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ARTICLE

A water quality investigation around an oil refinery in Hungary using the *Fontinalis antipiretica (HEDW.)* as bioindicator

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ABSTRACT In this study the aquatic moss *Fontinalis antipyretica (Hedw.)* was used to indicate the relative levels of water pollution by ten heavy metals: Cd, Cr, Cu, Ni, Pb, V, Zn, Al, Fe and Pb at the territory of an oil refinery at the river Danube in Hungary. For the sake of complex comparison of environmental loads, CO_2-gas exchange and chlorophyll-fluorescence parameter Fv/Fm were measured as complementarity to elemental analysis. A 36 days long period was studied in the summer of 2007. The water biomonitoring did not indicate the significant increasing of elemental load by the oil-refinery. **Acta Biol Szeged 52(1):75-77 (2008)**

KEY WORDS

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Monitoring the air and water quality near to an oil-refinery has been a long–standing community concern, particularly when such heavy industrial activities are located near urban areas. Among the most relevant atmospheric pollutants (sulphur dioxide, nitrogen oxides and PAHs), the investigation of the heavy metal level is primarily important (Westaway 1978). Fossil oils, mostly heavy oil contain higher concentration of heavy metals (VB.-VIIIB. columns of the periodic table) (Amoli et al. 2006).

In long and short term bioindication research bryophytes, especially green mosses, are preferred as they are excellent indicators of environmental conditions (Pócs et al. 1987). Bryophytes together with the lichens, are indicators of water supply, soil pH, heavy metals, policyclic aromatic compounds and UV-B radiation, etc., (Pócs et al. 1987; Bruns et al 1997; Tuba et al. 1997; Takács et al. 1999; Ötvös et al. 2003). They have the ability to accumulate heavy metals with high efficiency and low selectivity. The other advantage of monitoring by mosses is its low cost, and high tolerance of these living organisms to different environmental conditions (Meenks et al. 1991; Csintalan et al. 2005).

The aim of the present work is the determination of water quality and spatial distribution of the above mentioned pollutants over the period from July to August 2007 at the area surrounding an oil-refinery located near to river Danube (Hungary). This study is a part of a long period survey at the heavy industrialized area of the city Százhalombatta.

Materials and Methods

Elemental analysis

The samples were transplanted as active biomonitoring to the area next to an oil refinery at the River Danube, Hungary according to Tuba and Csintalan (1993). The aquatic and moss *Fontinalis antipyretica (Hedw.)* was used as bioindicator.

Equal weights of bunched mosses were used in plastic bottles to protect the samples. Three parallel bunches were placed at every site kept on the top of river by a float about 10 m distance from the water-front. We investigated about 4 km long part of the river (5 sampling point placed starting from the sewer of oil-refinery along the flowing of river). Point No.1 in the sewer, No.2 approx. 20 m under the estuary of drain. The remaining 3 points were transplanted lower. The point No. 6 as inner control was placed at the estuary of the power plant Százhalombatta, approx. 3 km upper, from the estuary of oil-refinery's drain on river Danube. Two other control area were used: as a 'medium' polluted at the lake of botanical garden of SIU, Gödöllő and an „unpolluted" at the West-Mátra mountain in Csörgő creek.

The investigated area was monitored from July to October 2007. In this study we present the summer period of July to August 2007. The samples were placed in this study for 36 days. The *Fontinalis antipyretica* (Hedw.) origined from a fresh water lake in Hungary. All plant material were gather at the early summer of 2007 from the same population.

The digestion of samples for elemental analysis followed the protocol described by Tuba et al. (1994). The samples were stored until digestion in plastic bags. The upper green

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Table 1. Ratios of the elemental content in *Fontinalis antipyretica* (Hedw.) (after transplantation compared to the untransplanted values) 1-6: water biomonitoring plots from river Danube. C1: water monitoring control site from Godollo, C2: Matra water control. Data are presented as mean±SD, n=9.

Plots / Elements	1	2	3	4	5	6	C_1	C_2
V	0.67±0.17	1.05±0.23	1.65±0.26	1.15±0.44	1.16±0.35	1.27±0.23	0.88±0.08	0.64±0.03
Cr	2.74±0.53	3.09±0.87	4.92±1.70	3.44±1.57	3.65±1.74	3.80±0.62	0.60±0.09	0.23±0.02
Co	0.44±0.12	1.81±0.25	3.04±0.53	2.24±0.94	1.82±0.32	1.70±0.38	0.41±0.02	0.14±0.01
Ni	0.88±0.12	1.65±0.42	2.52±0.32	1.68±0.64	1. 65±0.49	1.98±0.43	0.35±0.04	0.07±0.001
Cu	0.87±0.03	3.26±0.28	4.58±0.59	3.07±0.72	3.07±0.57	2.82±0.34	0.86±0.04	0.85±0.12
Zn	0.27±0.06	0.57±0.12	0.62±0.12	1.31±0.71	0.62±0.14	0.54±0.16	0.61±0.07	1.08±0.06
Cd	3.92±1.45	4.28±2.61	4.74±3.16	3.27±1.91	4.74±4.88	1.95±0.82	2.15±2.67	0.85±0.07
Pb	0.42±0.11	0.36±0.25	3.72±2.00	0.66±0.47	1.34±0.30	0.84±0.39	1.34±0.30	0.84±0.28
Fe	0.80±0.19	1.41±0.37	2.32±0.42	1.58±0.66	1.52±0.45	1.81±0.42	0.30±0.02	0.79±0.08
Al	1.39±0.23	3.87±1.02	6.04±1.83	4.35±1.88	3.95±2.10	4.90±1.04	0.34±0.07	4.07±0.63

3-4 cm long younger fresh plant „branches" from *Fontinalis antipyretica (Hedw)* were cut for further analysis. Standards from the Finnish Forest Research Institute, Muhos Research Station (No. 805) were used for better comparison. The concentrations of Cd, Cr, Cu, Ni, Pb, V, Zn, Al, Fe and Pb in the digested samples were determined by ELEMENT2 High resolution ICP-MS instrument Thermo Electron Corp.

One-way ANOVA followed by Tukey's test was performed to reveal significant differences between element content and physiological parameters of plots.

Measurements of CO_2 gas-exchange rate

CO_2 gas-exchange rate was measured using a LICOR-6200 type IRGA system, operated in differential mode at 900 $\mu mol^{-2} sec^{-1}$ (PAR) light intensity.

Chlorophyll-fluorescence measurements

Chlorophyll fluorescence was measured using a Hansatech (King' Lynn, UK) MFMS l modulated portable Hansatech (PEA) fluorometer. Calculation of fluorescence parameters and conventions for symbols follow Schreiber & Bilger (1993), in equation: Fv/Fm = (Fm-Fo)/Fm.

Results and Discussion

Bioindication of metal pollution in water at the region of an oil-refinery see Table 1.

The experimental plots at the oil-refinery, showed decreasing element content in the case of Zn except site 4th, and in case of Pb but not sites 3th and 5th. For all other elements and plots remarkable increase was observable except for site 1th. The analysis of variance in case of most of the elements

Table 2.'a' Changes of CO_2 gas-exchange rates measured at 900 $\mu mol^{-2} sec^{-1}$ radiation (PAR) intensity in the control and the transplanted aquatic moss, the *Fontinalis antipyretica* (Hedw.). 'b' Fv/Fm values in photosynthetically fully active moss branches afer 15 min. dark adaptation. Data are presented as mean±SD n=5, 1 to 6= water plots at the oil-refinery, C=Control of Gödöllő.

Sampling plots	a' before transplantation	a' after transplantation	b' before transplantation	b' after transplantation
	CO_2 assimilation (μmol CO_2 $kg^{-1} sec^{-1}$)		Fv/Fm parameters (relative unit)	
1	5.03±1.20	-12.47±9.93	0.79±0.01	0.65±0.04
2	2.36±0.87	0.28±0.03	0.77±0.03	0.75±0.02
3	5.66±1.64	0.42±0.01	0.80±0.01	0.79±0.01
4	4.10±2.49	0.68±0.07	0.79±0.01	0.79±0.01
5	3.19±0.88	- 0.12±0.01	0.82±0.06	0.78±0.02
6	5.04±1.37	0.12±0.02	0.78±0.01	0.75±0.03
C	6.17±0.27	0.35±0.04	0.76±0.01	0.78±0.03

at plot 3th confirmed (except Cd and Cr) significant pollution compared to other sites. The alterations at site 6th were similar to site 3th, but only in case of Al was significancant. Similarly to the change in element content among the plots 4th, 5th and 2th except Zn. This homogenity suggests pollution from the same sources. The alterations were remarkable, if the monitored area is compared to controls, but no significant differences were found in case of Zn, Cd and Pb. Only Al differred between the control of Gödöllő and Mátra. The control areas are eligible reference points as background pollution except Al and Pb.

CO_2 gas exchange responses

The CO_2 assimilation rate was markedly decreasing at all plots a month after transplantation compare to the untransplanted values see Table 2.

Chlorophyll-fluorescence responses

The characteristic ratio of fluorescence parameter Fv/Fm is suitable for the detection of abiotic stress. Significant decrease of Fv/Fm ratio was observed after 36 days transplantation at sites 1th and 6th.

From our data we conclude that the element loading in water was not homogeneous in few cases. Element accumulation occurred more than 1.3 km lower in the river from the estuary of oil-refinery's drain. The living Danube's results could be seen as homogeneous and no appreciable difference was obsereved down the river from the drain except the 3th site. The deviation might be consequence of the deposition of river's sludge. The samples from site 3th were high polluted with slob. This indicates local pollution, but not from the refinery. Moreover, the wastewater contained significantly less V, Co, Ni, Cu, Fe, Al, compared to the average river's loading. The Pb, Zn, Cr content in sewage were lower, but not significantly compared to that of Danube. The increased element content, except Cd and Cr, in River Danube was most probably due to background deposition (sludge, precipitated aerosoles) or different industrial plants, but not due to the oil-refinery. The significantly decreasing fluorescence parameter and CO_2 gas-assimilation at these sites (1th and 6th) indicate stress factors. Both parameters were decreasing markedly at the oil-refinery's drain. This may indicate other stress factors than heavy metal load in the sewage. The simultaneous measurement of elemental load and physiological parameters may help to identify the pollution source and biological strain.

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