

PEAT WETLAND AS A NATURAL FILTER OF EFFLUENTS FROM ADJACENT INDUSTRIAL AREAS

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Abstract

The main objective of the project is the study of a peat wetland functioning as recipient of effluents from former and present-day industrial activities. The investigation was focused on heavy metal contaminations and their probable mobilization or fixation. The studied peatbog is a typical Eastern European wetland, located in Hungary on the border between medium mountains (Bakony Mountains) and a Neogene basin (the Sárrét, an area under nature conservation). Watercourses and prevailing air currents can transport contaminants from industrial areas to the wetland. At first the basic parameters of surface waters and subsurface conditions (soils, groundwater) were investigated. These parameters (EC, Cl) are possible indicators of contamination. Subsequently, the amounts of heavy metals (Cd, Pb) extracted by solution in two steps (HCI, CaCl₂) were measured using atomic absorption spectroscopy (AAS). The extracted values indicate what amounts of which elements could be mobilized by human impact and/or production of humic acids, which occasionally emerges during the remediation works. The total heavy metal concentrations in the samples were investigated by X-ray fluorescence method. Based on the investigation, the peatbog is claimed to function as a natural filter.

Keywords: peatbog, heavy metal contamination, absorption, sequential extraction

1 INTRODUCTION

Among wetland functions the purification of contaminated water inflow takes an eminent place (Brinson et al., 1995). Although historically wastewater treatment has usually meant an uncontrolled sewage disposal and, as a result, valuable ecosystems have been irreversibly damaged (Rozkošny et al., 2014), the significance of this function has been maintained and is still valuable today. The wastewater treatment capacity of peat beds in industrial regions is under investigation in several countries (e.g. in Spain – Pérez, 2005).

In the surroundings of the studied peatbog industrial activities have been performed for more than a hundred years. In the Várpalota industrial region in the foreland of the Bakony Mountains, at first the operation of a lignite mine, subsequently the emissions from the local aluminium smelter and the Inota power plant (in a suburb of Várpalota) caused widespread environmental damage. In Pétfürdő (another suburb of Várpalota) the chemical fertilizer factory can also be a source of environmental problems. Based on monitoring data and documents the main contaminants have already been identified, but the question how they are mobilized has not yet been answered.

A few academic theses and papers (Blaskó, 2006; Ballabás, 2008, 2012; Tóth 2009) and manuscript reports (Enviroinvest Zrt., 2010; MAL Zrt. 2010) describe environmental risks in the area. The impacts of industrial activities on soil and groundwater quality in Pétfürdő were studied by Tóth (2009). Blaskó (2006) also concentrated on soil and groundwater contaminations in the area of the nitrogen fertilizer plant and pointed out high concentrations of several heavy metals. Air pollution in Várpalota was examined by Fülöp (2009) in a thesis. The emissions of the aluminium smelter and the power plant in Inota were documented by Pagony and Szilágyi (1974) and they found that south of the area the impairment shows a growing trend. Juhász (1992) warned that the poor environmental conditions in the environs of Inota require environmental monitoring. From these documents it was concluded that the level of environmental quality in the Central Transdanubian Region is below the national average (Ballabás, 2008). Berki (2011) focused on the Veszprémi-Séd watercourse, examined changes in its water quality and observed a year-to-year drop in the concentration of contaminants. The fixation and mobilization of heavy metals determine the opportunities for rehabilitation. In the course of the study of Csinger Creek's sediments Polgári et al. (2006) revealed the exact relationships between pH and the mobilization of heavy metals. Under alkaline conditions the rate of mobilization is usually low, but some heavy metals are particularly sensitive to environmental changes. Tamás and Farsang (2012) investigated heavy metals in fluvial sediments and claim that during the rehabilitation the easily exchangeable components represent the highest environmental risk.

The aim of the present research was the environmental monitoring of the peatbog of Nádasdladány and the fish-ponds near Várpalota with consideration to present and past industrial activities. In spite of large-scale industrial activities, no overall analysis has been performed there yet. The manuscript documentations prepared and monitoring data collected only focused on the immediate environs of the industrial area. The purpose of this examination was to prove or disprove the assumption that watercourses and prevailing air currents can transport contaminants from the industrial area into the present study area, the wetland.

2 STUDY AREA

The study area is a Tertiary basin located in Transdanubia, stretching between Lake Balaton and Székesfehérvár, in the southeastern foreland of the Bakony Mountains (Figure 1). The springs which feed the peatbog are located in the adjacent areas. The main watercourse of the basin is the Nádor Canal that drains the area since 1825. Conducting surface waters into the Sárvíz River, the channelization of the Nádor Stream caused severe desiccation in the basin (Dömsödi, 1977). In the course of the exploitation, started in the eighteenth century, high-quality peat was quarried and new ponds emerged. The remaining natural habitat is mostly peatbog with numerous ponds and connecting watercourses (Figure 1).



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The majority of industrial plants responsible for most of the environmental pollution are located to the north or northwest of the peatbog.



1. **0** 2. **0** 3. **0** 4.

Figure 2. Map of polluting industrial plants and sampling sites (basic map: © OpenStreetMap contributors, CC BY-SA). 1 – industrial plant; 2 – deponies; 3 – water (w) and solid (s) sampling sites; 4 – only water sampling. SI – Aluminium Smelter of Inota; CMD – Coal mine deposits in Várpalota; PP – power plant of Inota; PPD – its slag deposits; PCFF – Pétfürdő Chemical Fertilizer Plant

These are the following (Figure 2):

- Lignite mine deposits (on the map: CMD) at Várpalota caused air pollution (CO, CO₂, SO₂) until the open-pit mines were closed down in 1996. Since then the refuses contaminated the soil and water and increased acidity.
- The aluminium smelter (ASI) of Inota also generates air and soil pollution (CO, CO₂, SO₂), also loading the environment with fluoride and dust. In the reservoir of the plant 30,000 tonnes of hazardous waste have accumulated (leading to cyanide and fluoride contamination).
- The power plant of Inota (PP) and its slag deposits (PPD) also gave rise to SO₂, CO₂ and dust emissions. In the reservoir huge amounts of sulphate accumulated.

• In Pétfürdő the chemical fertilizer plant (PCFF) is the main source of pollution. It loaded the area with NH₃, NO_X, CO and heavy metals (Zn, Se, Mo) mostly deriving from the catalysis process.

3 METHODS

The sampling sites were selected with considerations to the drainage network and wind directions. Solid samples were collected through augering from soils, pond sediments and fluviatile sediments. Most of the water samples are taken at the same sites as the solid samples. For basic chemical examinations 1 litre of water was stored in glass bottles and another 1 litre for heavy metal examinations in a plastic bottle. HNO₃ was used as a preservative.

At first the basic parameters of groundwater, ponds, streams and solid samples were measured: pH, chloride ion, alkalinity, conductivity, humus content, relative calcareous matter and organic matter. The quantity of organic matter was determined using a gravimetric method (Hegedűs et al., 1980). The dried samples were burned out through heating to 600°C. From the difference between dried and burned weights the amount of organic matter was calculated. The humus content was investigated by Székely method which is a photometrical method using K₂Cr₂O₇ and H₂SO₄ (Hegedűs et al., 1980). The particle-size distribution was determined employing sieving and laser-particle sizer (FRITSCH Analysette A22_32).

Heavy metal concentrations were examined by the AAS and X-ray fluorescent method (XRF). The heavy metals Cd and Pb were analysed using atomic absorption spectroscopy with a SpektrAA-400 VARIAN graphite-oven atomic absorption spectrometer. For this technique 25 cm³ of 0.1M HCl or 0.1M CaCl₂ were added to 10 g of solid sample, which was put into an ultrasonic extractor for two hours. The total heavy metal concentrations of the samples were investigated by X-ray fluorescent method using Niton XL3t 600 XRF Analyser (50 KV/100µA, Au X-ray source).

4 RESULTS AND DISCUSSION

Most of the solid samples are calcareous except the ones from sampling sites 1S and 9S. These areas are at higher elevation and probably leached. In the case of organic matter the values are high. Where they are above 30%, they indicate the presence of peat (Table 1).

sample number	depth in cm	type organic matter (%)		relative calcareous matter [×]		
15	0-15	soil 11.84 ^{xx}		0		
15	15-30	soil	7.15 ^{××}	0		
15	30-50	soil	3.4 ^{××}	0		
28	0-50	pond sediment	52.64	XX		
28	50-100	pond sediment	7.23	XXX		
28	100-150	pond sediment	6.08	XXX		
38	0-30	pond sediment	49.82	XXX		
38	30-60	pond sediment	18.82	XX		
38	60-230	pond sediment	6.5	XXX		
4S	0-50	pond sediment	57.4	XXX		
4S	50-100	pond sediment	51.96	XXX		
4S	100-150	pond sediment	57.78	XXX		
58	0-50	pond sediment	17.33	XX		
6 S	0-50	fluviatile sediment	39.22	XXX		
6 S	50-100	fluviatile sediment	53.14	Х		
7S	0-50	pond sediment	53.75	XXX		
78	50-100	pond sediment	50.92	XX		
8S	0-50	fluviatile sediment	9.58	XXX		
98	0-50	fluviatile sediment	2.22	0		
105	0-50	fluviatile sediment	2.42	XXX		
115	0-50	fluviatile sediment	14.32	Х		
128	0-50	pond sediment	13.14	XXX		
12S	50-100	pond sediment	33.06	XXX		
138	0-50	pond sediment	16.48	XXX		
14S	0-50	pond sediment	8.12	XXX		
^x 0: not effervescent; x: poorly-; xx: moderately-; xxx: strongly effervescent						
**determination by SZÉKELY method						

Table 1. Organic matter and relative calcareous matter in solid samples

The sediments are alluvial clayey silt or silty clay. Coarser grains are only typical for streambeds (Figure 3).



Figure 3 Particle size distribution of the solid samples

The pH values show that the waters in the area are assessed as slightly alkaline to alkaline. This is explained by the calcareous geological background (streams springing from karstic limestone and dolomite mountains). P-alkalinity measured in the samples was close to pH 8. On three occasions chloride ion concentrations (limit value: 250 mg/l), while on two occasions values of conductivity (limit value: 2500 μ S/cm) were high or close to the limit (Table 2). The findings are explained by the fact that coal mine deposits are located in the close vicinity of the sampling sites.

sample number	type	UTM		EC	pH	p alkalinity	m alkalintiy	Cľ
			UIM	µS/cm	x	mg/l (CaO eq)		mg/l
1W	groundwater	288569.2257	5227954.3519	475	7.55	0.0	240.3	21.3
2W	still water	289321.0246	5227650.4050	1370	7.80	0.0	248.9	269.8
3W	still water	289380.3682	5227462.8240	1890	8.21	40.6	280.43	816.0
4W	still water	289198.2116	5227300.2907	388	8.22	11.4	163.11	35.5
5W	stream	289678.3884	5226576.9155	461	8.00	11.4	171.7	42.6
6W	still water	289678.5888	5226464.8521	510	8.30	14.3	203.17	49.7
7W	still water	289624.0688	5226645.3082	470	7.97	0.6	174.55	39.1
8W	stream	290200.0260	5224549.8328	528	8.28	17.1	266.13	63.9
9W	stream	286113.9524	5226034.6752	524	8.05	8.5	200.3	53.2
10W	stream	286154.9468	5226473.8880	489	7.97	8.5	188.8	14.2
11W	stream	287273.5718	5227075.2623	548	8.12	31.4	283.3	74.5
12W	still water	285676.3940	5228943.1816	525	8.90	48.6	174.55	92.3
13W	still water	283371.1935	5228625.6259	3150	8.20	17.1	123.0	230.8
14W	still water	284863.3937	5231160.7144	1440	8.14	28.6	148.8	134.9
15W	still water	286881.1260	5229866.5629	545	8.44	20.0	100.2	63.9
16W	still water	286153.2092	5229445.5342	491	8.76	51.5	186.0	39.1
limits, according to 2013/39/EU		steams in lowland	<1000	6.5-9.0	х	х	<60	
			mine pond	<1500	7.8 - 9.2	х	х	x

Table 2 Basic parameters determined in water samples (dark grey: over the limit, light grey: close to the limit of contamination)

In addition, we intended to measure those contaminants that are not restricted to only one factory, but can originate from any of them and can amplify the environmental risk to the peatbog. The results for Pb and Cd measured by AAS can be seen in Table 3.

During the sequential extraction 0.1M HCl and 0.1M CaCl₂ were chosen for solvents to determine the amounts of easily exchangeable components which can be mobilized by natural and anthropogenic processes. After treatment with CaCl₂ solution the measured values were higher than after treatment with HCl solution in most samples. The chemical bonds and competition of the heavy metal elements show greater differences due to the heterogeneity of solid samples, i.e. the quality of adsorption of organic materials and carbonate types. However, most of the HCl was consumed for the dissociation of carbonates. This process modified the role of the adsorption of isotherm types. This effect differs with the investigated elements (Cd and Pb). This assumption is confirmed by data in Figure 4. The relation between the measured values is rather random, caused by dependent higher values in one case (in the case of sampling site 6, at 100 cm depth).

Sample number	¹ Pb (µg/l)	² Cd (µg/l)			
1W	LOD	0.47			
2W	5.04	3.36			
3W	8.34	1.95			
4W	LOD	0.63			
5W	0.38	0.55			
6W	LOD	0.64			
7W	LOD	0.45			
8W	LOD	3.88			
9W	LOD	0.79			
10W	LOD	0.52			
11W	LOD	2.95			
12W	1.37	1.27 1.82			
13W	9.88				
14W	4.96	1.00			
15W	0.69	0.82			
16W	3.02	2.95			
¹ 10/2010. (VIII. 18.) VM: AA-EOS: 1.2 µg/l:					
MAC-EQS: 14 µg/l					
² 10/2010. (VIII. 18.) VM: AA-EQS: 0.25µg/l;					
MAC-EQS:1.5µg/l					
LOD: limit of detection					

Table 3 Pb and Cd contents in liquid samples, measured by AAS. The 10/2010.
(VIII. 18.) VM Hungarian ministry decree of contamination limits, harmonized with Directive 2013/39/EU of the European Parliament (European Parliament and Council, 2013). AA-EQS: Annual Average - Environmental Quality Standard. MAC-EQS: Maximum Allowable Concentration - Environmental Quality Standard



Figure 4 Amounts of heavy metals Pb and Cd (measured by AAS) in relation with different solvents

With XRF the total heavy metal concentrations of the samples were measured (Table 4). From the results it can be seen that Cd is under the detectable value and the Pb is under the limit value. On the other hand, further problematic heavy metals were discovered. Nine samples shows very high As concentration. It can originate from former coal mining, metallurgy or from petrochemistry. The first two samples show high Co, Cr, Ni, Cu, Zn contents. In this case these can relate to the railway line that runs close to the sampling sites. The central part of the peatbog (4S, 5S, 6S, 7S) also shows high heavy metal contents, mostly transported by watercourses.

		metal contaminants							
elements		Cd	Pb	Cr	Co	Ni	Cu	Zn	As
limit* (mg/kg)									
sample	danth in an	1	100	75	30	40	75	200	15
N.o.	depth in cm								
1S	0-15	LOD	20	110	110	40	50	90	40
1S	15-30	LOD	30	150	170	70	90	110	50
2S	0-50	LOD	20	10	LOD	30	20	40	30
2S	100-150	LOD	20	40	LOD	LOD	20	50	10
3S	0-30	LOD	LOD	LOD	LOD	LOD	LOD	10	10
3S	30-60	LOD	10	LOD	LOD	LOD	LOD	LOD	LOD
3S	60-230	LOD	10	LOD	LOD	LOD	LOD	10	LOD
4S	0-50	LOD	10	20	LOD	40	20	50	10
4S	50-100	LOD	10	LOD	LOD	LOD	LOD	10	10
4S	100-150	LOD	10	LOD	LOD	LOD	LOD	20	20
5S	0-50	LOD	80	100	LOD	20	100	810	10
6S	0-50	LOD	20	LOD	LOD	LOD	20	130	20
6S	50-100	LOD	20	10	LOD	LOD	20	100	20
7S	0-50	LOD	20	20	LOD	LOD	10	770	20
7S	50-100	LOD	40	30	LOD	LOD	30	970	20
8S	0-50	LOD	30	80	LOD	30	60	180	10
9S	0-50	LOD	20	140	LOD	30	LOD	40	10
10S	0-50	LOD	20	60	LOD	LOD	10	60	10
11S	0-50	LOD	20	60	LOD	30	20	70	10
12S	0-50	LOD	10	LOD	LOD	LOD	20	LOD	10
12S	50-100	LOD	10	LOD	LOD	LOD	LOD	10	10
13S	0-50	LOD	20	40	LOD	LOD	10	30	10
14S	0-50	LOD	10	LOD	LOD	LOD	10	20	20
* according to 6/2009. (IV. 14.) KvvM-EüM-FVM Hungarian regulation									
grey background: over the limit value									
LOD: lower limit of detection									

Table 4 Concentrations of the elements measured by XRF (according to KvVM-EüM-FVM 2009)

5 CONCLUSIONS

Our investigation provided evidence to the functioning of the peatbog as a natural filter between industrial areas and major watercourses.

The basic parameters analysed point to high levels of soil and water contamination. The high amounts of organic matter and carbonates enable the fixation of heavy metals. The higher heavy metal concentrations measured with XRF refer to the total sample, especially to Zn and As. The extent of contamination, however, is not constant. The contaminants are confined to particular sites mostly in the central part of the peatbog and are associated with well-defined deposits (Fig. 5). The findings of the study underline that the fixation of the studied heavy metals depends on the character of the geological background.



Figure 5 Accumulation of contaminants. A. Cl (mg/l); B. Electric conductivity (μS/cm); C. Zn (mg/kg); D. As (mg/kg). 1 – wetland; 2 – built-up area; 3 – ponds; 4 – watercourses, canals; 5 – railway; 6 - roads

In the water samples Cd and Pb concentration are occasionally close to or in some cases above the limit. They derive from equilibrium conditions between the geological background and the water bodies. It is assumed that higher values of these metals do not necessarily indicate actual contamination, but are remnants of formerly intensive industrial activities. The lighter solvent (CaCl₂) provided higher values than the stronger solvent (HCl). Both heavy metals produce poorly solvable compounds with carbonates. It could be an explanation that most of the HCl was used up to dissociate carbonates. It is certainly acceptable that the high values are not only due to pollutions, but also reflect the natural background values of the region. If pH is above 7.5, the mobility of the metals is reduced and they can be fixed. This situation can easily be achieved if root development is considered. The pH value can also be reduced to pH 4-5 by human impact (including, for instance, acid deposition). The extracted values indicate the amounts mobilized by humic acids due to human impact and occasionally. The metals Cr, Co, Ni and Cu mainly originate from illegal junkyards, from traffic (railways), agriculture, not exclusively from the operation of the chemical plant.

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