Interactions between microbial degradation of sedimentary organic matter and lake hydrodynamics in shallow water bodies: insights from Lake Sarbsko (northern Poland)

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ABSTRACT

In this paper we demonstrate spatial and seasonal changes in the pathways of microbial decomposition of organic matter within the surface sediments of Lake Sarbsko, a coastal water body located on the middle Polish-Baltic coast. We studied lake waters and bottom sediments at 11 sampling stations throughout the basin and in different seasons between November 2007 and September 2008. It was established that, in this very productive and shallow lake, microbial activity increases in warmer seasons and ceases during winter. In spring, bacterial activity is fuelled by increased influx of highly reactive planktonic organic matter, which is decomposed via methanogenesis, reduction of NO_3^- , SO_4^{-2} , and Fe and Mn oxides. On the other hand, during summer, oxidation processes (mainly oxidation of CH_4) tend to predominate. The change from reduction to oxidation is attributed to wind-induced vertical mixing of Lake Sarbsko waters and resuspension of bottom deposits. Degradation of sedimentary organic matter in Lake Sarbsko results in appreciable changes in the pH and the concentrations of red-ox sensitive ions in pore waters, but it has little effect on the chemistry of bottom and surface waters. However, release of PO_4^{-3} from the sediments might be a source of this nutrient in the lake. Internal loading of phosphates in Lake Sarbsko occurs under both oxic/mildly reducing and anoxic conditions.

Key words: microbial processes, geochemistry, lake sediments, pore waters, coastal lake, Poland

1. INTRODUCTION

Organic matter in lakes is prone to extensive chemical transformations during and after sedimentation. Organic compounds in lake water and sediments are oxidized by dissolved O_2 and/or oxygenated inorganic chemical species (i.e., NO₃⁻, FeOOH, MnO₂, SO₄²⁻, HCO₃⁻, etc.). These processes are mediated by heterotrophic bacteria and their intensity is the greatest at the sediment-water interface (Wetzel 1983; Müller *et al.* 1997).

Microbial processes in sediments exert widespread geochemical and ecological effects. Bacterial decomposition of sedimentary organic matter contributes significantly to greenhouse gas (CH₄, NO₂, CO₂) production in lakes (Mengis *et al.* 1997; Lojen *et al.* 1999; Jędrysek 2005; Bange 2006; Schubert *et al.* 2010). Moreover, microbial redox processes within lake sediments drive early diagenesis (Berner 1980) and consequently, owing to reductive solubilisation of sedimentary N, S, Fe and Mn compounds, are likely to affect chemical composition of near-bottom waters, especially in shallow water bodies (Stumm & Morgan 1981). Early diagenetic release of phosphorus from the sediments (internal loading) is to increase the process of eutrophication.

Availability of reactive organic matter is a prerequisite for bacterial activity in sedimentary systems (Wetzel 1983). Therefore, lagoons and coastal lakes, being very productive environments, provide favourable conditions for bacteria to develop. However, owing to spatial variation of organic matter content in the sediments within any given coastal lake or lagoon, the abundance and the composition of bacterial communities may change in time and space (Wetzel 1983). In addition, microbial consortia in the surface deposits in shallow water bodies can be strongly affected by wind-driven turbulence and current stirring, which drastically change pore water chemistry (Engle & Melack 2002; Bussmann 2005; Abesser & Robinson 2010; Niemistö *et al.* 2011).

The rate and pathways of microbial reactions in the sediments of coastal lakes on the Polish coast are rather poorly recognized, despite the intensity and complexity of bacterial metabolism in this geosystem being appreciably high (Mudryk & Donderski 1997) and despite the fact that the knowledge of geomicrobiological processes is essential for the evaluation of management and protection strategies for lake environments.

Therefore, using Lake Sarbsko (Gardno-Leba coastal plain) as an example, in the present study we attempt (i) to identify the mechanisms of microbial reactions in coastal lakes and (ii) to show their spatial and temporal variability in relation to sediment lithology and lake hydrodynamics.



Fig. 1. Location and bathymetry of Lake Sarbsko.

2. STUDY AREA

Lake Sarbsko is a coastal lake situated in the middle part of the southern Baltic coast, on the Gardno-Leba coastal plain (Fig. 1). The lake is separated by the Sarbsko Barrier from the Baltic Sea. The lake area is 6.5 km^2 and its average depth is 1.4 m, with a maximum of 3.5 m in the mid-eastern section of the basin. The lake is oriented parallel to the coastline and to the predominant westerly winds. Lake Sarbsko is fed by the Chelst River from the east and a stream from the south. The outflow (the Chelst outlet) is situated in the western part of the basin, from where lake water discharges to the Leba River (Fig. 1). As Lake Sarbsko has no direct connection to the Baltic Sea, freshwater input has the greatest influence on chemical composition of its water (Cieśliński 2007). On the other hand, during severe storms on the Baltic Sea, Lake Sarbsko is occasionally supplied with marine water via the Leba River mouth and the Chelst outflow channel (Woszczyk et al. 2010). Seasonal variations in water level are in accordance with changes of the Baltic level (Majewski 1972; Woszczyk et al. 2010). Higher lake water levels are observed between autumn and spring, while lowstands occur in summer. Lake water temperatures during sampling campaigns varied from 3.3-3.6 °C in December 2007, 5.1-5.5 °C in April 2008, 19.9-21.3 °C in July 2008, and 18.4-19.1 °C in September 2008.

3. METHODS

3.1. Sampling

Eleven sampling sites from different parts of the lake (Fig. 1) were selected for geochemical analyses. The number of sampling sites was dictated by difficulties with selecting one representative sampling site in the very dynamic ecosystem of this coastal lake. Chemical parameters of lake waters were measured *in situ* in surface (5-10 cm below the surface) and nearbottom layers (5-10 cm above the bottom). Pore waters from the top 5 cm layer of bottom deposits were analyzed in the laboratory.

Pore waters, together with surface sediments, were taken with a gravity corer (Tylmann 2007) and extracted by centrifugation (3000 rpm). To water samples in which stable C isotopes were determined, $HgCl_2$ was added to protect from bacterial activity.

Lake water was sampled on 13 December 2007, 10 April 2008, 10 July 2008, and 17 September 2008. Determinations of the chlorophyll-*a* concentrations were made in November 2007, February 2008, May 2008, and August 2008. Surface sediment samples (top 5 cm) for geochemical analyses were collected in July 2008 using the gravity corer mentioned above. Prior to the analyses, sediment samples were stored at -20 °C, freeze-dried, and homogenized in an agate mill Pulverizette 2.

3.2. Analytical methods

Dissolved oxygen and pH in Lake Sarbsko were measured with a WTW Multi 350i sensor. The concentrations of dissolved Fe (Fe_{diss}) and Mn (Mn_{diss}), as well as those of NH₄⁺, NO₃⁻ and PO₄³⁻ were analyzed spectrophotometrically with a Spectral PhotoLab WTW spectrophotometer and using Spectroquant tests (Merck). As Fe_{diss} and Mn_{diss} are mainly in reduced forms (Fe²⁺ and Mn²⁺, respectively), their concentrations must be regarded as minimum ones owing to possible oxidation during transport and laboratory handling. SO₄²⁻ concentrations were determined nephelometrically using a spectrophotometer (Photo Lab6 WTW). Sulphates were precipitated with BaCl₂ as BaSO₄ at slightly

Tab. 1. Bulk chemical composition of surface sediments from Lake Sarbsko. ^{a)} terrigenous (detrital) silica; ^{b)} biogenic silica (diatom frustules); ^{c)} total inorganic carbon (carbonates); ^{d)} according to Schnurrenberger *et al.* (2003); ^{e)} mean diameter [phi] acc. to Folk & Ward (1957); ^{f)} standard deviation acc. to Folk & Ward (1957).

Sample		Componer	ts [wt %]		Sediment		TOC/N		
number	SiO _{2ter} ^{a)}	SiO _{2bio} ^{b)}	TIC ^{c)}	TOC	type ^{d)}	M _Z ^{e)}	$\sigma_1^{(f)}$	Lithology	(molar)
SAR1	97.66	0.01	0.36	0.85	Clastic	2.013	0.516	Fine sand, well sorted	7.6
SAR2	17.60	13.70	3.00	17.35	Biogenic	5.814	2.097	Coarse silt, very poorly sorted	9.4
SAR3	12.04	19.11	3.24	18.50	Biogenic	6.314	1.745	Medium silt, poorly sorted	8.6
SAR4	37.10	10.86	2.88	11.30	Biogenic	5.450	2.152	Coarse silt, very poorly sorted	8.7
SAR5	66.22	4.86	1.20	6.82	Clastic	4.009	2.535	Very coarse silt, very poorly sorted	9.1
SAR6	83.56	2.10	1.20	2.42	Clastic	1.695	1.560	Medium sand, poorly sorted	7.6
SAR7	22.48	13.55	3.00	16.37	Biogenic	5.803	2.241	Coarse silt, very porly sorted	8.6
SAR8	17.05	14.44	3.24	17.20	Biogenic	6.436	1.962	Medium silt, poorly sorted	8.8
SAR9	98.84	0.01	0.12	0.34	Clastic	1.846	0.604	Medium sand, moderately well sorted	5.7
SAR10	22.05	13.65	3.12	12.11	Biogenic	5.807	2.048	Coarse silt, very poorly sorted	8.6
SAR11	30.28	12.22	2.52	15.15	Biogenic	5.519	2.146	Coarse silt, very poorly sorted	10.0

acidic pH. HCO_3^- was titrated with HCl (0.1 mol L⁻¹) using methyl orange as indicator. Chlorides were analyzed using argentometric titration (AgNO₃) with K_2CrO_4 as indicator, at neutral/slightly alkaline pH.

Chemical analyses of lake water were performed within two days of collection. Stable C isotope in lake water DIC were analyzed in 2 mL aliquots of the lake water samples. Lake water was transferred to glass vials; the air was then evacuated and the vials were flooded with He. CO_2 was released from the samples by addition of H₃PO₄. Samples were then heated to 40 °C. The isotopic measurements were carried out using a Delta isotope-ratio (ir) mass spectrometer attached to the MultiFlow system (Micromass Ltd., UK). Results were reported relative to the PDB reference material, using external standards.

The chlorophyll-*a* was analyzed spectrophotometrically in 200 mL aliquots of surface water filtered through GF/C Whatman filter following the Lorenzen method after 90% acetone extraction and corrected for phaeopigments (Kokociński *et al.* 2010).

To determine the contents of terrigenous (SiO_{2ter}) and biogenic (SiO_{2biog}) silica in the sediments, powdered samples were combusted at 550 °C for 4 h and subsequently digested in aqua regia at 100 °C for 2 h. The residue after acid treatment was assumed to represent total SiO₂ (SiO_{2tot}) . SiO_{2ter} and SiO_{2biog} were separated by extraction of biogenic opal (SiO_{2biog}) with 0.5 n NaOH on the water bath at 100 °C for 2 h (Bechtel *et al.* 2007). The content of SiO_{2biog} was calculated as SiO_{2biog} [%] = SiO_{2tot} - SiO_{2ter}.

The total carbon (TC) and total nitrogen (TN) contents were determined using a Vario Max elemental analyser (Elementar Analysensysteme GmbH, Germany). Carbonates were determined by loss on ignition (Heiri *et al.* 2001). TIC was calculated as TIC [%] = $0.27 \cdot \text{LOI}_{925}$, where LOI₉₂₅ is the content of CO₂ evolved from the sample, as defined by Heiri *et al.* (2001). The organic carbon content (TOC) was derived from TC after subtraction of TIC.

Grain size analyses were performed in organic matter-free samples using a laser particle size analyser (Malvern Mastersizer 2000). Organic matter was removed with 30% H₂O₂. Grain size parameters were

calculated according to formulas proposed by Folk & Ward (1957).

3.3. Hydrodynamic calculations

The potential effect of wind action on surface sediments of Lake Sarbsko during sampling campaigns was evaluated in terms of the depth of water mixed layer (D_{WML}). When the water in any given point of a lake is lower than D_{WML} , the surface sediment is resuspended. D_{WML} was calculated using the formulas provided by Douglas & Rippey (2000). Effective wind fetch (F_W) was derived from the equation employed by Nöges & Kisand (1999). The calculations were performed for maximum daily wind speeds and for the mean daily wind directions during the days of sampling.

4. RESULTS

4.1. Bulk chemical composition of the lake surface sediments

Surface deposits of Lake Sarbsko are represented by clastic and biogenic sediment classes (*sensu* Schnurrenberger *et al.* 2003). The former are defined on the basis of over 50% detrital silicate (SiO_{2ter}) content, while the latter are distinguished by the predominance of carbonaceous and fossiliferous biological remains (Schnurrenberger *et al.* 2003).

Bulk composition of the samples is summarized in table 1. Surface sediments of Lake Sarbsko are characterized by TOC contents between 0.3 and 18.5 wt% (Tab. 1). Most samples are rich in organic carbon (TOC >5 wt%). The colour of the sediments is dark oliveblackish. In reaction with HCl at room temperature, H₂S is liberated, which indicates the presence of FeS. Molar TOC/N ratio is relatively low and varies between 6 and 10. Clastic sediments are found in the westernmost part of the lake, where a back delta of the Chelst River is located (Szopowski 1962), in the SE section of the lake, and in the central part of the basin in front of the river mouth. On the other hand, increased concentrations of TOC, biogenic silica (SiO_{2biog}) and carbonates (TIC) were mainly recorded in close proximity to the Sarbsko Barrier and in the deepest part of the lake. Clastic sedi-





ments are composed mainly of sand of different degrees of sorting (Tab. 1). The mineral matrix of biogenic deposits is dominated by medium and coarse silt and displays poor and very poor sorting.

4.2. Lake water chemistry

Throughout the year, Lake Sarbsko water was very well oxygenated. Between December 2007 and September 2008, dissolved O_2 levels in the lake varied between 14.7 and 9.3 mg L⁻¹ in surface water and between 10.4 and 7.7 mg L⁻¹ in near-bottom water. The highest oxygenation occurred in winter and spring, and the lowest O_2 concentrations occurred in summer (Fig. 2). Changes in lake water pH showed well-pronounced seasonality (Fig. 3). During winter, surface and bottom-water pH was lower and varied from 7.35 to 8.11. Between spring and autumn, pH was relatively invariant and ranged from 7.97 to 8.70.

Concentrations of dissolved species, except for bicarbonates (Fig. 4), in lake surface and bottom waters were rather similar and displayed rather low spatial changes. Owing to the above similarities in table 2, we included only the data for bottom waters to demonstrate geochemical distinction between lake water column and pore waters.

The most abundant components in Lake Sarbsko bottom waters were bicarbonates, chlorides, and sulphates. The highest concentrations of bicarbonates were noted during summer (107-174 mg L^{-1}); however, in July 2008, HCO₃⁻ revealed appreciable variation throughout the lake. In contrast, the lowest alkalinity of

Lake Sarbsko waters occurred in September 2008, with HCO_3^- concentrations of 88-116 mg L⁻¹. Lake water chlorinity was relatively low. The maximum of 72.7-97.9 mg L⁻¹ occurred in December 2007, while the lowest values (5.7-63.1 mg L⁻¹) were noted in July 2008. Sulphates revealed a very similar temporal trend. Maximum $SO_4^{2^-}$ concentrations varied between 46-56 mg L⁻¹ in winter and 30-<25 mg L⁻¹ in mid-summer. Biogens (NO₃⁻, NH₄⁺, and PO₄³⁻) were distinctly depleted in lake waters throughout the study period, with nitrates and ammonium being slightly more abundant in December 2007 and July 2008.

The concentrations of dissolved Fe and Mn were very low, albeit dissolved Fe displayed a distinct spring maximum (0.13-0.17 mg L⁻¹), and in the abundance of Mn_{diss}, summer depletion can be identified (0.18-0.03 mg L⁻¹). In most of sites, Mn_{diss} dominates over Fe_{diss}. Stable C isotope ratios in lake waters varied greatly throughout the sampling period (Tab. 2). In April 2008 lake water was highly enriched in heavy C isotope, while in mid-summer very low $\delta^{13}C_{DIC}$ signatures were obtained (-5.09 to -7.07‰). In December 2007 and September 2008, $\delta^{13}C_{DIC}$ were similar and ranged from -2.15 to 2.59‰ and -0.08 to 2.49‰, respectively.

Chlorophyll-*a* concentrations were as high as 15.88-46.84 μ g L⁻¹ with two peaks: in February 2008 (46.50-111.87 μ g L⁻¹) and August 2008 (91.50–146.84 μ g L⁻¹).

4.3. Chemical composition of pore waters

Spatial and temporal changes in the composition of pore waters from Lake Sarbsko are summarized in table 2.



Fig. 3. pH of surface, bottom and pore waters of Lake Sarbsko in different seasons. Seasons are indicated by the colour of columns.



Fig. 4. Comparison of chemical composition of bottom and surface waters of Lake Sarbsko. **A)** the concentrations of Fe_{diss} (as an example of red-ox sensitive form); **B)** the concentrations of Cl⁻ (non-sensitive to microbial metabolism); **C)** the concentrations of HCO₃⁻. SW – surface waters; BW – bottom waters. Note positive correlations of data and similar ranges of the concentrations of chemical species in bottom and surface waters. In cases of red-ox sensitive ions, some outliers may be found.

Site	SO4 ²⁻ (mg L ⁻¹)		HCO_3^- (mg L ⁻¹)		$\frac{\text{NO}_3}{(\text{mg L}^{-1})}$		PC (mg	PO_4^{3-} (mg L ⁻¹)		NH4 ⁺ (mg L ⁻¹)		Fe _{diss} (mg L ⁻¹)		Mn_{diss} (mg L ⁻¹)		δ ¹³ C _{DIC} (‰, PDB)	
	PW	BW	PW	BW	PW	BW	PW	BW	PW	BW	PW	BW	PW	BW	PW	BW	
Decembe	er 2007																
SAR1	50	48	192	134	12.7	6.2	0.61	< 0.09	0.04	0.22	< 0.03	0.09	0.22	0.15	2.86	2.59	
SAR2	25	56	160	163	58.8	3.0	0.81	< 0.09	1.77	0.12	0.34	0.03	0.14	0.11	2.73	-0.27	
SAR3	40	52	166	131	24.2	9.8	0.39	< 0.09	0.07	0.18	0.04	0.11	0.08	0.09	1.22	-0.44	
SAR4	50	46	169	128	15.7	8.9	0.37	< 0.09	0.04	0.22	< 0.03	0.07	0.10	0.10	0.43	-2.15	
SAR5	70	49	178	131	11.2	6.0	0.37	< 0.09	0.07	0.26	0.06	0.09	0.12	0.16	2.72	-1.28	
SAR6	39	49	204	131	9.6	9.8	< 0.09	< 0.09	0.05	0.15	< 0.03	0.04	0.04	0.08	-0.39	-1.80	
SAR7	66	51	143	134	8.8	7.1	0.13	< 0.09	0.08	< 0.04	0.04	0.04	0.11	0.09	0.86	-1.20	
SAR8	32	56	149	157	35.2	12.3	0.33	< 0.09	0.05	0.07	0.03	0.03	0.07	0.09	2.77	1.03	
SAR9	25	47	218	140	21.7	14.8	< 0.09	< 0.09	0.07	0.10	0.07	0.05	0.06	0.11	0.13	0.77	
SAR10	69	47	169	149	3.3	8.7	0.16	< 0.09	0.09	0.04	0.05	0.03	0.12	0.09	-1.05	-0.31	
SAR11	72	48	175	131	10.8	7.0	< 0.09	< 0.09	0.05	0.06	< 0.03	0.09	0.04	0.13	1.94	0.95	
April 200)8																
SAR1	39	35	239	128	2.3	2.7	0.86	0.06	26.10	0.11	0.38	0.17	0.25	0.19	-	2.18	
SAR2	26	46	195	131	1.9	7.1	0.61	0.04	20.50	0.07	0.44	0.14	0.18	0.13	5.49	6.02	
SAR3	33	37	186	128	1.7	4.2	0.16	0.06	2.31	0.16	0.74	0.15	0.12	0.11	2.77	3.45	
SAR4	28	34	149	131	1.3	3.0	0.04	0.07	1.37	0.09	0.73	0.15	0.11	0.12	-2.89	0.78	
SAR5	32	30	204	128	0.9	2.3	0.68	0.08	10.92	0.13	0.37	0.16	0.18	0.18	-	4.67	
SAR6	38	35	122	131	1.5	2.6	0.05	0.1	0.91	0.29	0.37	0.16	0.10	0.11	1.94	5.38	
SAR7	35	34	61	128	2.2	2.0	0.52	0.06	2.80	0.08	0.91	0.14	0.14	0.12	5.13	2.47	
SAR8	25	36	119	128	3.0	5.4	0.05	0.06	1.01	0.07	0.56	0.17	0.10	0.10	1.65	4.82	
SAR9	24	33	159	128	1.2	3.9	0.13	0.05	1.19	0.08	0.86	0.15	0.09	0.13	-1.83	3.61	
SAR10	17	48	96	125	0.9	4.7	0.41	0.06	8.46	0.07	0.75	0.13	0.17	0.12	7.30	6.17	
SAR11	31	50	159	122	2.6	2.6	0.84	0.09	4.42	0.09	1.23	0.15	0.15	0.15	5.96	4.97	
July 2008	8																
SAR1	25	<25	73	171	< 0.9	9.1	0.04	0.43	0.48	0.06	0.03	0.01	0.28	0.04	-4.39	-7.07	
SAR2	27	25	113	159	< 0.9	3.8	< 0.3	< 0.03	0.61	2.25	0.02	0.07	0.26	0.02	-5.15	-6.30	
SAR3	<25	30	67	153	2.0	20.2	0.4	0.14	0.54	0.42	0.03	0.02	0.27	0.06	-7.48	-6.32	
SAR4	<25	<25	58	159	3.3	2.6	0.06	0.06	0.46	4.06	0.03	0.18	0.16	0.08	-2.08	-6.16	
SAR5	26	33	104	174	< 0.9	6.9	0.04	0.03	0.51	1.10	0.03	0.13	0.19	0.09	-6.03	-5.09	
SAR6	34	25	113	153	2.8	4.7	< 0.03	0.03	0.44	1.41	0.03	0.13	0.17	0.15	-4.91	-6.33	
SAR7	25	30	113	137	6.2	5.4	< 0.03	< 0.03	0.41	0.80	0.03	0.10	0.23	0.05	-4.61	-5.15	
SAR8	25	25	119	153	1.4	4.5	< 0.03	0.10	0.44	3.95	0.03	0.08	0.26	0.03	-1.69	-6.15	
SAR9	<25	<25	64	101	1.6	4.5	< 0.03	< 0.03	0.43	1.88	0.03	0.03	0.14	0.03	-5.93	-5.65	
SAR10	27	30	119	140	1.0	7.3	< 0.03	0.08	0.23	0.07	0.03	0.18	0.12	0.18	-6.20	-6.86	
SAR11	<25	28	122	107	<0.9	<0.9	0.03	0.11	0.22	0.07	0.05	0.05	0.11	0.11	-6.73	-5.82	
Septemb	er 2008																
SAR1	27	28	113	113	0.2	0.1	0.06	0.04	0.14	0.14	0.02	0.06	0.15	0.12	1.82	2.01	
SAR2	25	27	116	113	0.4	0.1	0.07	0.05	0.29	0.11	0.02	0.03	0.12	0.11	0.04	0.58	
SAR3	27	31	110	107	0.2	0.1	0.05	0.04	0.11	0.12	0.02	0.09	0.09	0.09	0.13	0.84	
SAR4	29	26	109	107	0.1	0.1	0.05	0.05	0.12	0.13	0.03	0.03	0.08	0.08	1.98	1.42	
SAR5	30	26	104	104	0.6	0.2	0.04	0.05	0.16	0.18	0.05	0.07	0.11	0.13	0.93	1.87	
SAR6	39	33	98	110	0.4	0.0	0.06	0.04	0.28	0.13	0.02	0.04	0.06	0.05	2.19	1.46	
SAR7	27	33	116	88	n.a.	n.a.	0.04	0.04	0.19	0.06	0.02	0.03	0.09	0.75	2.13	2.49	
SAR8	30	33	223	101	0.4	0.2	0.03	0.02	0.46	0.18	0.03	0.03	0.08	0.11	0.07	0.81	
SAR9	35	29	134	101	0.4	0.7	0.04	0.05	0.17	0.11	0.06	0.04	0.09	0.13	1.55	0.97	
SAR10	30	28	125	116	0.1	0.6	0.03	0.03	0.14	0.18	0.04	0.03	0.14	0.11	0.69	0.98	
SAR11	30	30	110	110	0.3	0.3	0.04	0.04	0.11	0.12	0.02	0.08	0.04	0.13	-0.11	-0.08	

Tab. 2. The concentrations of chemical species involved in microbial processes in bottom and pore waters of Lake Sarbsko during the study period (PW-pore waters, BW-bottom waters). Location of sampling sites shown in figure 1.

Between December 2007 and September 2008, chlorinity displayed considerable decrease from 351.7-71.3 mg L⁻¹ to 31.7-8.0 mg L⁻¹. Cl⁻ concentrations in the western part of the lake were distinctly higher than in other locations, especially in the December 2007 data set.

Lake water pH showed only minor variations in time and space (Fig. 3). In December, April, and September, pH was between 7.9 and 8.5, except for the SAR8 site, in which in September 2008 pH dropped to 7.3. On the other hand, in mid-summer, pore water pH dropped significantly to 6.3-7.9, especially in the westernmost and easternmost sections of the lake.

In the course of the study period, pore waters in Lake Sarbsko displayed considerable variation in the concentrations of NO_3^- , NH_4^+ , SO_4^{2-} , HCO_3^- , PO_4^{3-} , and Fe_{diss} and Mn_{diss} (Tab. 2). In December 2007, pore solutions revealed increased concentrations of NO_3^- , SO_4^{2-} ,

 HCO_3^- and PO_4^{3-} , as well as very low contents of NH_4^+ , Fe_{diss} , and Mn_{diss} . The concentrations of PO_4^{3-} and Mn_{diss} in the December data set displayed an overall eastward decline. SO_4^{2-} exhibited three local maxima located in the western and eastern margins of the lake and along the Sarbsko Barrier. HCO_3^- was evenly distributed throughout the lake.

In April 2008 the concentrations of SO_4^{2-} dropped from 25-72 mg L⁻¹ to 17-39 mg L⁻¹ and remained low to the end of the study period. In contrast, concentrations of Fe_{diss} and PO₄³⁻ increased distinctly at most of the sites. Dissolved Fe revealed a tendency to increase towards the east. Mn_{diss} was slightly higher than in December and displayed an overall eastward decline. Bicarbonates were at the same level as in December 2007; however, in the western part of the lake the concentrations of HCO₃⁻ were slightly higher than in winter.

Tab. 3. The depth of wind-induced vertical mixing of Lake Sarbsko during sample collection periods calculated using hydrodynamic formulas. Numbers in bold indicate resedimentation of lake bottom deposits. Climatological data were obtained from the Institute of Meteorology and Water Management (IMGW), Gdynia, Poland. # - measured in November 2007. D_w : mean daily wind direction; V_w : maximum daily wind speed; F_w : effective wind fetch; D_{WML} : depth of water mixed layer.

	Water 13 th December 2007						10 th April 2008				10 th Jul	y 2008		17 th September 2008			
	depth [#] (m)	D_{w}	V_w (m s ⁻¹)	F _w (m)	D _{WML} (m)	D_w	V_w (m s ⁻¹)	F _w (m)	D _{WML} (m)	D_w	V_w (m s ⁻¹)	F _w (m)	D _{WML} (m)	D_w	V_{w} (m s ⁻¹)	F _w (m)	D _{WML} (m)
SAR1	0.5	15	6.03	130	0.5	53	6.03	400	0.9	254	9.00	110	0.6	64	7.00	860	1.5
SAR2	0.8	15	6.03	430	0.9	53	6.03	1020	1.5	254	9.00	260	1.0	64	7.00	1320	1.9
SAR3	0.8	15	6.03	50	0.3	53	6.03	70	0.3	254	9.00	110	0.6	64	7.00	110	0.5
SAR4	1.5	15	6.03	250	0.7	53	6.03	700	1.2	254	9.00	590	1.5	64	7.00	1100	1.7
SAR5	1.7	15	6.03	50	0.3	53	6.03	300	0.7	254	9.00	600	1.5	64	7.00	610	1.2
SAR6	1.6	15	6.03	340	0.8	53	6.03	800	1.3	254	9.00	910	1.9	64	7.00	1040	1.7
SAR7	1.5	15	6.03	50	0.3	53	6.03	200	0.6	254	9.00	800	1.8	64	7.00	400	1.0
SAR8	2.5	15	6.03	330	0.8	53	6.03	610	1.1	254	9.00	1110	2.2	64	7.00	720	1.4
SAR9	0.8	15	6.03	460	0.9	53	6.03	570	1.0	254	9.00	1020	2.1	64	7.00	590	1.2
SAR10	1.5	15	6.03	50	0.3	53	6.03	110	0.4	254	9.00	1160	2.2	64	7.00	150	0.6
SAR11	1.8	15	6.03	210	0.6	53	6.03	310	0.7	254	9.00	1380	2.4	64	7.00	330	0.9

Moreover, pore water became enriched in ammonium, and the highest concentrations of NH_4^+ were observed in the westernmost part of the lake, in front of the barrier head, and in the eastern section of the basin. After the spring peaks, the concentrations of NH_4^+ as well as those of HCO_3^- , PO_4^{3-} , and Fe_{diss} declined significantly in subsequent months. During the summer, pore waters were enriched in Mn_{diss} .

During winter and spring, pore waters revealed higher concentrations of dissolved chemical species than overlying solutions, while in the summer, vertical concentration gradients were less pronounced. In mid-summer, bottom waters displayed slightly higher concentrations of SO_4^{2-} , Cl⁻, PO_4^{3-} , NH_4^+ , NO_3^- , HCO_3^- and Fe_{diss} than pore waters. Only dissolved Mn was evidently more abundant in pore waters. In September 2008 the concentrations of most ions in bottom and pore waters were similar except for the SAR8 site, where HCO_3^- and NH_4^+ were higher within the sediments.

Spatial distribution of the above chemical species in pore waters of Lake Sarbsko display irregular patterns. However, some inter-correlations between the dissolved components and correspondence between the composition of water and bottom sediments were found. The distribution of HCO₃⁻ in Lake Sarbsko during winter was highly negatively correlated with TIC in the sediments (r = -0.88). Mn_{diss} in pore waters displayed positive relationships with Cl⁻ and PO₄³⁻ in both December 2007 (r = 0.72 and r = 0.68, respectively) and April 2008 (r = 0.52 and r = 0.85, respectively). In July 2008 the correlations were missing and in September 2008 they were very weak.

Pore waters revealed considerable changes in stable C isotope composition of dissolved inorganic carbon (DIC) (Tab. 2). δ^{13} C varied significantly in time and space. In December, $\delta^{13}C_{DIC}$ were between -1.05 and 2.86‰. In April 2008, stable C signatures rose and ranged from -2.89 to +7.30‰ and were rather unrelated to both sediment composition and pore water chemistry. In July 2008, $\delta^{13}C_{DIC}$ dropped to -1.7 - -7.5‰, and the lowest values occurred in the sites where $\delta^{13}C_{DIC}$ in

April were high. In September, $\delta^{13}C_{DIC}$ were positive in most sites and varied from -0.11 to 2.19‰.

4.4. Surface sediment mixing

As shown in table 3, the depth of lake water mixing in Lake Sarbsko varied between 0.3-0.9 m in December 2007 and 0.6-2.4 m in July 2008. The deepest mixing during summer was due to the high speed of westerlies, resulting in very long values of effective wind fetch, especially in the central-eastern section of the lake. In contrast, calm water conditions in winter were mainly caused by low effective fetch of northerly wind over the lake. Surface sediment resuspension was most effective in July 2008. From theoretical considerations, it emerges that, during summer, redeposition occurred in 7 out of the 11 study sites. In the littoral part of Lake Sarbsko, spread along the southern shore (SAR2 and SAR9), sediment mixing occurred throughout the whole study period. On the other hand, in the sites located along the Sarbsko Barrier (SAR3 and SAR5) and in the deepest part of the lake (SAR8), sediment stirring was rather unlikely.

5. DISCUSSION

Enrichment of bottom deposits of Lake Sarbsko in TOC indicate high organic matter supply and/or its good preservation (Barnes & Barnes 1978). High organic matter input is in accordance with enhanced productivity of the lake, reflected in the concentrations of chlorophyll-a, which fits the range typical for highly eutrophic turn. good preservation waters. In indicates anoxic/suboxic conditions below sediment-water interface. Relatively low molar TOC/N ratio argues for the predominance of autochthonous organic matter, with minor contribution of terrestrial compounds (Meyers & Teranes 2001). The fresh phytoplankton-derived organic matter tends to be very reactive in sedimentary systems and prone to microbial decomposition. The distribution of clastic sediments shows the extent of hydrodynamically active sections of the lake bottom, where sediment stirring by wind waves and currents occurs permanently.

Within these zones organic matter reveals rather low TOC/N ratios, which indicates that in the high water energy parts of the lake organic matter is very quickly decomposed, so that freshly deposited organic matter can be retained only for a relatively short time.

Seasonal changes in chemical composition of pore solutions in Lake Sarbsko's surface sediments can be explained in terms of bacterial activity, because microbes use inorganic dissolved species as electron acceptors during the processes of sedimentary organic matter decomposition. These processes tend to occur in anoxic/suboxic conditions within the surface layer of bottom deposits. In shallow-water and highly productive lakes, rich in plankton-derived organic matter, such conditions can develop within surface deposits despite the presence of free oxygen in near-bottom waters (Krevs *et al.* 2006).

The effect of temporal changes in salinity on microbial processes in pore waters in Lake Sarbsko seems not to be high. Saltwater ingressions to the lake, expressed in the concentrations of Cl⁻, were encountered in December 2007 in the westernmost part of the lake and along the Sarbsko Barrier (Woszczyk et al. 2010). However, there were no statistically significant relationships between chlorinity and the concentrations of chemical species involved in microbial processes, except for the concentrations of Mn. Overall positive covariance of Cl⁻ and Mn_{diss} during winter and spring, together with rather low concentrations of dissolved manganese (Tab. 2), might indicate that saltwater inflows to Lake Sarbsko cause local density stratification of lake waters - which can be seen in the much higher Cl⁻ concentrations in pore solutions - and thus create mildly reducing conditions within surface deposits, which in turn favours reductive solubilisation of Mn. Nevertheless, this process delivers appreciably low amounts of manganous Mn to the lake waters.

The pattern of temporal changes in the concentrations of dissolved chemical species shows that bacterial degradation of sedimentary organic matter in the lake mainly occurs during spring and summer, which is in accordance with data from other studies (Wetzel 1983; Hamilton-Taylor *et al.* 1996; Falcão & Vale 1998; Lojen *et al.* 1999). According to Lojen *et al.* (1999), this can be explained by greater availability of labile phytoplanktonic organic matter and higher water temperatures. Mudryk & Donderski (1997) reported that temperatures below 15 °C abruptly inhibit activity of protein-decomposing bacteria.

The enhancement of microbial processes is indicated by the increases in lake water DIC (HCO₃⁻) and by the concentrations of ammonium and phosphates together with diminished concentrations of sulphates (Lojen *et al.* 1999).

Increased concentrations of ammonium in the lake can be related to microbial decomposition of proteins and nitrogenous organic compounds (Wetzel 1983) and to reduction of nitrates (Stumm & Morgan 1981). The former was found to be the most important bacterial metabolic process in coastal lakes of the Polish coast (Mudryk & Donderski 1997), and the latter is indicated by the coincidence of NH₄⁺ enrichment with the drop in the concentrations of NO_3^- (Tab. 2). On the other hand, Rozan et al. (2002) reported that ammonium is produced during bacterial reduction of SO_4^{2-} , which is evidenced by the coincidence between the increase in NH_4^+ and lowering in the concentrations of sulphates. Bicarbonates are direct products of different pathways of oxidation of organic compounds (Furrer & Wehrli 1996); however, their spatial distribution throughout the sediments of Lake Sarbsko can be, at least partially, determined by precipitation/dissolution of CaCO₃, as indicated by the correlation with carbonate content mentioned above. From our calculations it appears that in December 2007 pore waters in Lake Sarbsko were slightly supersaturated with respect to calcite [SI between 0.13 and 0.70 (unpublished data by the authors)], which suggests that the pool of microbially released HCO3⁻ could have been depleted owing to precipitation of CaCO₃. In contrast, during summer, measured concentrations of bicarbonates were affected by dissolution of sedimentary carbonates, as indicated by SI_{calc} in the range from +0.16 to -2.09 (a positive value was obtained in only one site).

On the other hand, phosphates participate only inactively in bacterial processes in sediments. The increase in PO_4^{3-} concentrations in pore solutions is mainly related to reduction of amorphous Fe/Mn oxides, which are effective scavengers for PO_4^{3-} ions in lakes (Gächter & Müller 2003). This mechanism provides a reasonable explanation for the spring maximum in PO_4^{3-} in Lake Sarbsko, as enrichment in phosphates coincides with the increase in Fediss and Mndiss. The former two are mainly attributed to ferrous Fe and manganous Mn, respectively, because oxidized forms of Fe and Mn tend to be depleted in lakes owing to their insolubility in water (Stumm & Morgan 1981; Wu et al. 1997). The link between the release of phosphates and reduction of metal oxides in Lake Sarbsko is shown by positive correlation between the concentrations of PO₄³⁻ and Mn_{diss}. On the other hand, increased concentrations of PO₄ during winter are surprising and cannot be explained conclusively. It seems, however, that enrichment in PO_4^{3-} is related to high NO_3^{-} concentrations and increased pH. Jensen & Andersen (1992) and Niemistö et al. (2011) showed that in shallow, polymictic and well-oxygenated lakes, high pH favours desorption of phosphates from aerobic sediments by OH⁻ exchange with PO_4^{3-} ions bound to metal oxides. In turn, NO_3^{-} additions to pore waters contribute to PO_4^{3-} release from the sediments owing to overall stimulation of bacterial activity (Jensen & Andersen 1992). Alternatively, release of phosphates in winter could be related to reduction of Mn oxides, as indicated by positive corre-



Fig. 5. Schematic representation of temporal changes in lake water chemistry and the sequence of microbial processes within surface deposits of Lake Sarbsko.

lations between PO_4^{3-} and Mn_{diss} in the December 2007 data set.

The mechanism of P release to lake waters under oxic/mildly reducing conditions in winter can fuel late winter/early spring biological productivity, mirrored in the enhanced concentrations of chlorophyll-*a* in Lake Sarbsko in February 2008. Moreover, this process may contribute significantly to eutrophication of the lake, especially because release of phosphorus from the bottom deposits in winter is followed by reduction of sedimentary Fe oxides in spring (Tab. 2; Fig. 5), which hinders refixation of PO₄³⁻ in sediments and makes it available for lake phytoplankton.

On the other hand, other chemical species produced during decomposition of sedimentary organic matter (namely, NH_4^+ , Mn_{diss} , and Fe_{diss}) seem to have limited influence on the composition of overlying waters. Their concentrations in bottom waters were low throughout the study period, presumably owing to oxidation at or above the sediment-water interface.

In April 2008, together with distinct enrichment in HCO₃⁻, NH₄⁺, Fe_{diss}, and PO₄³⁻, pore waters in some locations within the lake displayed very high values of $\delta^{13}C_{DIC}$ (5.1-7.3‰) (Tab. 2), which can be associated with methanogenesis (Lojen *et al.* 1999). The presence

of bubble microbial methane in Lake Sarbsko was shown by Woszczyk *et al.* (2009).

Microbial processes alter lake water alkalinity and pH. Sulphate reduction and Fe/Mn-oxide reduction produce alkalinity and increase pH (Furrer & Wehrli 1996; Soetaert et al. 2007). Denitrification in turn exerts the opposite effect, albeit resulting in only slight acidification (Furrer & Wehrli 1996; Soetaert et al. 2007). Consequently, these processes cannot explain a distinct drop in pore water pH between spring and summer 2008. A negative effect on pH can be attributed to re-oxidation processes, mainly oxidation of CH₄. However, a minor contribution from oxidation of Fe²⁺ cannot be ruled out (Davison 1993; Hamilton-Taylor et al. 1996; Soetaert et al. 2006). Oxidation of methane is evidenced in strong depletion of lake water DIC in heavy C isotope between April and July 2008, and oxidation of Fe is inferred from a distinct drop in the concentration of Fe_{diss} in pore waters (Tab. 2).

Nevertheless, oxidative processes in July 2008 occurred not only in the sediments but also in the lake water column, as indicated by very negative $\delta^{13}C_{DIC}$ in bottom waters (Tab. 2). Since methane oxidation involves dissolved oxygen (Liu *et al.* 1996), it can be responsible for significant decrease in O₂ concentrations

in bottom waters during summer. In July 2008, pore waters in Lake Sarbsko displayed increased concentrations of Mn_{diss} , which can be explained in two ways.

The first possibility is that the release of Mn from the sediment solid phase resulted from dissolution of calcite in acidified pore waters, in which SI_{calc} was very negative in most sites. The link between Mn and carbonates can be explained by the fact that manganous Mn often substitutes for Ca²⁺ in crystal lattices, owing to the similarity of ionic radii of these two ions (Shen *et al.* 2007). Incorporation of Mn²⁺ in carbonates precipitating from the water column in Lake Sarbsko can be supported by a distinct drop in the concentrations of Mn_{diss} in lake bottom waters in July 2008, when supersaturation with respect to calcite was achieved [SI_{calc} between 0.66 and 1.18 (unpublished data by the authors)] and spontaneous precipitation of CaCO₃ was possible.

More likely, however, is the possibility that high concentrations of Mndiss indicate reduction of Mn oxides within surface sediments. According to Davison (1993), this chemical or microbially-mediated process occurs rapidly whenever manganese oxides enter an anoxic environment and ferrous iron and sulphides act as the most important reducing agents. Distinctly depleted Mn_{diss} in bottom waters in July 2008 provides the evidence for the enhanced oxidation and thus precipitation of manganese in the lake water column, which is often observed during summer at elevated water temperatures (Davison 1993; Abesser & Robinson 2010). The rate of reduction of Mn in pore waters seems to be related to the intensity of oxide precipitation from bottom waters, as suggested by a strong negative correlation between the concentrations of Mn_{diss} in pore and bottom waters (r = -0.66) (Tab. 2). Moreover, reduction of sedimentary Mn oxides contributes to immobilization of $\ensuremath{\mathsf{Fe}_{\mathsf{diss}}}$ and decreases pH within surface sediments, according to the reaction: $2Fe^{2+} + MnO_2 + H_2O \rightarrow Fe_2O_3 + Mn^{2+} + 2H^+$ (Davison 1993).

Temporal changes in chemical composition of interstitial waters indicate that the pathways of bacterial decomposition of organic matter in Lake Sarbsko sediments vary with time (Fig. 5). Enhanced microbial activity commences in spring with degradation of amino acids and/or reduction of NO₃⁻, SO₄²⁻ and Fe/Mn oxides, as well as with methanogenesis. As a result, the concentrations of Fediss, Mndiss, NH4⁺, and PO4³⁻ in pore waters increase and the concentration of SO_4^{2-} declines. These processes are followed by aerobic methane oxidation with a minor contribution of MnO₂ reduction during summer, as indicated by the significant decrease in $\delta^{13}C_{DIC}$ and enrichment in Mn_{diss} in July 2008. Summer increase in the rate of consumption of CH₄ in the lake is in accord with the observations of Utsumi et al. (1998), Ford et al. (2002), and Kuznetsova & Dzyuban (2005) from shallow and polymictic water bodies located in different environmental conditions.

Aerobic oxidation of methane in lakes is often attributed to vertical water mixing and resuspension of bottom deposits (Engle & Melack 2002; Bussmann 2005), which deliver oxygen to methane-rich bottom and pore waters. However, very high oxygenation of lake waters is harmful for methane-oxidizing bacteria (Rudd *et al.* 1976; Ford *et al.* 2002), which require some dissolved nitrogen compounds to become oxygen-insensitive (Rudd *et al.* 1976).

On the other hand, the cycling of CH_4 in shallow lakes is influenced by lake level fluctuations. Engle & Melack (op. cit.) found that, during lake level low-stands, diffusive flux of methane from the bottom deposits to overlying oxygenated waters increases, thus stimulating the activity of methanotrophic bacteria.

We believe that the combination of the above mechanisms (i.e., water mixing and drop in lake water level) was critical for initiating aerobic oxidation of CH_4 in Lake Sarbsko during summer.

This hypothesis is corroborated by hydrodynamical considerations. Table 3 shows how the depth of windinduced lake water mixing in Lake Sarbsko changed between sample collection periods. The calculations indicate that, despite the polymictic character of this water body in December 2007 and April 2008, anemometric conditions were rather unfavourable for deep water mixing, owing to low effective wind fetch (winds from N and NE) and relatively low wind speed. On the other hand, westerly winds in mid-July resulted in complete lake water overturn throughout a major part of the lake and stirring of bottom deposits (Tab. 3). Moreover, the water level in Lake Sarbsko during summer tends to be at its yearly minimum (Woszczyk et al. 2010), and the lake depth is ca 50-60 cm lower than in autumn highstands, which could further expose the surface deposits for resedimentation.

In July 2008 the concentrations of most dissolved species (Mn is an exception) in lake bottom waters were higher than in pore solutions (Tab. 2). We hypothesize that these inverse hydrochemical gradients were due both to sweep up of dissolved ions from the sediments to overlying waters during lake water overturn and to resuspension of bottom deposits. Vertical mixing brought some NH₄⁺ and CH₄ to oxygenated bottom waters and thus fuelled the activity of methanotrophs. Utsumi et al. (1998) demonstrated that during lake water movements methanotrophic bacteria can be displaced together with chemical species and sediment particles and can thrive in an oxic water column. On the other hand, enrichment in Mn_{diss} in pore waters is explained by a high rate of MnO₂ reduction, which can be chemically or biologically consumed within several minutes (Davison 1993). Thus, higher concentrations of Mn_{diss} are not contraindicative of removal of pore solution from the sediments due to stirring, because manganous ions could build up shortly after resedimentation of suspended particles. In September 2008, oxidation of CH_4 stopped. This resulted in the increase in pore water pH and $\delta^{13}C_{DIC}$. However, the concentrations of dissolved species were appreciably low, indicating that, within the surface deposits, oxic conditions prevailed. In winter, bacterial activity is suppressed, and consequently pore waters reveal higher concentrations of oxygenated chemical species (mainly nitrates), and bottom waters display very high levels of oxygenation.

6. CONCLUSIONS

The intensity and pathways of microbial processes in Lake Sarbsko display appreciable spatial diversity, which cannot be conclusively explained. However, it is clear that intensity and pathways of microbial decomposition of organic matter in the lake are rather unrelated to bulk sediment composition and only slightly influenced by changes in lake water salinity. Microbial processes in the surface sediments are mainly active in spring and summer. During spring, chemical composition of pore water is affected by degradation of organic matter at the expense of inorganic chemical species under suboxic/anoxic conditions. In summer, aerobic oxidation of organic compounds (mainly methane) predominates. The switch from anaerobic to aerobic processes is driven by lake water mixing during lowered lake water level. Aerobic oxidation of methane significantly contributes to depletion of dissolved oxygen in lake waters during summer. In Lake Sarbsko, internal loading of phosphorus from bottom sediments occurs under both oxic/mildly reducing and anoxic conditions. The former was observed in winter and enabled late winter/early spring increase in bioproductivity in the lake.

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