

Some characteristics of the sediments of healthy and degraded reed stands at Lake Fertő/Neusiedler See

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Abstract. Changes in the electric conductivity, pH, redox potential, temperature, PO_4^{3-} , NH_4^+ , NO_3^- , SO_4^{2-} , S^{2-} , Cl^- , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , total carbon (TC), total organic carbon (TOC) and total nitrogen (TN) concentrations of the sediment interstitial water and in the electron transport system activity (ETS), litter associated fungal biomass (as ergosterol), organic matter content (LOI) of the sediment were studied in healthy and degraded reed stands at the Hungarian part of Lake-Fertő /Neusiedler See. Based on the results of the multivariate statistical analyses, significant differences have been found between the healthy and die-back sites.

INTRODUCTION

In wetland ecosystems, which are among the most productive ecosystems (Mann & Wetzel, 2000), the largest part of the organic material production is formed by emergent macrophytes, playing an important role in the detritus food chain (Wetzel, 2001). This macrophyte originated detritus is finally accumulated in the sediment, where it undergoes through different physical, chemical, and microbiological transformations.

At Lake Fertő/Neusiedler the largest input of organic matter is originated from the high *Phragmites australis* (Cav. Trin. ex Steudel) production (Dinka *et al.*, 2010). *Phragmites australis* is a cosmopolitan plant species, it has functionally adapted to the anaerobic conditions of the sediment by transporting oxygen into the rhizosphere (Armstrong & Armstrong, 1998) and favouring the oxidation of the reduced chemical compounds as well as the microbial oxidation processes (Azzoni *et al.*, 2001).

The microbial mineralization of organic matter – which is carried out by microbial communities of variable compositions (Fenchel & Blackburn, 1979), using sequentially different electron acceptors (Jones, 1985) – is highly influenced by the presence or absence of oxygen and has a remarkable influence on the chemical composition of the sediment and sediment interstitial water

(Berner 1980). The products of bacterial metabolism (CO_2 , CH_4 , NO_3^- , NH_4^+ , H_2S , PO_4^{3-}) enter into the sediment interstitial water (Gaillard, 1993). In the sediments the majority of microorganisms are attached to the sediment surface and only a minor portion of them may be found in the sediment interstitial water (Hirsch & Rades-Rohkohl, 1988; Griebler, 1996).

In the Hungarian part of Lake Fertő/Neusiedler the purposeful hydrobiological research began in the 1970s with a gradually increasing spectrum and became an international field of interest for hydrobiologists (Dinka, 2007). The previous comprehensive studies on sediment and water chemistry conducted at Lake Fertő have been concentrated mainly on the open water areas and inner ponds (Dinka, 1994).

In the last few decades several authors have reported changes in the structure of the reed (Ostendorp, 1989; Armstrong *et al.*, 1996), which is connected with the reed degradation processes. The analyses of the influence of reed stands on the biogeochemical cycles in the aquatic ecosystems and the degradation processes which have been observed in Central-Europe stimulated the comparative investigations of the healthy and degraded reed stands. Based on these analyses, aligned research was carried out in 8 countries from 1993 to 1999 in the frame of EU-EUREED I–II program and it was pointed out among the

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others that the quality of water and sediment had a direct influence on reed die-back (e.g. Čížková *et al.*, 2001; van der Putten, 1997).

The studies conducted in the framework of EUREED program at Lake Fertő/Neusiedler See, have elucidated that the reed stands with different health conditions differ in many aspects from each other (Dinka & Szeglet, 1999, 2002). These previous findings have justified the wider investigation of the sediments of reed stands at Lake Fertő/Neusiedler See (Dinka, 1998, 2001; Ágoston-Szabó, 2004, 2007), which may also influence the habitat diversity.

The aim of this study was to compare the healthy and degraded reed stands on the basis of the chemical parameters of surface and sediment interstitial water and the microbial activity of the sediment. The hypothesis was that the sediment interstitial water chemistry and the microbial activity of the sediment are significantly different in the healthy and degraded reed stands.

Study area

Lake Fertő or Neusiedler See (Hungarian and Austrian name, respectively) situated on the Hungarian–Austrian border (47° 42' N, 16° 46' E, Fig. 1) has a surface area of 309km² (Hungarian part 75km²), with a mean depth of 1.1m. 54% of the whole lake and 85% of the Hungarian part is covered by reed, characterised by an enhanced detritus accumulation and mixing effect of the wind, therefore the sediment water interactions are more intensive.

Sampling sites were selected in the Hungarian part of the lake. The chemical characteristics of the water and interstitial water were examined at three sampling sites (Fig. 1):

– Site 2 is a homogenous reed area, situated in a healthy reed stand, with consistent gray coloured sediment.

– Site 3 is a degraded reed area, characterised by clumped distribution of the culms, consistent, black coloured sediment with negative redox conditions, high organic matter content and S²⁻ con-

centrations, which induce the callus blocking of aerenchyma channels (Armstrong *et al.*, 1996).

– Site 3.1 is a replanted, young reed area in the reedless region of the degraded reed stand (site 3) with less consistent, black coloured sediments. At this site (3.1) samples were taken both from the water among reed shoots and the unvegetated areas of the thinned reeds area. The different character of these plots will be referred as "in" (in reed tussocks, among reed shoots) and "out" (unvegetated area around the reed tussocks) in the figures.

MATERIALS AND METHODS

Surface and interstitial water

Interstitial water was taken from 0–20 and 20–40cm sediment layers (from plastic sampling tubes previously set at the sampling sites); the reason for choosing these layers was that 80% of the reed rhizome system is found in the above 40cm sediment layer.

The electric conductivity, pH, temperature of the water and interstitial water were determined on the spot. The redox potentials were determined in the laboratory with calomel electrode (Pt), and expressed versus normal hydrogen electrode by adding +240mV (Eh of saturated calomel electrode).

The Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻, NO₃⁻ concentrations were determined by Dionex ionchromatograph (DX-120). The PO₄³⁻ and NH₄⁺ concentrations of the interstitial and surface water were determined with standard chemical analysis (Felföldy 1980, Golterman *et al.* 1978), while the S²⁻ concentration was measured with iodometric titration, after ZnCl₂ precipitation (Golterman *et al.* 1978).

The total carbon (TC), the total organic carbon as non-purgeable organic carbon (TOC) and the total nitrogen (TN) concentrations of the sediment interstitial water were determined by TOC analyser (liqui TOC).

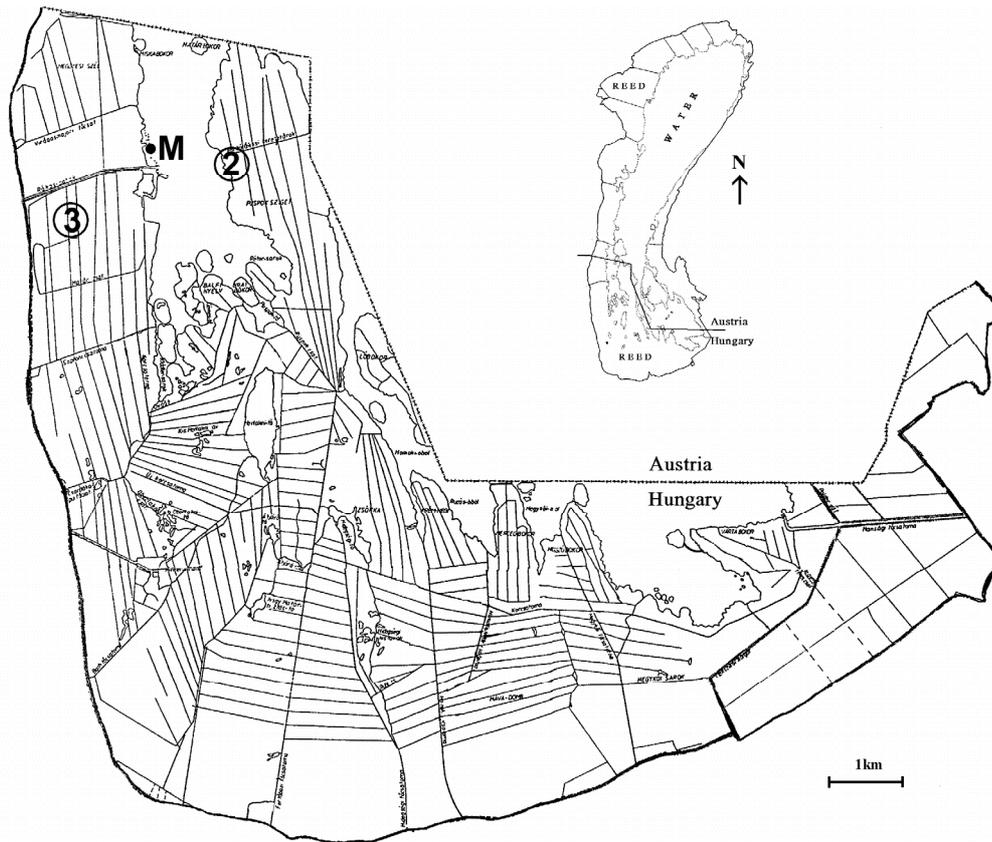


Figure 1. Sampling sites at Lake Fertő. 2 – healthy reed stand site, 3 – degraded reed stand site (including site 3.1 which is not indicated on the map), M – Meteorological Station

Sediment

Sediment cores were collected at each sampling site with plastic sampling tubes of 1 meter (diameter: 19.5cm). Subsamples from the 0–5cm, 19–20cm and 39–40cm layers (in which most part of the rhizome system occur) were placed in a crucible, and dried to constant weight at 105 °C for 24h for determination of the moisture content, then combusted at 450 °C (Molnár & Dinka, 1997; Jungwirth, 1979) for 4h in a muffle furnace for determination of organic matter content by loss on ignition method (LOI).

Litter associated fungal biomass was estimated by extracting and quantifying ergosterol from sediment samples (Gessner & Newel, 1997; Bååth, 2001).

The electron transport system (ETS) assay described by Kenner & Ahmed (1975), Owens &

King (1975), and modified by Broberg (1985) was used to determine the potential microbial respiratory activity of the sediment.

Data analysis and statistical methods

An analysis of variance, Pearson's correlation and cluster analysis were performed using the Statgraf 1.0 for Windows and Past software packages (Hammer *et al.*, 2001) and only the results of the statistical analyses are given in this study.

Data of sampling

Samples were collected on 19/09/2006, when the water level of the lake was 96cm (115.47m above the Adriatic Sea level, which is an average water level) at the gauge of Fertőrákos.

RESULTS

Surface and interstitial water

In situ measured parameters

The temperature of the surface water varied between 19.1–19.2 °C and decreased in the function of the sediment depth with 0.3–1.0 °C until the 0–20cm sediment layer, and by 0.3–0.5 °C until the 20–40cm sediment layer.

The redoxpotential of the surface water varied between (-53.0) – 183.4 mV, the lowest values were recorded at site 3.1 (Fig. 2). The redox values decreased (but not significantly, $p > 0.05$), in the function of the sediment depth.

The pH values in the surface water ranged from 7.9 to 8.5 (Fig. 2), and significantly ($p < 0.05$) decreased in the function of the sediment depth at each sampling site.

The electrical conductivity of the surface water varied between 3.5–4.2 mS cm⁻¹ and significantly ($p < 0.05$) increased with the sediment depth (except for site 2) (Fig. 3). At site 2 it was lower than at site 3 and 3.1 both in the water and sediment interstitial water.

Nutrient concentrations

The PO₄³⁻ concentrations of the surface water ranged from 0.03 to 1.51 mg l⁻¹ (Fig. 2), and increased with the depth of the sediment until the 20cm, then decreased until the 40cm, but these variations were not significant at $p < 0.05$ level.

The NH₄⁺ concentrations varied between 0.18–0.46 mg l⁻¹ and the NO₃⁻ concentrations between 0.06–0.44 mg l⁻¹ in the surface water (Fig. 2), the concentrations of both compounds increased with the depth of the sediment, but significantly ($p < 0.05$) only the NH₄⁺ concentrations at sites 3 and 3.1 in.

These redox sensitive nutrient compounds

(PO₄³⁻, NH₄⁺, NO₃⁻) showed a strong negative correlation with the redoxpotential both in the water and sediment interstitial water (with the exception of PO₄³⁻ in the 20–40cm sediment layer) (Tab. 1).

The TC concentrations varied between 387.8–733.9 mg l⁻¹, the TOC between 163.8–377.8 mg l⁻¹ and the TN concentrations between 5.9–10.9 mg l⁻¹ in the surface water, and the highest values were measured at site 3.1 (Fig. 2). The TN concentrations significantly increased ($p < 0.05$) in the function of sediment depth (with the exception of site 3.1 out), while the TOC and TC concentrations showed a significant increase ($p < 0.05$) only at site 3. The highest TOC and TN concentrations were measured in the sediment interstitial water of site 3.

In each of the investigated samples a strong positive correlation was found between the TOC-TC, TOC-TN concentrations and between the TIC-TC, TIC-TN concentrations, respectively (Tab. 1).

Strong negative correlation was found among the TC, TOC, TN concentrations and the pH, redoxpotential of the sediment interstitial water (Tab. 1).

The TN concentrations of the water showed a stronger positive correlation with the NO₃⁻ ($R^2 = 0.99$) concentrations than with the NH₄⁺ concentrations ($R^2 = 0.71$), while it was inverse in the deeper sediment layers (0–20cm: $R^2_{\text{TN-NH}_4} = 0.60$, $R^2_{\text{TN-NO}_3} = 0.47$; 20–40cm: $R^2_{\text{TN-NH}_4} = 0.86$, $R^2_{\text{TN-NO}_3} = 0.08$). The TOC concentrations of the sediment interstitial water showed a strong correlation with the LOI of the sediment (0–20cm: $R^2_{\text{TOC-LOI}} = 0.87$, 20–40cm: $R^2_{\text{TOC-LOI}} = 0.97$).

The TC:TN molar ratio in the surface water ranged from 75.6 to 83.4, and it was higher than in the sediment interstitial water (0–20cm: 61.8–80.9 and 20–40cm: 56.97–88.5).

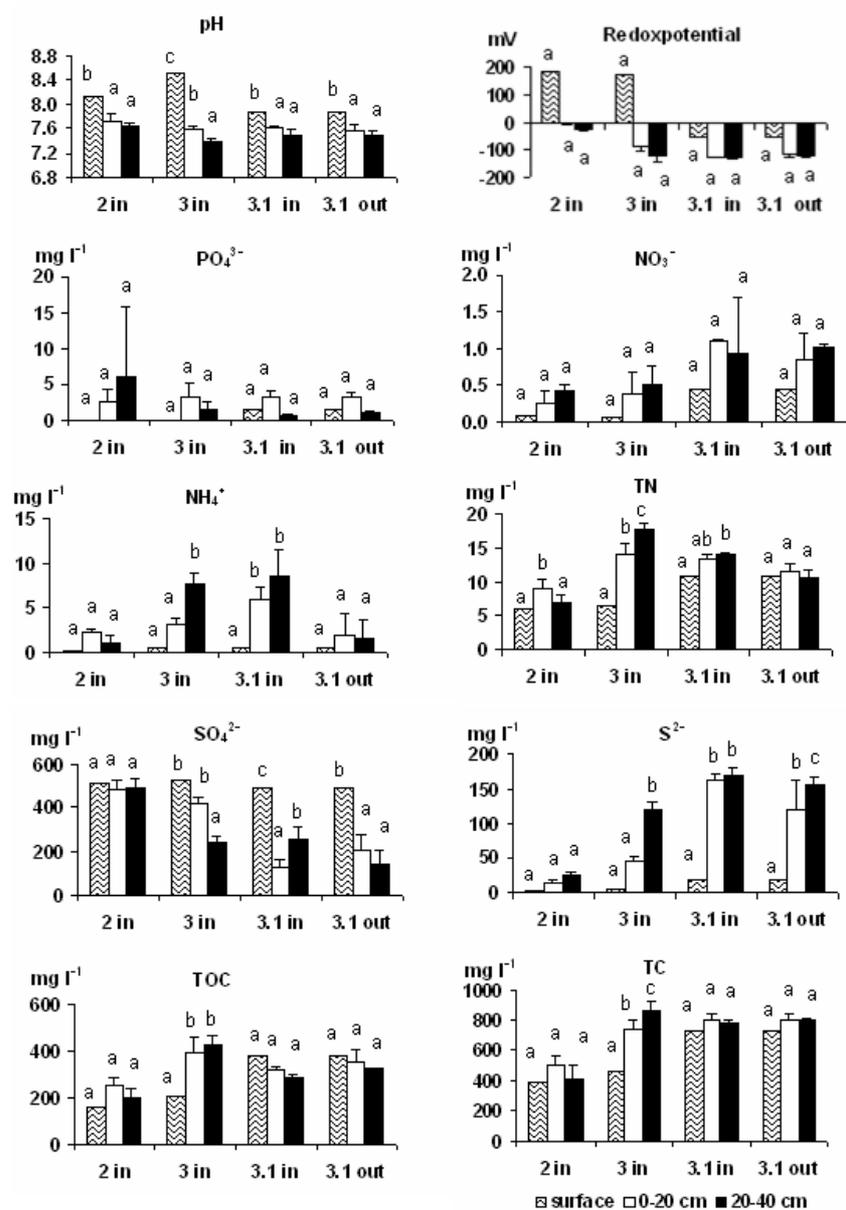


Figure 2. Changes in the chemical parameters of the surface and sediment interstitial water (values followed by different letters are significantly different at the 0.05 probability level)

Changes in the concentrations of the main ions

The SO_4^{2-} concentrations of the surface water varied between 488.4–519.0 $mg\ l^{-1}$, the highest values were measured in the healthy reed stand (site 2). The SO_4^{2-} concentrations significantly ($p < 0.05$) decreased in the function of the sediment depth (with the exception of site 2) (Fig. 2).

The S^{2-} concentrations varied between 2.2–19.0 $mg\ l^{-1}$ in the surface water, the highest values were recorded at site 3.1, and significantly ($p < 0.05$) increased in the function of the sediment depth (with the exception of site 2) (Fig. 2). The highest decrease in SO_4^{2-} concentrations and increase in S^{2-} concentrations were recorded at site 3.1.

Table 1. Pearson's correlations between some chemical parameters

	surface	0-20 cm	20-40 cm
TOC-TC	1.00	0.74	0.88
TOC-TN	1.00	0.82	0.89
TIC-TC	1.00	0.92	0.94
TIC-TN	0.98	0.62	0.69
TOC-pH	-0.72	-0.85	-0.97
TOC-redox	-0.99	-0.67	-0.75
TC-pH	-0.69	-0.97	-0.95
TC-redox	-0.98	-0.99	-0.98
TN-pH	-0.77	-0.78	-0.96
TN-redox	-1.00	-0.80	-0.77
SO ₄ ²⁻ -redox	0.92	0.83	-0.96
S ²⁻ -redox	-1.00	-0.85	0.99
SO ₄ ²⁻ -NH ₄ ⁺	-0.31	-1.00	-0.98
S ²⁻ -NH ₄ ⁺	0.70	1.00	0.97
SO ₄ ²⁻ -PO ₄ ³⁻	-0.92	-0.51	0.98
S ²⁻ -PO ₄ ³⁻	1.00	0.53	-0.98
SO ₄ ²⁻ -NO ₃ ⁻	-0.94	-1.00	-0.57
S ²⁻ -NO ₃ ⁻	1.00	1.00	0.85
PO ₄ ³⁻ -redox	-1.00	-0.91	1.00
NO ₃ ⁻ -redox	-1.00	-0.85	-0.69
NH ₄ ⁺ -redox	-0.66	-0.51	-0.63

The SO₄²⁻ concentrations positively, while the S²⁻ concentrations negatively correlated with the redoxpotential values both in the water and sediment interstitial water (Tab. 1). The NH₄⁺, PO₄³⁻ and NO₃⁻ concentrations positively correlated with S²⁻ concentrations and negatively with the SO₄²⁻ concentrations (with the exception of PO₄³⁻ in the 20–40cm sediment layer) (Tab. 1).

The concentrations of the main cations: Na⁺, K⁺, Ca²⁺, Mg²⁺ and of the Cl⁻ in most cases significantly ($p < 0.05$) increased with the depth of the sediment (Fig. 3). A close correlation ($R^2 = 0.828–0.999$) was found among the Na⁺, Mg²⁺, Cl⁻ concentrations and electrical conductivity both in the water and sediment interstitial water.

Changes in sediment characteristics

Organic matter content as loss on ignition (OM_{LOI}) varied from 10.5–58.0% (Tab. 2). At site 2, 3 and 3.1 in (in reed tussocks, among reed

shoots) increased, while at site 3.1 out (unvegetated area) decreased in the function of the sediment depth. This increase was 2–9 times higher at sites 3 and 3.1 than at site 2.

ETS-activity varied from 0.17–0.27 mg O₂ g⁻¹ h⁻¹ in the surface sediment layer (Tab. 2) and decreased in the function of the sediment depth at each sampling site (by 11–71% until the 1–20cm and by 36–63% until the 39–40cm sediment layer).

The highest ETS activity values were measured at sampling site 3, where the loss on ignition values was also the highest. As comparing the site 3.1 in and 3.1 out higher ETS-activity, and higher loss on ignition values were measured outside the reed stand.

The correlations between the sediment ETS-activity and the chemical parameters of the sediment interstitial water can be seen on Tab. 3. Almost in each of the examined cases the ETS-activity of the sediment showed a strong positive correlation with the loss on ignition of the sediment.

Fungal biomass (as ergosterol concentrations) of the surface sediment layer varied from 8.3–41.5 µg l⁻¹, in most cases decreased in the function of the sediment depth (Tab. 2). Similarly to the ETS-activity and to the loss on ignition, the highest fungal biomass was measured at sampling site 3.

Comparison of sampling sites

According to the results of the two-way ANOVA analysis, (first component: site; second component: depth), there were significant differences ($p < 0.05$) between the sampling sites.

Based on the chemical parameters of the surface and interstitial water, site 2 significantly differed from sites 3, 3.1 in and 3.1 out, while among the sites: 3, 3.1 in and 3.1 out there were no significant differences.

Taking into consideration the investigated microbial parameters of the sediment site 2 also

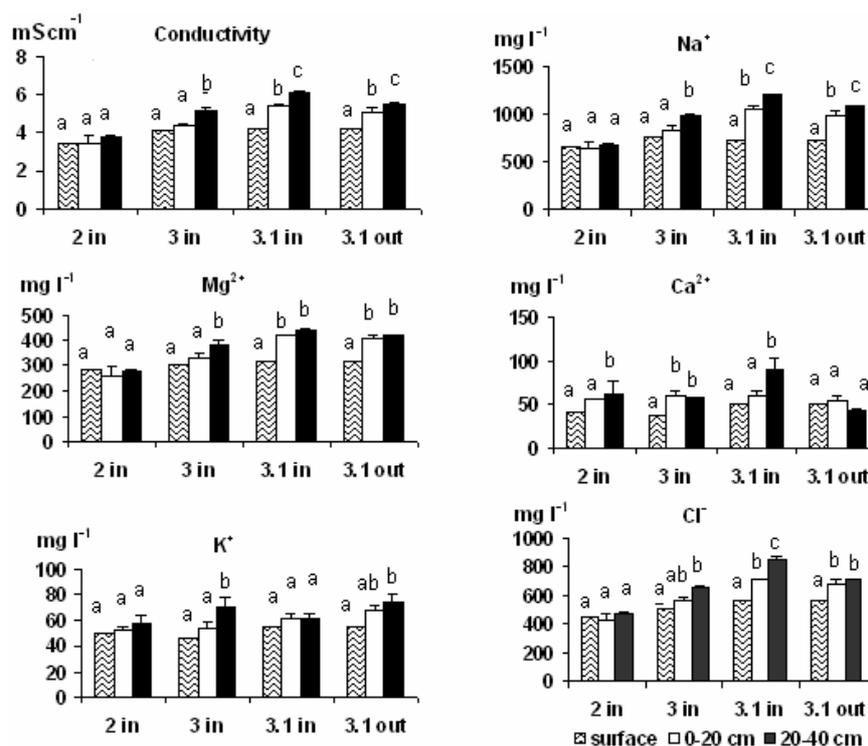


Figure 3. Changes in the electrical conductivity, Cl^- , Na^+ , K^+ , Mg^{2+} , Ca^{2+} concentrations of the surface and sediment interstitial water

Table 2. Changes in the ETS-activity, fungal biomass as ergosterol (ERG) and organic matter content as loss on ignition (LOI) of the sediment

sites	LOI [%]			ETS [$\text{mg O}_2 \text{g}^{-1} \text{h}^{-1}$]			ERG [$\mu\text{g g}^{-1}$]		
	0-5 cm	19-20 cm	39-40 cm	0-5 cm	19-20 cm	39-40 cm	0-5 cm	19-20 cm	39-40 cm
2 in	10.7	11.8	12.0	0.17	0.15	0.10	16.9	8.4	12.12
3 in	56.2	75.4	67.9	0.27	0.08	0.17	41.5	93.1	13.52
3.1 in	10.5	8.8	22.3	0.08	0.06	0.03	8.3	4.6	29.63
3.1 out	58.0	7.3		0.26	0.11		13.6	3.9	

significantly differed from sites 3, 3.1 in and 3.1 out; moreover, site 3 significantly differed from the sites 3.1 in and 3.1 out, but between the sites: 3.1 in and 3.1 out there were no significant differences.

The results of the PCA also reflected the separation of site 2 from the other investigated sampling sites both in the water and in the 0–20 cm and 20–40cm interstitial water (Fig. 4). In the 0–20cm sediment layer, site 3.1 in and 3.1 out were situated close to each other while in the 20–40cm layer a separation could be observed between them.

DISCUSSION

Chemistry of sediment interstitial water and the microbial activity of the sediment were analyzed in the function of the sediment depth and compared in healthy and degraded reed stands.

Similarly to the results of previous studies (Dinka 1998, 2001, Ágoston-Szabó 2004) the pH, redoxpotential, SO_4^{2-} concentrations, temperature decreased, while the electrical conductivity, cation, S^{2-} and Cl^- concentrations increased with sediment depth.

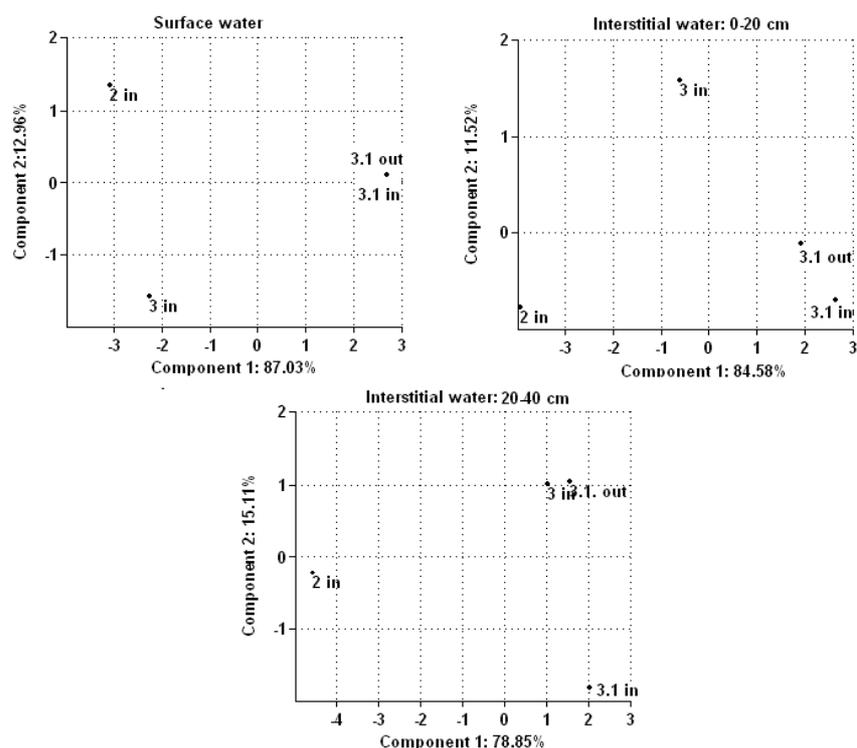


Figure 4. Principal component analysis of the sampling sites based on the chemical features of the surface and sediment interstitial water

Table 3. Pearson's correlations between the ETS-activity, fungal biomass (ERG) and the investigated chemical parameters

	ETS			ERG		
	0-5 cm	20 cm	40 cm	0-5 cm	20 cm	40 cm
Redox	0.83	1.00	0.06	0.68	-0.19	-0.51
pH	1.00	0.96	-0.38	0.98	-0.52	-0.83
Cond.	-0.17	-0.94	-0.39	0.07	-0.06	0.20
S2	-0.81	-0.80	-0.34	-0.64	-0.37	0.25
SO4	0.98	0.78	-0.06	0.92	0.39	-0.61
NH4	-0.14	-0.84	-0.12	0.10	-0.30	0.46
PO4	-0.83	-0.93	0.16	-0.68	0.60	-0.42
NO3	-0.86	-0.78	-0.78	-0.72	-0.39	-0.30
TOC	-0.75	-0.70	0.60	-0.57	0.87	0.95
TC	-0.72	-1.00	0.17	-0.54	0.30	0.69
TN	-0.80	-0.95	0.34	-0.63	0.55	0.81
LOI	0.88	-0.27	0.77	0.97	1.00	0.99
ETS	0.00	0.00	0.00	0.97	-0.27	0.83
ERG	0.15	0.83	0.38	0.00	0.00	0.00

The SO_4^{2-} concentration decrease in the function of the sediment depth was paralleled by the S^{2-} concentration increase due to the sulphate reduction, which is one of the dominant processes in the sediment of Lake Fertő/Neusiedler See

(Armstrong & Armstrong, 1998; Dinka, 2001; Ágoston-Szabó, 2004).

The differences in the redox potential values and sulphide concentrations in the interstitial wa-

ter of the healthy and degraded areas may be due to the differences in the sediment organic matter content and in the *Phragmites* mediated oxygen transport, which influences the redoxpotential and the concentrations of the redox sensitive compounds in the sediment (Armstrong & Armstrong, 1998). Healthy reed shoots transport oxygen more efficiently into the rhizosphere than the die-back shoots (in which callus occlusion of aerenchyma frequently occurs Armstrong *et al.* 1996), where creates favourable conditions to the oxidation of reduced compounds and the detoxification of the sediment (Azzoni *et al.*, 2001).

Usually the increase in PO_4^{3-} concentrations in the function of sediment depth is the reason for the release of the iron bound phosphate and the decomposition of organic matter in reductive conditions (Istvánovics, 1988), unlike at Lake Fertő/Neusiedler See, where the organic matter content of the sediment is high and according to Dinka (1994), 60–78.5% of the sediment TP is bound to the Ca, 13–28% to the organic matter and only 14% is NaOH hydrolysable.

The analysis of inorganic nitrogen speciation in our study indicated an NH_4^+ -N dominance in the surface and interstitial water, which suggests that the nitrate reduction may have been the dominant processes in N transformation in the sediment. The elevated NH_4^+ concentrations in the interstitial water may have been the result of degradation of N-containing organic matter (Van Lujin *et al.* 1999).

The organic matter content measured as TOC concentrations of the surface water accounted for 42–51% of TC and of the sediment interstitial water for 40–53% (0–20cm) and 37–49% (20–40 cm) of TC, respectively. The high total organic carbon concentrations at sites 3, 3.1 in (vegetated areas) and out (unvegetated area) can be related by the anaerobic environment at these sites, demonstrated by the low redoxpotential values of these sites. The mineralization of organic matter is

slower under anaerobic conditions (Esteves *et al.*, 2001).

The high TC:TN molar ratio found in the surface and sediment interstitial water indicated a N limitation. The negative correlation of the TC, TOC, TN concentrations with the pH, redoxpotential and the positive correlation of the ETS-activity with the pH, redoxpotential of the sediment interstitial water indicated that the concentrations of the TC, TOC, TN are influenced by the impact of the pH and redox conditions on the microbial activities.

The increase in the concentrations of Na^+ , Ca^{2+} , K^+ , Mg^{2+} , Cl^- in the function of the sediment depth suggest that these ions are diffusing from the deeper sediment layers toward the sediment surface. Batty & Younger (2004) found that the depth profile of the Ca^{2+} is influenced by the degree of Ca^{2+} uptake by plants.

The positive correlation between the ETS activity, ergosterol concentrations of the sediment with the TOC, LOI indicated that the microbial activity is strongly interrelated with the sediment organic matter content.

CONCLUSION

Significant differences were found between the healthy and degraded sites based on the sediment characteristics, which demonstrated that the changes in the chemical parameters of the sediment interstitial water and in the organic matter content and microbial activity of the sediment are strongly interrelated with the condition of the reed stands. The correlation analysis showed that the microbial activity of the sediment was interrelated with organic matter content, pH and redoxpotential of the sediment. At die-back site there were no significant differences between the natural and replanted reed stands.

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