an impact of analyzed parameters describing bottom sediment on the dissolved oxygen concentrations in the waters studied.

Equally, the analysis of the influence of variables on the value of O<sub>2</sub> using multiple regression found that the value of the required independent variable in relation to the remaining dependent variables was best described by the function:

$$O_2 = -4.7427 + 1.1880Mn - 1.7099pH \quad (1)$$

The summary of the regression in relation to O<sub>2</sub> (Table 4) shows how the above-mentioned model can account for 65% of the variability noted for the dependent variable. Incorporation of additional dependent variables does not improve the parameters of the model significantly, and, as

**Table 3.** Influence of bottom sediment parameters on water oxygen content expressed as Pearson coefficient (R)

Parameters	Fe	Mn	pH	Fe/Mn
O <sub>2</sub>	0.36586	0.31225	-0.49837	0.294298

**Table 4.** Summary of the multiple regression analysis

Statistics	Value
R of multiple correlation	0.8093
R <sup>2</sup> of multiple correlation	0.6549
Corrected R <sup>2</sup>	0.5608
F(3.11)	6.9588
P	0.0068
Error of the estimation	0.4618

is clear from the above, the changes in the pH of reservoir bottom sediments have the greatest influence on the values recorded for O<sub>2</sub>.

The validity of the model was further demonstrated by analyzing the correlations between the sampled values for O<sub>2</sub> and theoretical values (deriving from Eq. 1) (Fig. 2). Further confirmation is offered by the distribution of residuals close to the normal distribution (Fig. 3).

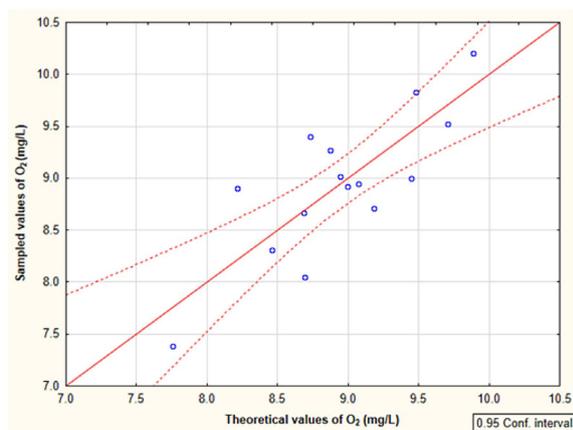
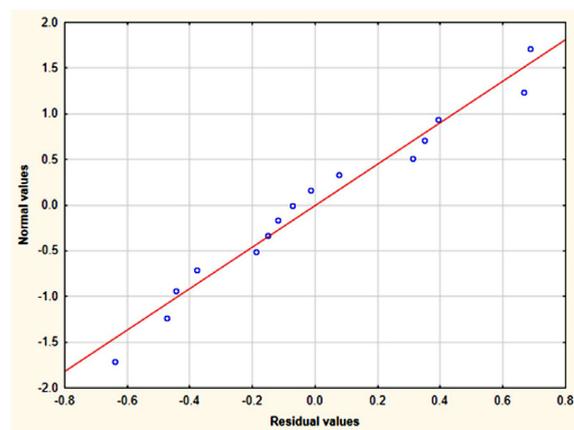
## DISCUSSION

The observed concentrations of Fe and Mn in the bottom sediments of the reservoirs studied were lower than those obtained for other ecosystems in southern Poland. Czaplicka et al. [2017] reported the Fe concentrations in Czorsztyn, Dobczyce, Goczałkowice and Rybnik reservoirs of approx. 30 g/kg, with Mn in the 1.33–3.27 g/kg range. The differences may result from the nature

and management of the catchment areas examined, e.g. reflecting slope or various potential origins of the elements [Karwacka et al. 2015].

The mobility of Mn reflects the occurrence in various forms under different redox conditions. Where anoxia is present, releases of Mn and Fe from the sediment into overlying water are observed, and this should theoretically dampen any growing deficiency of oxygen in overlying waters [Hou et al. 2013]. Given the lack of any significant relationship between the 100·Mn/Fe ratio and oxygen deficits arising in waters, there may be confirmation of the idea that both are released into the water column with similar efficiency. Nevertheless, the oxidation of Fe(II) is known to proceed more rapidly than that of Mn(II) [Naeher et al. 2013], while the involvement of numerous interdependent transformation processes leads to a complex pattern describing the presence of the redox-sensitive trace metals.

However, the Fe present in waters is not necessarily there on account of redox-related remobilization, as it can also be a tracer for terrigenous sources [Naeher 2012]. In light of this, the observed lack of a correlation with oxygen content in waters that was found to characterize the concentration of Fe in the sediment (and indirectly the release of that element from sediment) may indicate the diverse ways in which this element is transformed. In turn, the contribution of Mn to the multiple correlation model may confirm the

**Fig. 2.** Correlation between sampled values for O<sub>2</sub> and theoretical values deriving from Eq. 1**Fig. 3.** Multiple regression results: the distribution of residuals close to the normal distribution

predominance of Mn release into overlying water in association with phosphates, with the result of the presence of the latter being decreased oxygen content [Bryant et al. 2011]. Furthermore, while this impact is significant statistically (Table 4), it is less so in quantitative terms. From the model (Eq. 1), it appears that an increase in the concentration of Mn in sediments by 1.18 g/kg d.m. (or in fact a reduced release of such a charge), enriches water by 1 mg/L of oxygen. However, the Mn concentrations in sediments are only about one-tenth as high, so an analogous proportion of the influence of the independent variable on the dependent should be assumed.

In addition, the model (Eq. 1) implies that a lowering of the pH value of the sediment by 1.70 units again enriches water in oxygen, by 1 mg/L, with the proportions similar to those above again being maintained. Nevertheless, an inverse proportional effect of pH on the oxygen content in the supernatant is in fact reported widely [Hou et al. 2013, Wu et al. 2013].

## CONCLUSIONS

1. The waters of the reservoirs studied are relatively well-oxygenated, though both supersaturation and anoxic conditions are observed seasonally, perhaps indicating the presence of autochthonous organic matter.
2. Bottom sediments are alkaline, and the concentrations of Mn and Fe varied between the studied sites across a wide range of values, albeit with the latter still lower than in other reservoirs of this geographical zone.
3. No direct impact of bottom-sediment Fe or Mn content, Mn/Fe ratio or pH on oxygen conditions in the reservoir waters could be detected.
4. Multiple regression analysis nevertheless allowed for the identification of a significant influence of the Mn content and sediment pH on the oxygen concentration in the waters studied. In essence, an increase in the Mn content and a reduction in pH both result in more favorable aerobic conditions in waters.

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