Thesis of Doctoral (PhD) Dissertation

COMPARATIVE EXAMINATION OF DIFFERENT WATER BODIES AND THEIR SEDIMENTS

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Debrecen, 2011

1. INTRODUCTION

The water is one of the most important limiting factor in the terrestrial ecosystems, and in the aquatic ecosystems it is an ecological medium. Therefore, the water is such an environmental element, which is ultimately necessary for the biosphere. The water is the base of the life and a natural resource at the same time.

The influence of the global climate change brings the water to the centre of wiev of the 21st century (*Láng et al.,* 2007; *Stern,* 2007). The biosphere have existed for 3.5 billion years without fossil energy sources, however, the life is not possible without water.

In 23rd october, 2000, the European Union released the Water Framework Directive, which main purpose is the preservetion and improvement of the good ecological and qualifical status of the surface- and groundwaters.

The base of the Hungarian water qualifying process is the MSZ 12749 standard, which mainly involves the chemical parameters of the water body. Based on the Water Framework Directive the government released the 31/2004. KvVM decree, which involves the ecological state of the water body as well.

The natural wetlands are between the terrestrial and the aquatic ecosystems. They have a high biodiversyty, which importance is well emphasized by the Ramsar convention (1971).

One of the main feature of the artificial wetlands is the intensive community metabolism, therefore, these ecosystems are able to process the higher organic loads, as a „living machine".

The water body and the sediment of the aquatic ecosystem is makes an organic unit, which strongly influences the material cycling (*Janurik - Szabó*, 1985; *Chapman - Reiss*, 1999). There are living community level examinations, which give information on the structure and composition of the microbial community (*Csizmarik*, *1992*). However, the functional examinations are important for researching the activity of microbial communities, because the sediment is one of the most important mineralization compartment of the aquatic ecosystems.

The sediment is strongly influences the quality of the water body, because it is a nutrient depo, therefore influences the eutrophication. The sediment accumulates the dead organic matter, therefore it has an important role in the saprobity and the oxygen cycle of the aquatic ecosystems.

2. THE OBJECTIVES OF THE RESEARCH

The main goals of the research were to develop more methods in the aquatic environment assesment. Also, the research of the water and sediment quality is important for the aquatic ecosystem modelling. The measurements were conducted at the Szarvas - Kákafok deadarm, compared to an atrificial wetland, constructed at the Research Institute for Fisheries, Aquaculture and Irrigation, Szarvas.

The objectives of the research were the following:

I. Examination of the environmental factors of the Szarvasi-Kákafok deadarm and an artificial wetland:

- Examination of the quality of the water body;
- Examination of the oxido-reduction potential of the sediment and its relation to the water quality;
- Examination of the sedimentation rate of the deadarm.

II. Composition a suitable measurement system for examining the microbial decomposition in the sediment:

- Testing the possibilities of the *in vitro* and *in situ* measurements;
- Examination of the mineralization by measuring the CO_2 emission.

III. Examination of the microbial decomposition:

- Examination of the microbial respiration in the fish pond – makrophyte system;
- Examination of the microbial respiration in the Szarvas-Kákafok deadarm.

3. MATERIALS AND METHODS

Sampling sites

The Szarvas-Békésszentandrás Holt Körös ("Kákafok Deadarm") is the biggest deadarm of Hungary. Its basin area is 927 km^2. The overall length is 29.2 km, the average width is 71 m, the surface area is 207 ha, the average water depth is 2.2 m, and the water quantity is 4.5 million m^3. The water quality is generally meso-eutrophic, and meso-saprobic. 20 sampling sites were determined (*Figure 1*).

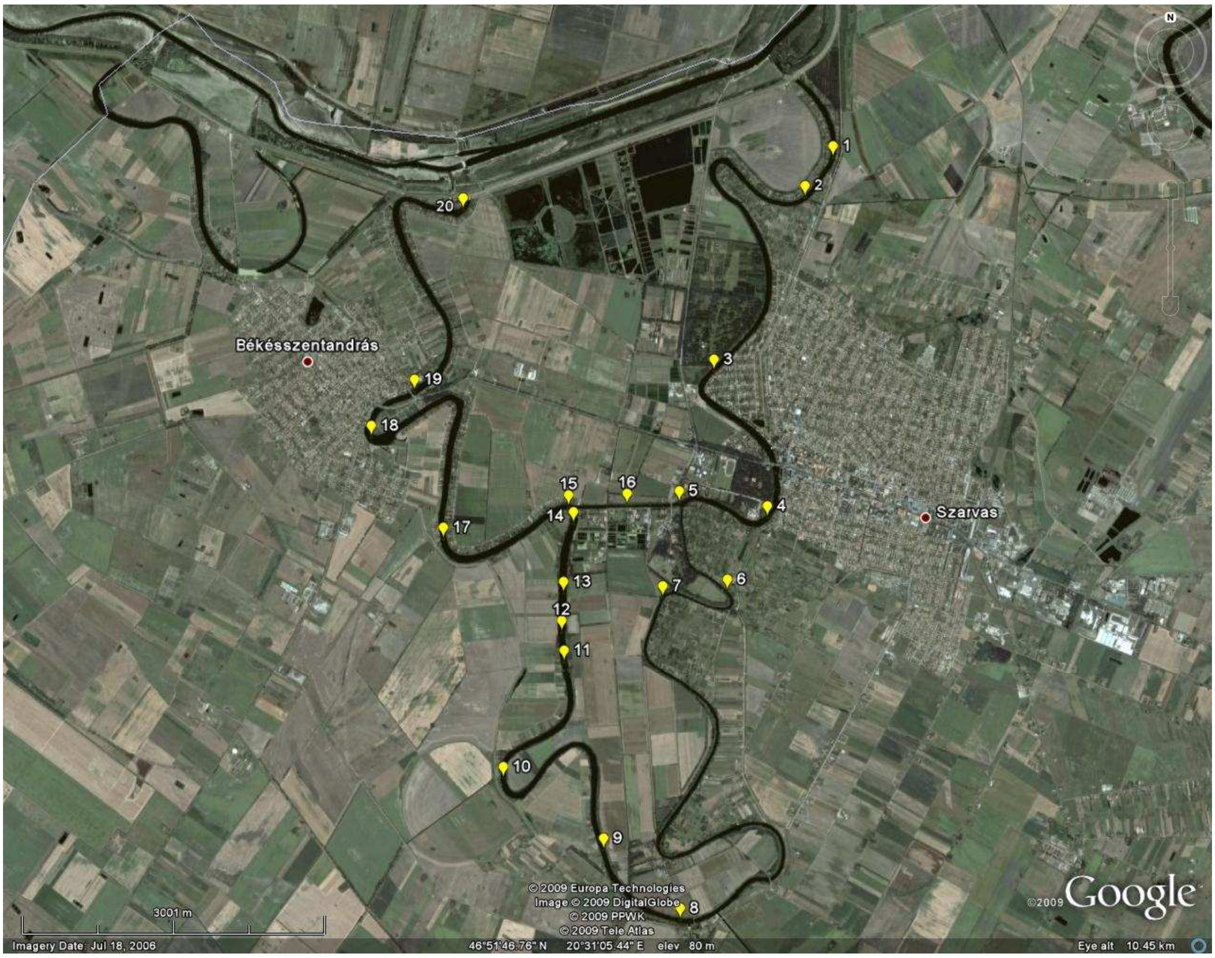

Figure 1: Sampling sites (by GoogleEarth)

The other sampling area was an eutrophic – polysapbrobic artificial wetland, constructed at the Research Institute for Fisheries, Aquaculture and Irrigation, Szarvas. The system consisted of two fish ponds and two makrophyte ponds. The surface area of the fish ponds were 2500 m^2, the average water depth was 1,2 m, the water quantity was 3000 m^3. The surface area of the makrophyte ponds were also 2500 m^2, the average water depth was 0.5 m.

Measurements in the field

The oxido-reduction potential of the sediment was measured by a COLE-PARMER type 59002-60 ORP-pH meter (mV/pH). The examinations of the water body of the deadarm were conducted by a HORIBA type U-10 instrument. The conductivity, the pH, the temperature and the oxygen content were measured parallelly. The water depth and the thickness of the soft sediment were measured as well.

Determination of the dry material

The dry mass was measured by the MSZ ISO 6060: 1991. standard after drying to constant weight at 105 °C, followed by cooling in an exiccator.

Potentiometric laboratory methods

The measurements of pH were conducted by a METTLER TOLEDO MPC 227 pH and conductivity meter due to the MSZ 260-4:1971. standard.

The measurements of the conductivity were conducted by a METTLER TOLEDO MPC 227 pH and conductivity meter due to the MSZ 448-32:1977. standard.

The measurements of the oxido-reduction potential were conducted by a TOA ORP METER RM-20P instrument (TOA ELECTRONICS Ltd. Japan).

Measurement of theTotal Organic Carbon (TOC)

It was measured directly from the original sample by a TOC 5000A Total Organic Carbon Analyzer (SHIMADZU).

The principle of the method is to oxidize the organic material in the sample in a liquid phase, at 750 °C temperature by platinum catalyst. The CO_2 is measured by an infrared detector.

Examination of the respiration

A Brüel & Kjaer type 1302 multi-gas monitor was applied. The instrument is a photoacoustic spectrometer.

Photoacoustic gas measurement is based on the same basic principles as conventional IR-based gas analyzers - the ability of gases to absorb infrared light. However there are some important differences between PAS and these conventional techniques.

The absorbtion is measured directly. This means that PAS is highly accurate and sensitive, with very little instability.

At the *in vitro* measurements a closed system was applied, the gases were recirculated. The volume of the measuring flasks were 766 ml, the incubation temperature was 25 °C.

In order to check the air-tightness of the system an artificial CO_2 emission was measured.

First, silicone tubing was used, however, in this case a CO_2 loss was detected.

After this teflon tubing was applied, and the air-tightness of the system have been secured (*Figure 2*). Thus CO_2 loss could not be detected, even at long time measurements.

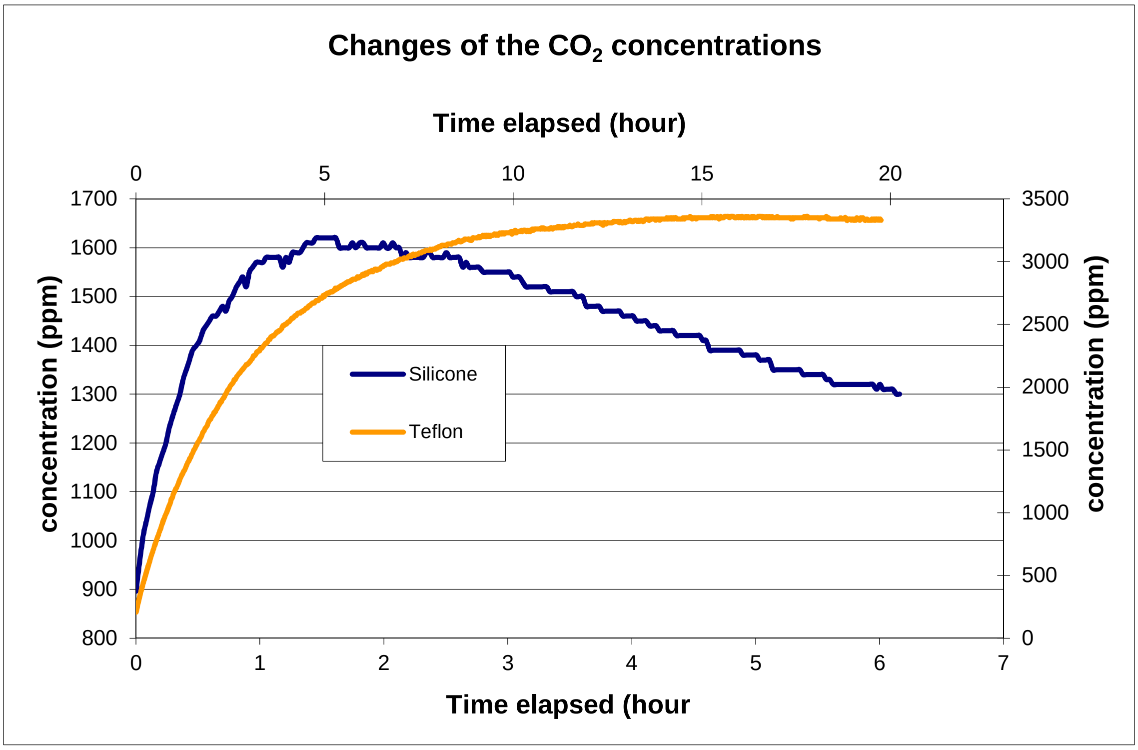

Figure 2: Changes of the CO_2 concentrations in a non living measurement system connected by silicone and teflon tube

Because of the small gas volume and the closed system the gas emission could show a saturation curve. The linear part of the curve should be considered for calculating the respiration (*Figure 3*). It is important to chose the correct incubation time and the correct sample-gas volume ratio. If the volume of the sample is too high, an overpressure can develop, which causes measurement errors. If the volume of the sample is too low, the emitted gas concentrations may below the detection limit of the gas analyser.

The correct sample – gas volume ratio was found at 20/80 %. In this case the gas emission was well detectable and linear, even for a 10 hours period (Figure 4).

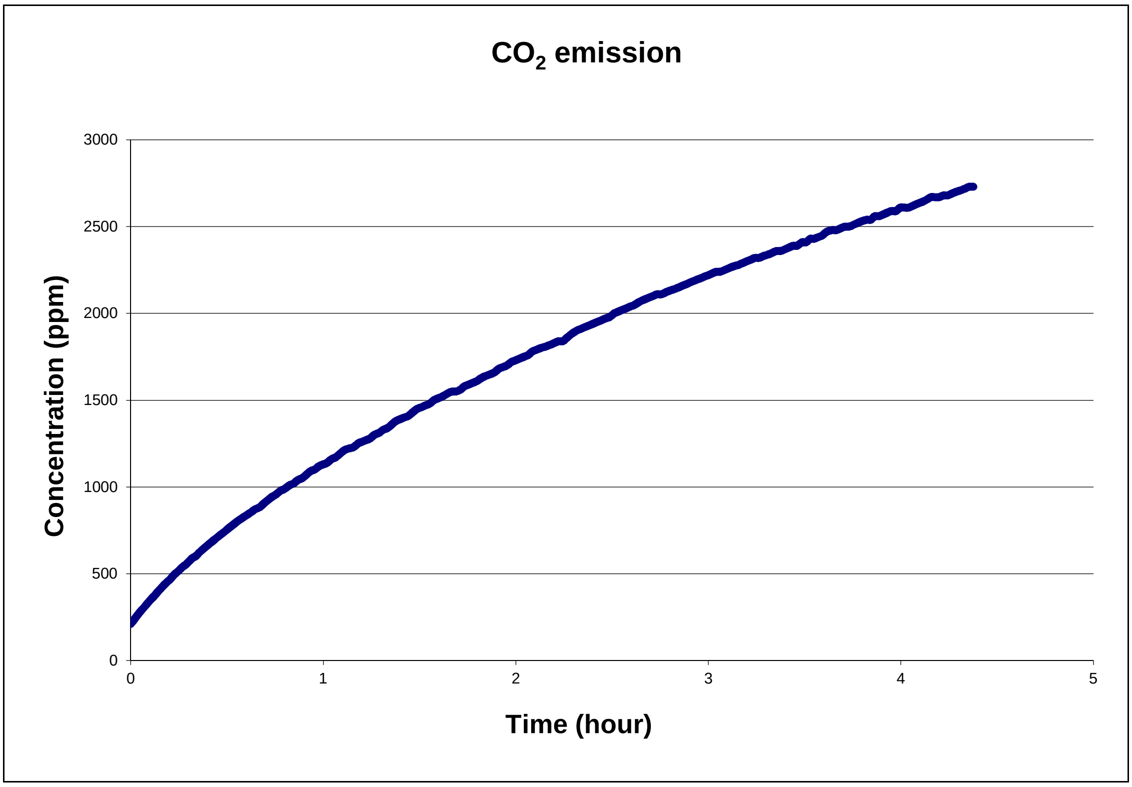

Figure 3: Calibration of the measurement system by measuring CO_2 concentrations

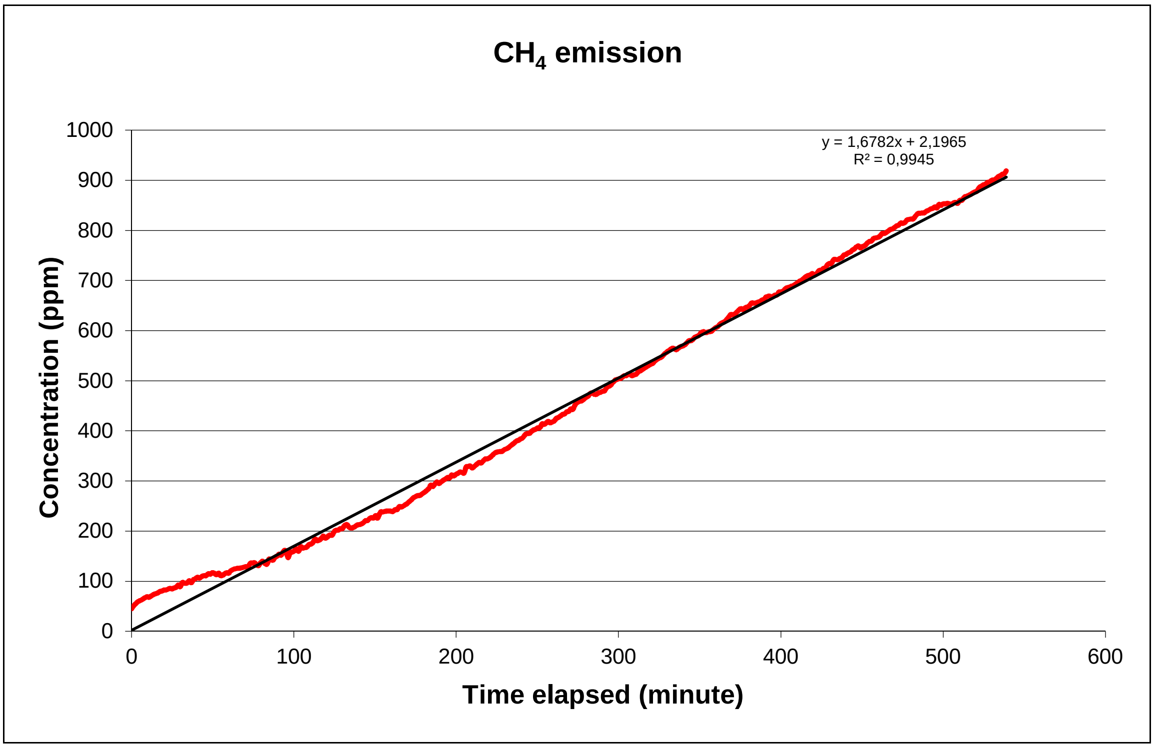

Figure 4: Calibration of the measurement system by measuring CH_4 concentrations

The CO_2 concentration can be converted to molar quantity by the next equation:

$$N = \frac{P \times V}{R \times T}$$

N = molar quantity

P = Pressure in the measuring system

V = gas volume (calculated by the measured concentration, in ppm)

R = R constant

T = Temperature

The molar quantity can be converted to mass and the emissions can be expressed as carbon unit per time unit per sample unit.

$$E = \frac{\Delta M}{M_s \times T_{inc}} \quad \left(\frac{mgC}{g \times hour}\right)$$

E = Emission

ΔM = difference of carbon mass during the incubation time

M_s = Mass of the sample

T_{inc} = Incubation time

The measure system is able to conduct *in situ* examinations (*Figure 5*) In this case the respiration should be related to the sediment surface area (mg C $hour^{-1}$ m^{2-}).

Figure 5: in situ measurement composition

4. RESULTS AND DISCUSSION

Examination of the Szarvas-Kákafok deadarm

Estimation of the sedimentation in the deadarm

The thicknesses of the soft sediment of the deadarm were measured in 1992 and in 2006, at 20 sampling sites.

The sedimentation rate is influenced by more environmental factors:

- communal waste organic matter;
- agriculture originated plant nutrients, therefore the eutrophication;
- the hydrological parameters of the deadarm;
- the compactation of the sediment.

At the 7th sampling site dredging was conducted before the measurements, therefore it may serve as a reference point for calculating the sedimentation rate. The thickness of the soft sediment was 50 mm in 1992, and 90 mm in 2006, thus 40 mm have sedimentated for 14 years. Therefore, the sedimentation rate is 2.9 mm year^{-1}.

The 5th sampling site is a good example for illustrating the influence of the water current.The water stream decreased the thickness of the sediment from 580 mm to 70 mm.

The sediment thickness significantly increased at the sampling sites 9-11, and 12. This increase can be explained by the organic and inorganic nutrient load from a fis cum duck system, and an intensive aquaculture system (*figure 6*).

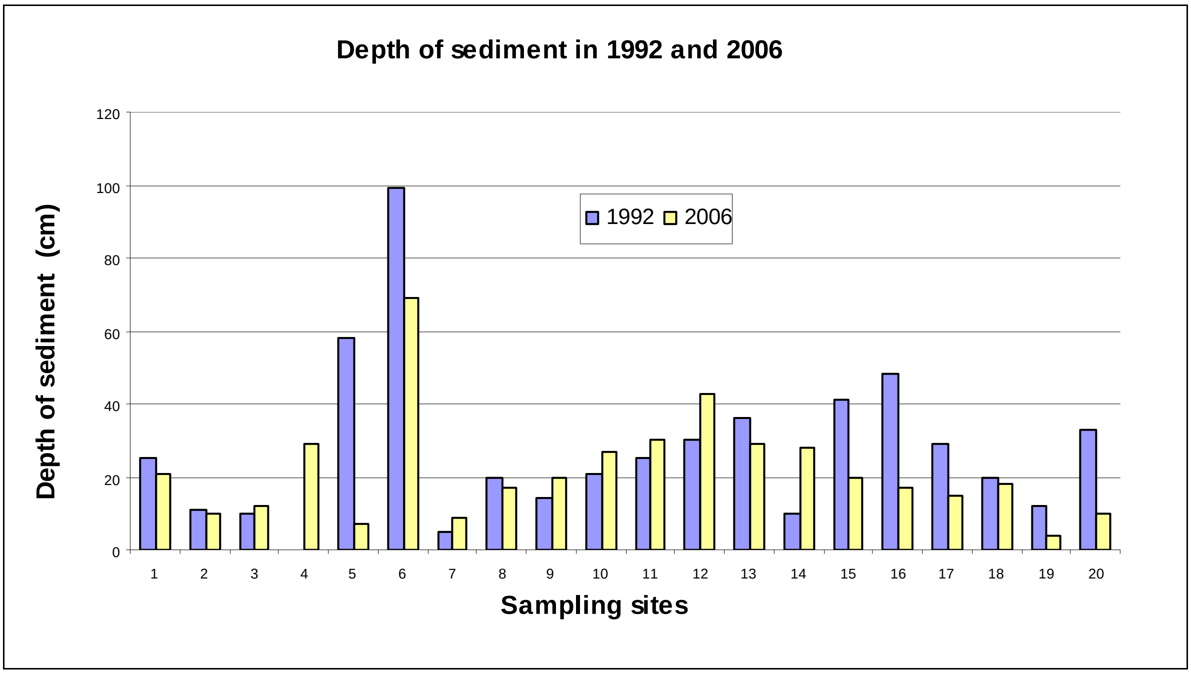

Figure 6: Thickness of the sediment in the deadarm at the sampling sites

The average sedimentation rate is estimated as 4-5 mm in a year.

Examination of the water quality in the Szarvas-Kákafok deadarm

The water body of the deadarm was examined in September, 2006 and August, 2008 *in situ*. The oxygen content, the conductivity, the temperature and the pH were measured in the field. The oxido-reduction potential of the sediment was measured immediately after the sampling (*Table 1*). The pH and the oxigen content showed much bigger variations, the oxido-reduction potential of the sediment was more equalized. In 2008 an algal boom was recorded in some part of the deadarm, which resulted high pH and oxigen values. *Figure 7* shows that the ORP values were lower, than in 2006, which can be explained by the increased production of the deadarm.

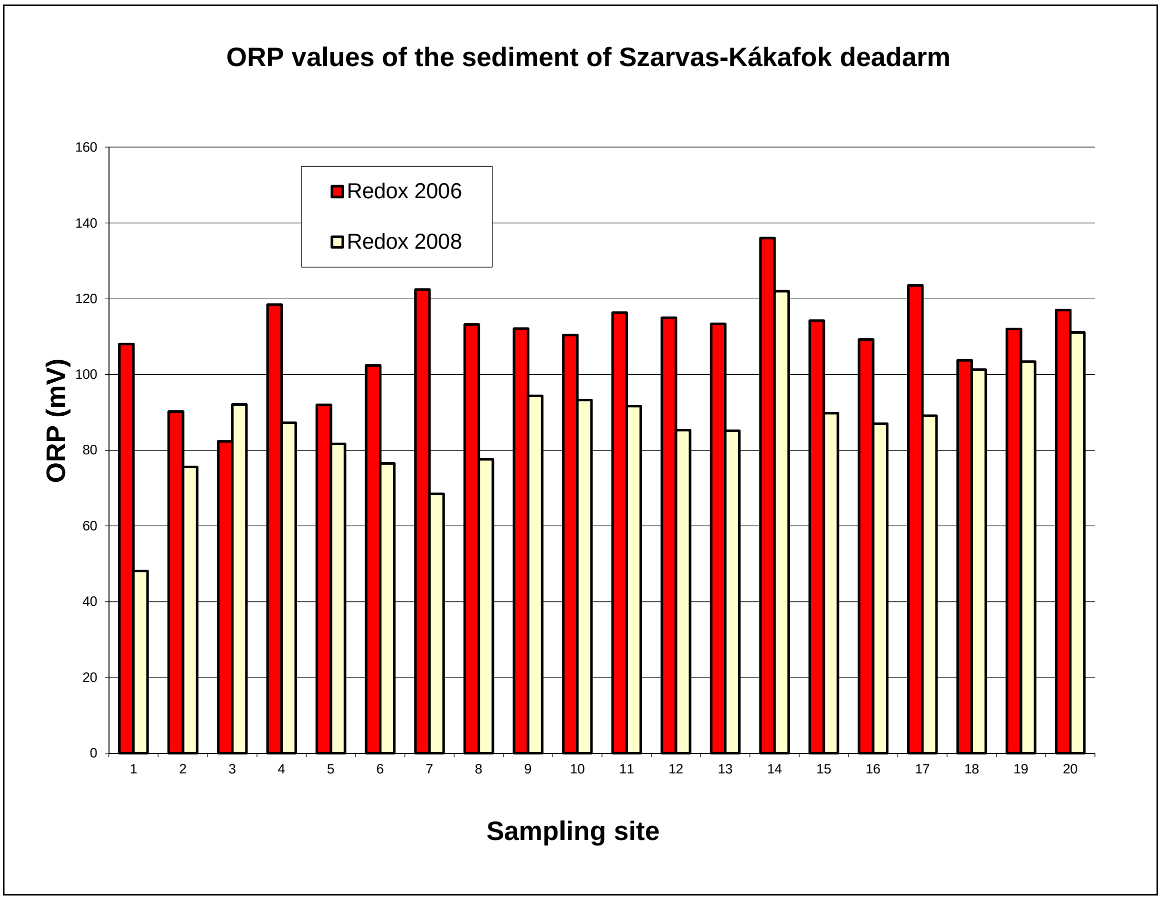

Figure 7: The values of the oxido-reduction potential in the sediment of the deadarm

Table 1: Measurements in the Szarvas- Kákafok deadarm *in situ*

Sampling site	Sampling time	ORP sediment mV	pH	Conductivity µS cm^{-1}	O_2 mg l^{-1}	Temperature °C
1	2006	108	7.6	415	7.1	18.3
	2008	48.1	8.38	383	8.4	24.6
2	2006	90.2	7.74	428	7.8	18.4
	2008	75.6	8.32	386	4.5	24.8
3	2006	82.3	7.68	412	7.9	18.4
	2008	92.1	9.2	345	7.8	24.9
4	2006	118.4	7.5	426	7.5	18.4
	2008	87.2	9,85	334	13.2	25.3
5	2006	92	7.68	430	7.1	18.6
	2008	81.7	9,7	338	10.9	25.3
6	2006	102.4	7.52	445	6.2	18.6
	2008	76.5	9.5	338	9.9	24.7
7	2006	122.4	7.52	420	6.2	18.8
	2008	68.5	9.3	341	8.45	24.6
8	2006	113.2	7.72	434	8.5	19.5
	2008	77.6	8.8	346	7.9	25.7
9	2006	112.1	7.7	428	6.3	18.7
	2008	94.3	9.62	405	13.65	27.2
10	2006	110.4	7.49	425	6.8	19.4
	2008	93.2	9.83	414	16.1	27.2
11	2006	116.3	7.9	459	9.6	19
	2008	91.6	9.58	433	15.35	27.1
12	2006	115	8.15	474	11	19.3
	2008	85.3	9.68	436	16.14	27.3
13	2006	113.4	8.1	490	11.3	19.6
	2008	85.1	9.22	445	10.82	26.9
14	2006	165.2	6.85	681	11.6	19.7
	2008	122	8.72	367	7.56	25.8
15	2006	114.2	7.48	434	7.5	19
	2008	89.8	8.8	353	8.9	25.8
16	2006	109.2	7.46	431	7.9	19
	2008	87	9.4	340	15	26.3
17	2006	123.5	7.51	459	7.5	19.2
	2008	89.1	9.3	361	12.3	25.6
18	2006	103.7	7.25	442	6.8	19.3
	2008	101.3	8.5	387	11.75	26.7
19	2006	112	7.25	443	7.55	19.6
	2008	103.4	9.73	389	11.2	26.6
20	2006	117	7.48	455	6.2	19.2
	2008	111.1	8.12	439	5.1	26.9

It is recorded, that the pH can increase in the water body (*Kant - Raina*, 1990), therefore further measurements were conducted between july 26 and august 8, 2010, twice a day; in the morning and in evening.

Three water samples were collected horizontally, from the littoral zone, from the mid section, and from the centre line of the deadarm. The depths of the water body were 1 m, 2.4 m and 4 m. From the littoral zone the samples were collected from the surface and the bottom water body, while surface, middle part and bottom water samples were collected from the mid section and the centre line of the deadarm. The samples were measured immediately after the sampling in the flask, in order to obtain in situ data. The oxygen content, the conductivity, the pH and the temperature were recorded. The meteorological data were obtained from the Meteoroogical Station, Szarvas.

During the measurement period diverse weather conditions were detected. The daily average temperature and its standard variation was calculated (*Figure 8*). The lowest temperature was on 25th July, and the highest was on 4th August. The air temperature showed high daily variations, which are indicated by the high STD values. The changes in the water body were more balanced, however the highest temperature reached 27.1 °C. The low STD values indicate, that thermocline has not formed, even in the 4 m deep centre line section. Therefore, the oxbow-lake can be classified as shallow lake.

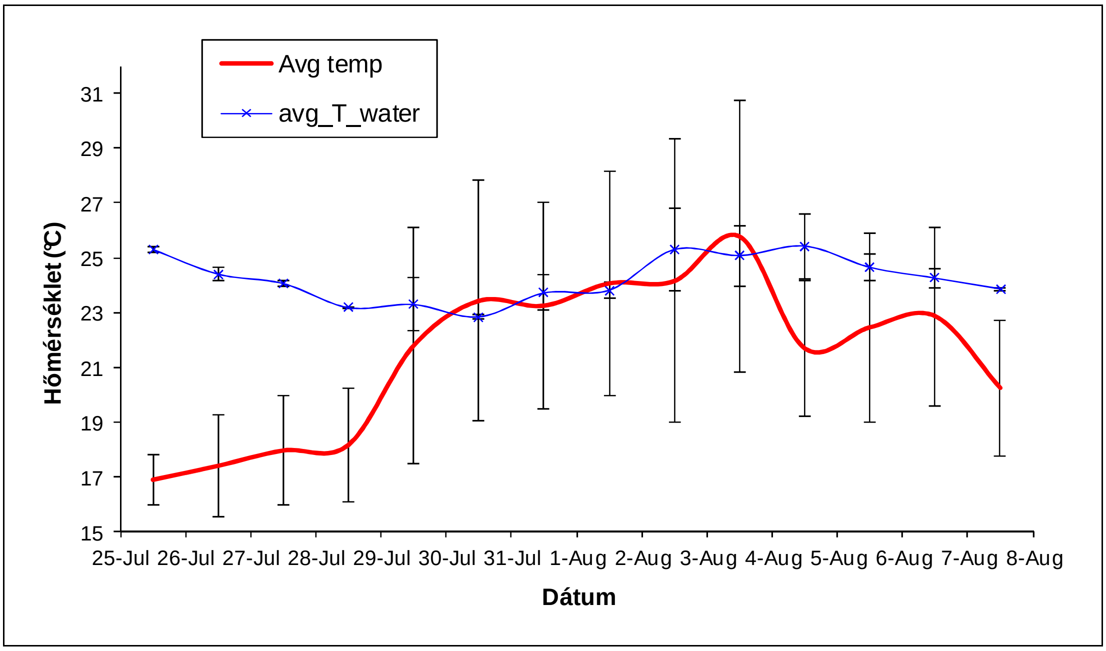

Figure 8: Changes of the average air temperature compared to the water temperature

The pH showed strong correlation with the temperature. As the water temperature started to rise, it led to an increasing photosynthesis, which lowered the CO_2 and HCO_3^- content of the water. Eventually it was showed in an increased pH (*Figure 9*). These results are well correlated with the observation of *Schwoerbel* (1999).

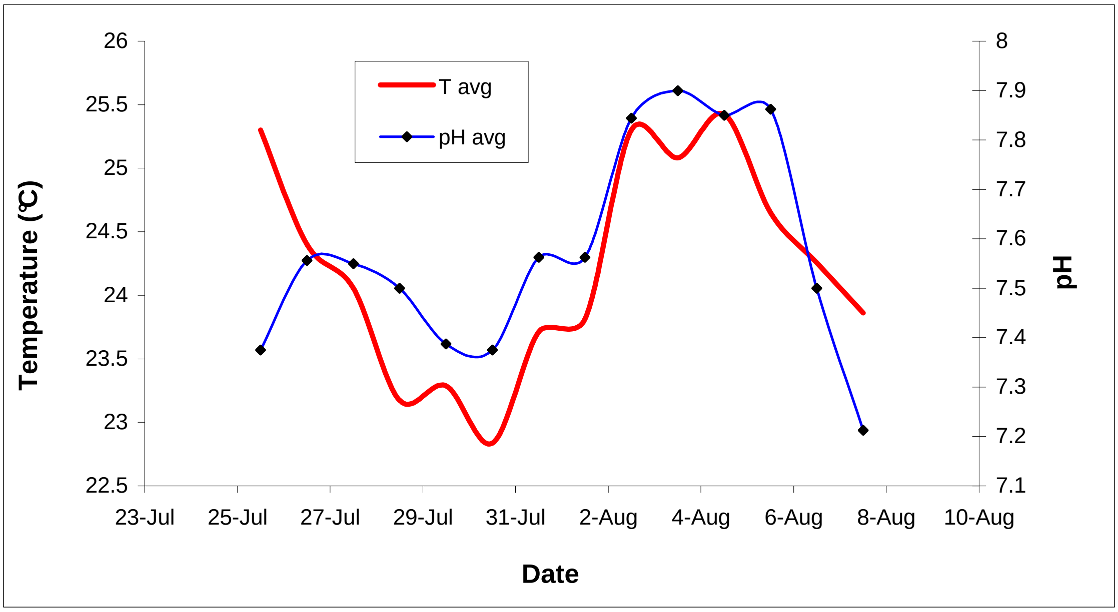

Figure 9: Changes of the pH compared to the water temperature

Due to a smaller flood on the river, the deadarm was closed between 30th July and 3rd August. As the very slow stream stopped, it dramatically changed the oxygen relations in the water body. In the littoral zone the oxygen content increased due to a photosynthetic activity and a still water. However the diffusion in the 1 m water body was able to supply sufficient O_2 into the bottom layer (*Figure 10*).

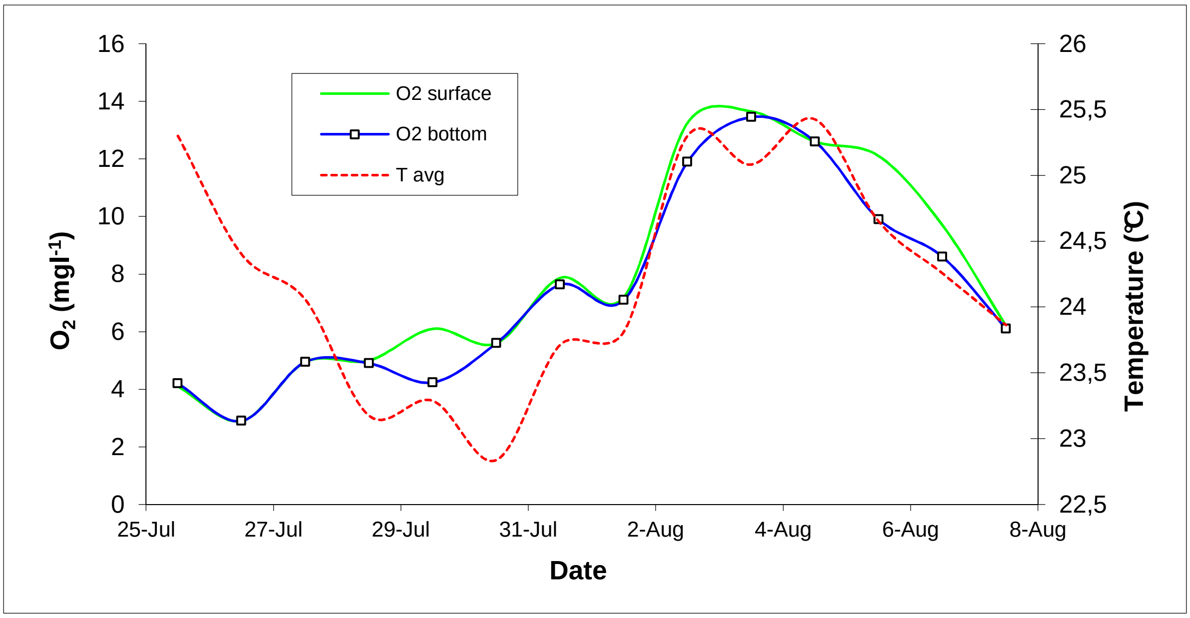

Figure 10: Changes of the oxygen content in the littoral region, compared to the water temperature

In the mid section the water was 2.4 m deep. While the constant stream supported sufficient mixing effect, in the still water oxygen stratification started due to the higher temperatures and higher photosynthesis (*Figure 11*). After the flood, the oxygen content decreased, but was more balanced in all depth.

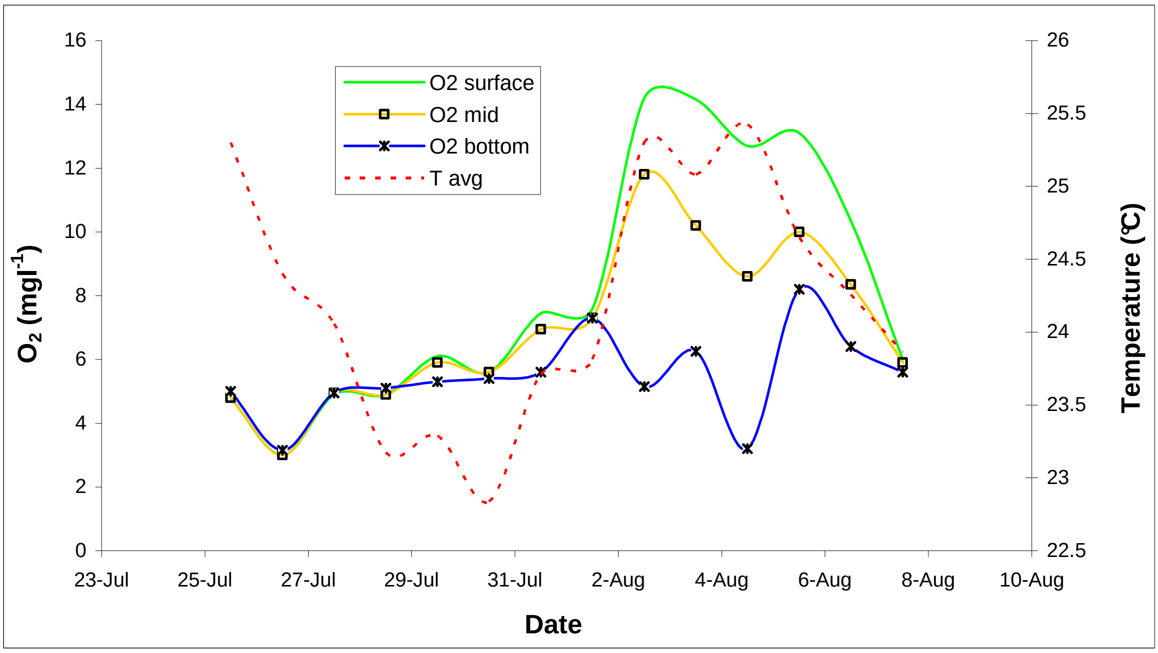

Figure 11: Changes of the oxygen content in the mid section, compared to the water temperature

In the deepest centre line region the changes were more stronger. On the surface the O_2 level reached the 18.2 mg l^{-1} value, while in the bottom layer decreased to 1 mg l^{-1} (*Figure 12*). After the water supply the O_2 content remained at 5 mg l^{-1} level.

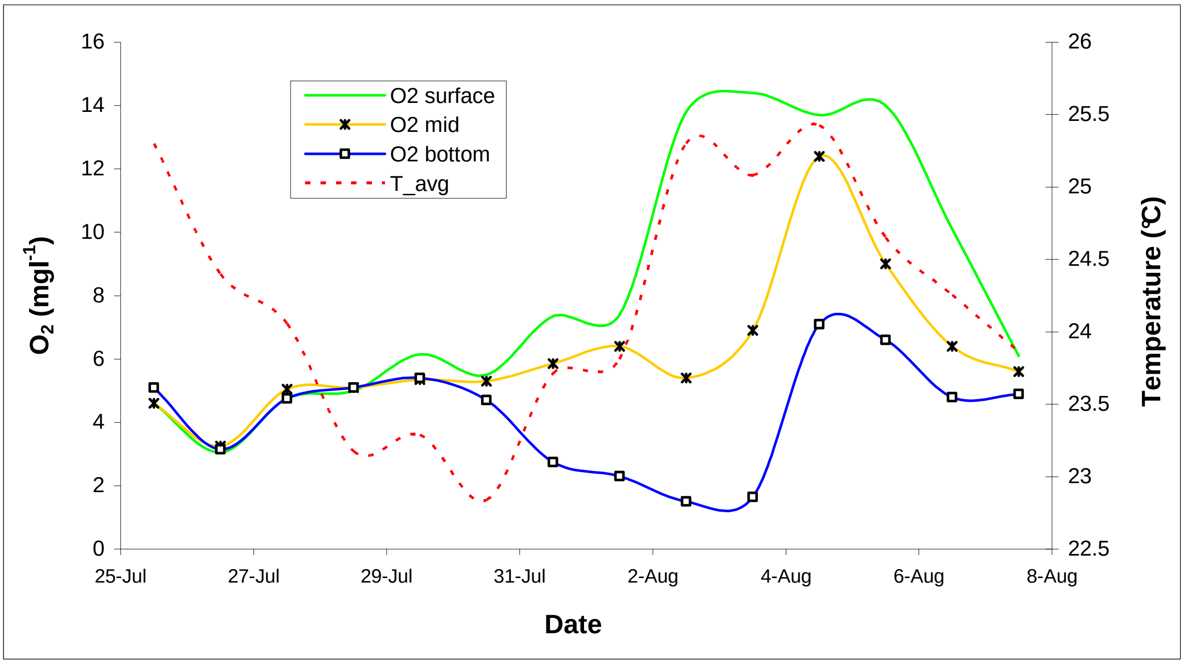

Figure 12: Changes of the oxygen content in the current line, compared to the water temperature

Examination of the artificial wetland

The effluent of the intensive aquaculture system transferred 31,6 mg l^{-1} particulated matter to the artificial wetland, which contained 57,3% organic fraction. The changes of the quantities of the organic matter was followed by TOC measurements in 2002 (*Figure 13*).

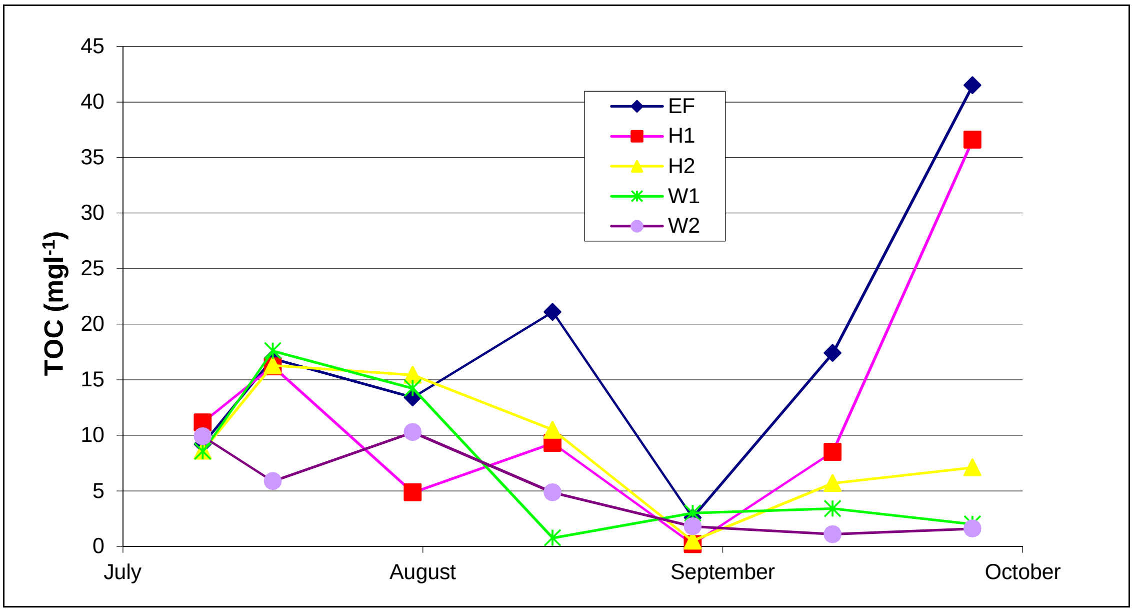

Figure 13: Changes of the TOC in the fish pond - makrophyte system

Due to the results of the measurements the system was able to process the organic load.

In the 2002nd year the oxygen content strongly varied, in some cases reached extreme low values (*Figure 14*).

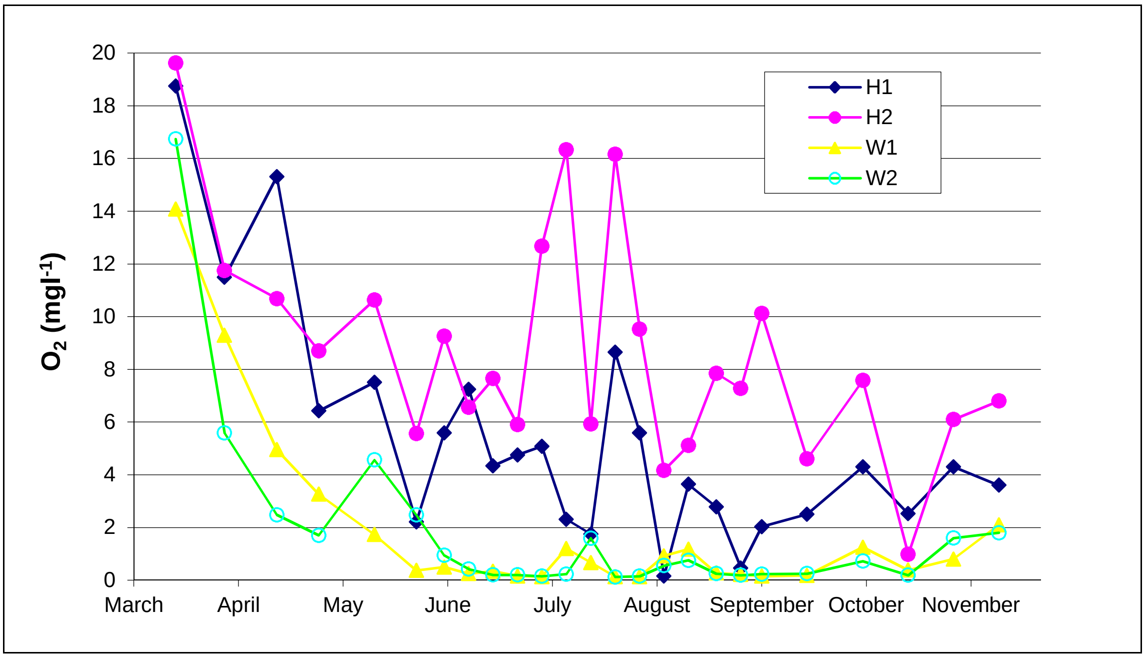

Figure 14: Changes of the oxygen content in the fish pond - makrophyte system

These changes were clearly observed in the case of the daily variations (Figure 15).

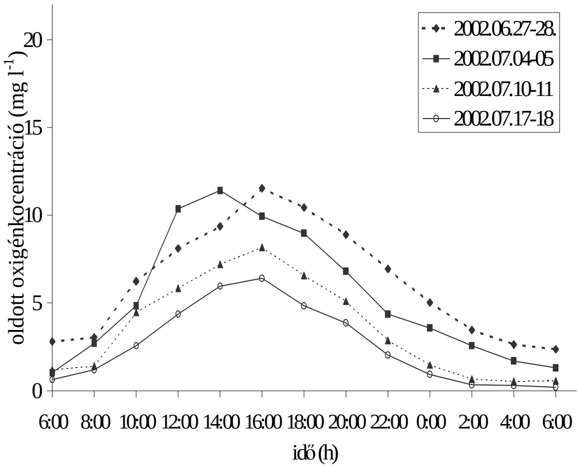

Figure 15: Daily variations of the oxygen concentrations in the fish pond 1. and 2.

Knud-Hansen (1998) states, that the oxigen content does not decrease below 3 mg l^{-1}, even in the most hypertrophic fis ponds, if the production is autochtonous. In our case the outer organic load decreased the oxygen level to 1 mg l^{-1} in the 1^{st} pond in the early morning. This value is critical for the fishes (*Horváth*, 2000), therefore artificial oxygen input was necessary. The ORP changes of the sediment showed higher variations, than in the deadarm (*Figure 16*).

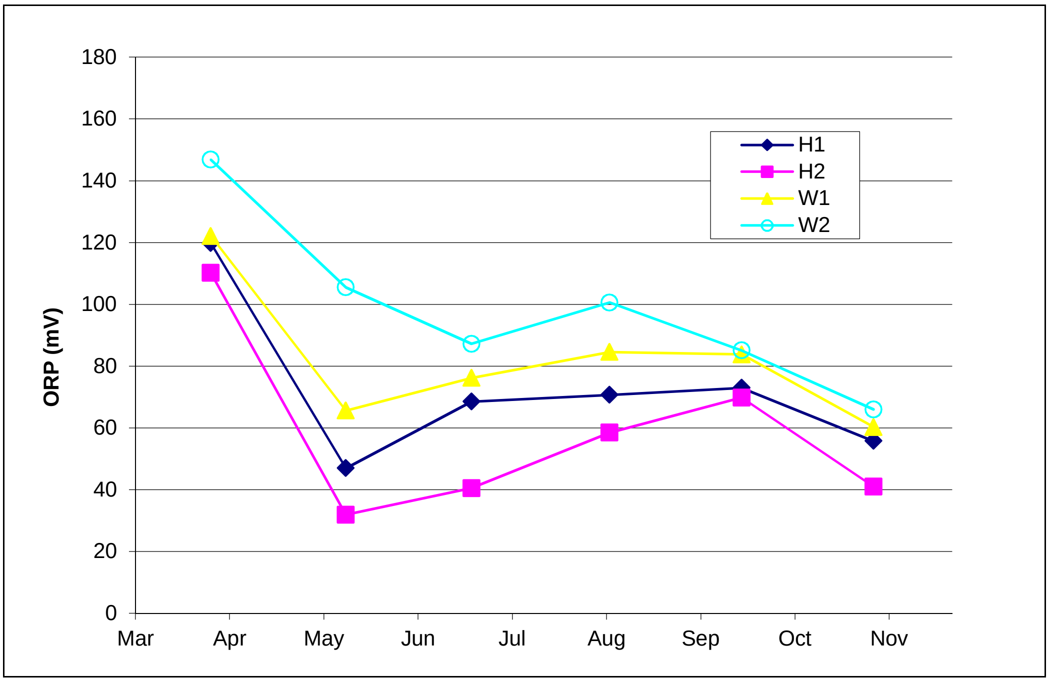

Figure 16: Changes of the ORP of the sediment in the artificial wetland system

Examination of the respiration

***In situ* examinations**

In November, 2002 the respiration in the sediment of the drained fish pond was determined by 1500 data, which were obtained during a 26 hour continuous measurement. The temperature data were recorded as well. The results are shown on the *Figure 17*. The respiration showed strong correlation to the temperature. The respiration rate followed the temperature variations by a one hour time shift. As the results indicates, the respiration continues at even 1 °C temperature. These results correlates with the examinations of *Thamdrup - Fleischer* (1998), who measured respiration and nitrification under arctic circumstances.

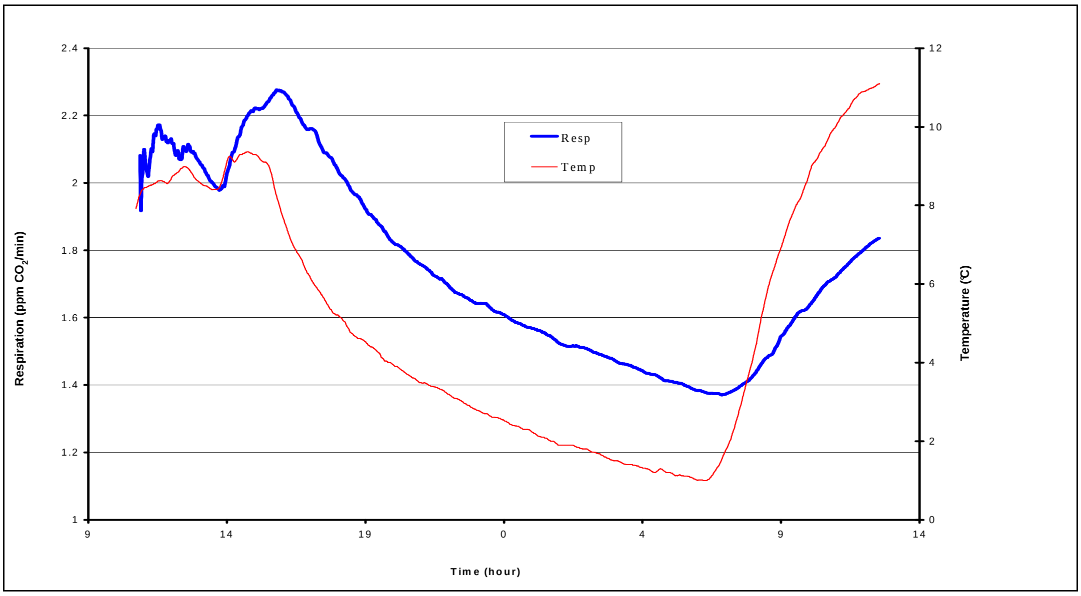

Figure 17: Respiration of the sediment in the drained fish pond

***In vitro* examinations**

The respiration of the sediment of the fish pond was examined *in vitro* as well. The main purpose of the measurements was to research the aeration influence for the sediment respiration. Therefore oxidative and anaerobic measurement flasks were used. The results are detailed on the *Figure 18*. Based on my measurements, the respiration was three times higher in the oxidative flask, which implies that the mineralization processes can accelerate in the wetlands. The result correlates with the observations of *Lin et al*. (2003), who examined the decomposition of the non soluble organic matter in the sediment.

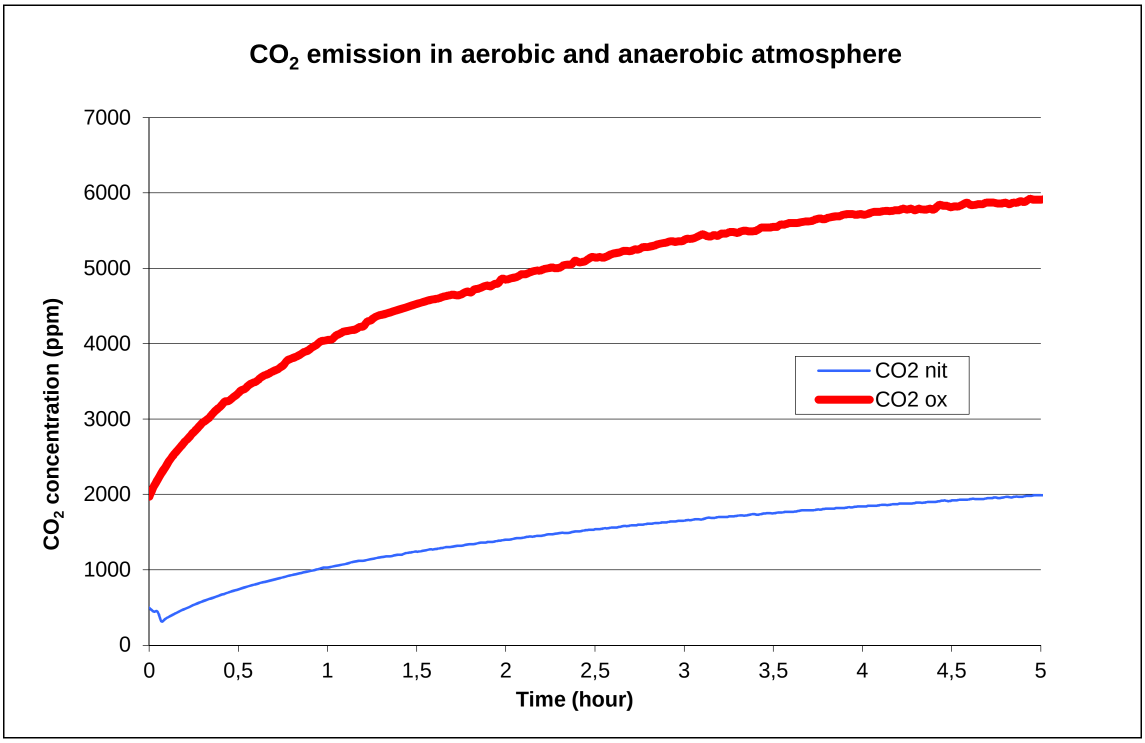

Figure 18: Respiration in oxidative and inert atmosphere

The developed method detect the gas form of the CO_2, therefore the *in situ* respiration measurements were not possible in the sediment of the Szarvas-Kákafok deadarm. The collected sediment samples were measured *in vitro*, in the laboratory. The values of the respiration and the oxido-reduction potencial are shown in the *Figure 19*. The pattern of th oxido-reduction potential and the respiration is remarkable. *Catallo* (1999) reported similar results . According his examinations, the respiration and the ORP are in dynamic balance..

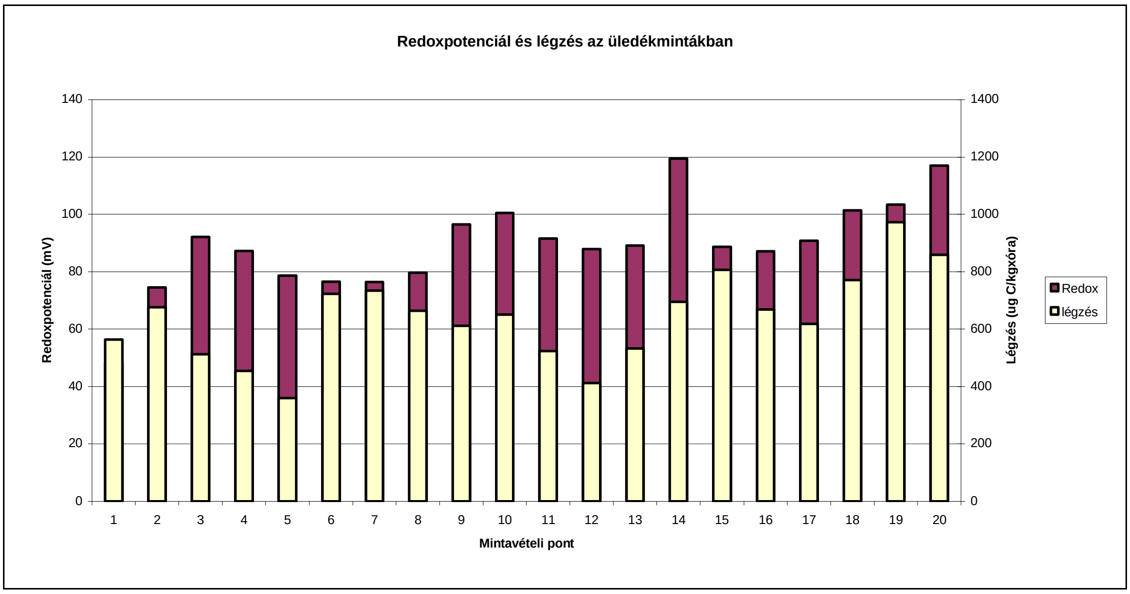

Figure 19: Changes of the ORP and respiration in the sediment

5. NEW SCIENTIFIC RESULTS

1. The sedimentation rate of the Szarvas – Kákafok deadarm was estimated by measuring the sediment depth in 1992 and 2006. Based on the measurement the sedimentation rate is 4-5 mm in a year. The sedimentation rate and the water quality measurements show, that the eutrophication of the deadarm is intensive.

2. A measurement system was developed based on the PAS technology for determination of the microbial respiration in the sediment. The method is based on the photoaqoustic detection of the CO_2, emitted by the respiration. One of the advantage is, that it is able to measure the respiration *in situ*. Furthermore, it is possible to monitor the time dynamics of the respiration.

3. Due to the *in vitro* experiments, the rate of the respiration was three times higher in an oxidative atmosphere, than in anaerobic circumstances. The influence of the aeration improves the mineralization rate of the sediment, therefore the organic load may decrease in the aquatic ecosystems.

4. The daily variation of the microbial respiration was monitored by 2 minutes time resulution *in situ*. The rate of the respiration strongly correlated to the changes of the temperature. Furthermore, the measurements proved, that the mineralization processes can take place at low, only 1 °C temperature.

5. In the aquatic ecosystems the changes of the water body are fast. The responses and the variation in the sediment is more equalized, the mineralization is strongly influenced by the oxido-reduction potential. It is advised to involve the oxido-reduction potential and the microbial activity of the sediment into the water qualifying process.

6. RESULTS, APPLICABLE IN PRACTICE

1. The sedimentation rate of the Szarvas – Kákafok deadarm was estimated by measuring the sediment depth The results show, that the eutrophication of the deadarm is intensive.

   Due to the Water Framework Directive, the controll of the pollution sources are neceessary.

2. The respiration was calculated by measuring the CO_2 emission. The advantage of the method is, that measuring the anaerobic respiration is possible. Therefore a more detailed wiev can be achieved on the carbon cycling of the sediment compartment of the aquatic ecosystems.

3. The developed method by the PAS technology makes possible *in situ* measurements, thus, the material cycling of the examined ecosystem can be researched in its environment in the field. Based on the measurements, the daily variations of the respiration of the sediment were calculated. The quickness of the developed method makes possible the monitoring measurements as well.

4. The aeration of the sediment accelerates the mineralization processes. In the case of the present river policy, the water cannot go out to the floodplain, therefore the self cleaning capabilities of the rivers are decreased.

5. The constructed fish pond - makrophyte wetland is able to process a significant organic load, which makes possible to develop a nature-friendly water cleaning technologies.

7. LIST OF PUBLICATIONS IN THE THESIS OF DOCTORAL DISSERTATION

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