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INFLUENCE OF THERMAL POWER PLANT TUZLA ON THE HEAVY METALS BURDEN IN THE SURROUNDING

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Abstract. The production of electricity through fossil fuel combustion has a significant impact on the conditions for sustained development, due to the fact that it depletes natural resources which can not be renewed, and through its greenhouse gas emissions. Power plants withdraw and discharge considerable quantities of water. Waterborne pollutants that may come into contact with ecological communities range from thermal discharge to a variety of metals suspended in soils, oil and grease and other oxygen demanding wastes. Fly-ash landfills and ponds are the predominant source of heavy metals, such as lead, cadmium, copper, zinc, mercury, etc. Heavy metals present moderate to high environmental hazard and ecological risk rankings due to known toxicity and persistence. Whether any of these metals are bio-available depends on complex chemical interactions between the metals and other parameters. For that reason investigations of heavy metals burden in the soil and in biota in the surrounding of thermal power plants presents the continuing task. The purpose of this paper is to correlate the pollution caused by the emission from thermal power plant Tuzla, since it is situated in populated area and in the vicinity of agricultural fields used by the inhabitants.

Keywords: heavy metals burden, soil, power plant emission.

AIMS AND BACKGROUND

Emmissions from thermal power plant Tuzla. Power plant Tuzla has the biggest capacity for electrical energy production (ca. 700 MW) in Bosnia and Herzegovina. It is located close to the city Tuzla, which is the administrative center of the biggest and most populated canton in Bosnia and Herzegovina.

Production of electrical energy presents nowadays the most important industrial capacity in this region. Monitoring of the pollution in the surroundings of thermal power plant showed the catastrophic situation in 1990, and measures were undertaken on the improvement of environmental situation and on technology improvement.

The data for the emissions in 1999 and 2000 are given in Table 1. Those emissions resulted as products of burning up of 4 809 772 t of local coal per year.

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Table 1. Emissions from thermal power plant Tuzla

Emission	1990 (t/year)	2000 (t/year)	Emission ratio 1999/2000 (%)
SO_2	73 589	27 974	38
NO_x	12 200	7 260	60
CO	4 591	1092	24
Solid particles	17 812	3864	21

Significant improvement in reducing the emissions of pollutants is the result of measures undertaken for the protection of the surrounding environment.

The plans for improvement were prepared for the achievement of international standards and norms (Protocols from Kyoto and Energy Climate).

In accordance to the future improvement of emissions for the period 2003-2006, Thermal power plant Tuzla should emit as follows:

- emission of SO_2 35831 t/year
- emission of NO_x 9904 t/year
- emission of CO 1312 t/year
- emission of solid particles 2032 t/year

It is expected that emissions will be decreased up to 48.6% of SO_2 , 81.18% of NO_x, 28.60% of CO and 11.40% of solid particles in comparison to the present values.

In accordance to the energy production, the European norms on emissions propose the limiting values as follows:

- solid particles 150 mg/N m^3
- SO_2 400-1000 mg/N m^3
- NO_x 650 mg/N m^3

Recent measurements showed that emissions of SO_2 and solid particles are increased and the measures should be urgently undertaken to decrease these emissions to tolerable levels.

Beside the pollution from thermal power plant, traffic pollution is significant since it is concentrated in a very narrow zone.

Acid deposition and heavy metals. Acid deposition affects the environment in several different ways. In aquatic systems acid deposition can affect ecosystems by lowering pH value. Aquatic systems with predominant sandstone lithologies are very sensitive to acid deposition, because they lack basic compounds that buffer acidification. Acidified waterbodies may also contain high concentrations of toxic heavy metals.

Heavy metals are naturally present in the surrounding soil and bedrock. Heavy metals are found lock in clay articles and minerals, but the acidification of terrestrial soils and bedrock can cause these metals to become soluble. In less buffered soils, vegetation is affected by acid deposition because:

1. Higher acidity results in the leaching of important plant nutrients, including calcium, potassium and magnesium;

2. Low availability of these nutrients may cause a decline in plant growth rates;

3. Heavy metals become more mobile in acidified soils and can interfere with plant uptake of other nutrients;

4. Important soil organisms can not survive in soils below a pH of about 6.0.

Heavy metals in soil. The soil samples were taken in accordance with standard procedures from four locations.

Heavy metal concentration in soils is very important due to their toxic effect in food through biologic chain: soil–plant–food. For this reason accurate monitoring of their concentration plays an important role.

During the course of the biogeochemical cycle through various compartments of the environment toxic trace metals can enter the food chain to man by various ways.

The uptake of the metals by soil depends on the chemical properties of the metal and of the soil, especially on its acidity and the content of humic substances. Some metals are rather firmly bound to humic substances of the soil, as Pb or Hg, others can be easily remobilised from the soil as Cd.

The monitoring of toxic heavy metals in the soil becomes a task of a high priority and significance in environmental research and protection, particularly in view of the rate at which chemicals are introduced into the surrounding environment. Maximal tolerant content (MTC) of heavy metals in agricultural soil is given below[1]:

– Pb	100-150 mg/kg of soil
– Cd	1-2 mg/kg of soil
– Cu	60-100 mg/kg of soil
– Zn	130-200 mg/kg of soil

EXPERIMENTAL

Four different locations were marked as significant with respect to heavy metal contamination, from which the soil samples and plant material as bio-indicators of heavy metal uptake were taken.

The soil samples and samples of plant material (*Trifolium repens)* were taken in accordance with standard procedure. Location 1 is approximately 100 m away from the thermal power plant; location 2 is in the vicinity of near-by traffic road (ca. 250 m away from thermal power plant); locations 3 and 4 are agricultural soils approximately one kilometer away from the thermal power plant. Four investigating sites mentioned above were situated in the area with significant emission of gases and solid particles from the power plant.

Sample pretreatment. The soil samples were taken into a precleaned polyethylene bag which was sealed. The samples were homogenised and air dried for 24 h, and then thermally treated at 500°C for 6 h, for the purpose of decarbonisation of organic matter. Portion of 2 g of finely ground soil was digested with suprapure HNO_3 (Merck). The entire digestion takes about 3 h. The unit firstly was heated up to 80°C for 40 min and temperature was raised gradually to 160°C as the sample was heated at this temperature for 40 min. Subsequently the sample was cooled down to room temperature. pH of soil was determined by standard method and on locations 1 and 2 was pH $\cong$ 5 and on locations 3 and 4 pH $\cong$ 6.

Plant material (*Trifolium repens*) grown on 4 locations was dried on 50°C and homogenised prior to thermal treatment at 500°C for period of 6 h, and thus decarbonised. Decarbonised samples were rinsed with 2M HNO_3 (supra pure) and transferred to 25 ml flasks.

Chemicals. All reagents were supra pure grade (Merck). Standard stock solutions of Pb, Cd, Cu and Zn were prepared from Merck Titrisol solutions. All laboratory ware was at first thoroughly cleaned and subsequently exposed to a mixture of half concentrated HNO_3 for several days and then rinsed thoroughly with ultra-pure water several times.

Method and equipment. Concentrations of heavy metals (Pb, Cd, Cu and Zn) in soil and plant samples were determined by electroanalytical method – DPASV (differential anode stripping voltammetry) which is standard method for trace metal determinations.

Voltammetric measurements were carried out with a Princetenon applied research (EG&G) potentiostat Model 303A. Voltammetric cell was made of Pyrex glass (10 ml) with hanging mercury drop electrode (HMDE) as working electrode and saturated Ag/AgCl electrode as reference electrode. The research electrochemistry software 4.3 was used for the control of voltammetric measurements.

Standard addition method was applied and in the course of calculations of concentrations of trace metals MATHCHEM-computer program was used.

RESULTS AND DISCUSSION

The analysis of soil on 4 locations showed that locations 1 and 2 are characterised as sandy and silty soils. The content of CaO and high percentage of glowing loss indicate the carbonaceous character. Lower content of SiO_2, Al_2O_3 and Fe_2O_3 in this soil indicates the deficite of humic component.

The content of Al_2O_3 and Fe_2O_3 on locations 3 and 4 as well as the content of MgO, CaO and value of the glowing loss indicate the higher clay content.

The results of soil analysis are given in Table 2.

Table 2. Soil analysis

Pollutant	Location 1	Location 2	Location 3	Location 4
SiO_2	71.90	48.59	69.40	70.61
Fe_2O_3	5.19	2.40	6.99	6.99
Al_2O_3	5.75	2.75	6.54	6.50
CaO	4.59	23.10	3.36	2.91
MgO	2.20	2.34	4.03	4.15
SO_3	0.58	0.44	0.55	0.57
Glowing loss	10.4	20.56	9.59	8.89

The results of voltammetric measurements for lead are given in Fig. 1 and for cadmium in Fig. 2. Standard addition method was applied, as it is illustrated for lead in Fig. 1.

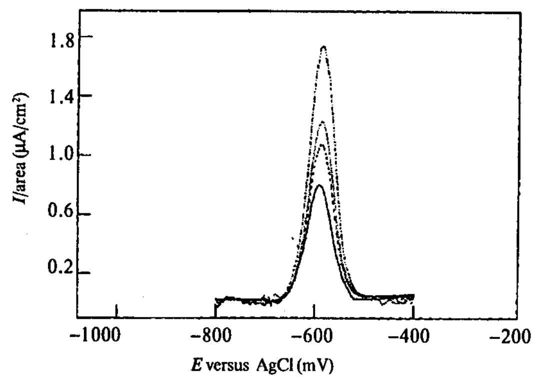

Fig. 1. Voltammetric curve for Pb in soil on location 2

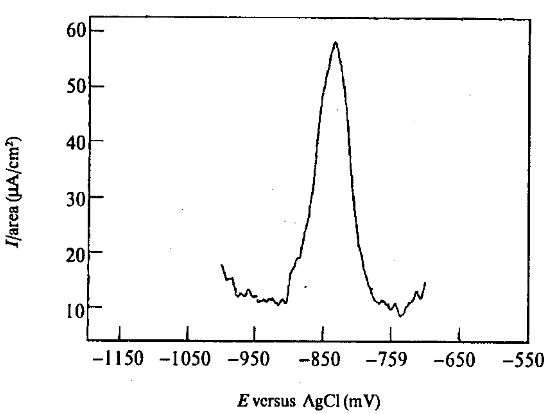

Fig. 2. Voltammetric curve for Cd in soil on location 2

The concentrations of heavy metals in soil (mg/kg) on 4 locations near the thermal power plant are given in Table 3.

Table 3. Concentrations of heavy metals

Metal (mg/kg)	Location 1	Location 2	Location 3	Location 4
Pb	468	680	525	394
Cd	5.85	10.2	8.8	6.8
Cu	284	330	225	158
Zn	158	190	364	290

The concentrations of heavy metals (mg/kg) of plant material (*Trifolium repens*) are given in Table 4.

Table 4. Concentrations of heavy metals in plant (*Trifolium repens*)

Metal (mg/kg)	Location 2	Location 4
Pb	203	198
Cd	1.5	2.5
Cu	250	120
Zn	170	137

Figure 3 illustrates heavy metal burden in soil on 4 locations. Figure 4 illustrates the heavy metals content that bio-indicating plan uptook on two locations.

The results obtained show that heavy metals burden of soil on 4 locations reached the levels up to five times higher than the maximum allowable limits and can be considered as contamination, especially on location 2, which is closer to the traffic road.

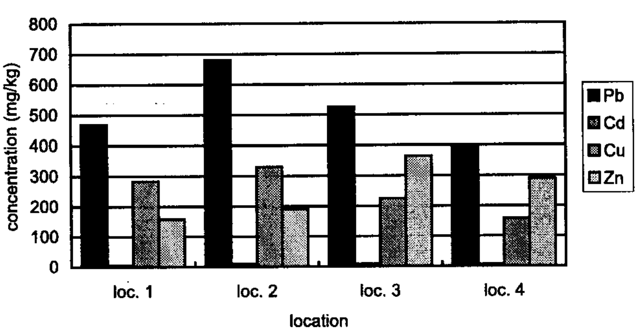

Fig. 3. Heavy metals in soil

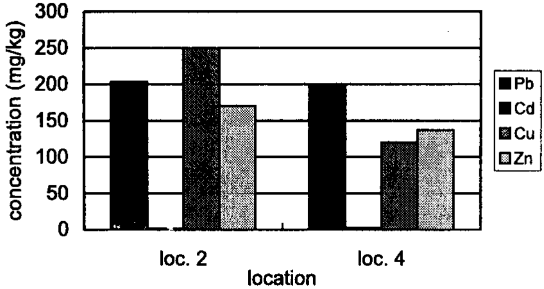

Fig. 4. Uptake of heavy metals in plant (*Trifolium repens*)

The intake of heavy metals by plant (*Trifolium repens*) was pronounced and the concentration range reflects the contamination of the soil. The concentrations of heavy metals in the plant material from location 4 (which is 1 km away from the thermal power plant) were lower due to the less pronounced emissions, but still can be considered above allowed limits, what presents the potential problem since it is the agricultural soil.

The acidity of the soil is caused by acid deposition nearby the thermal power plant and deposition of particles loaded with heavy metals. The acidification and the micro-biological activity disturbance directly affect the quality of organic matter. A first effect of this process is heavy metals mobility intensification up to five times as compared to the maximum allowed limits.

The second effect is the decrease of the humification intensity, because the organic matter has a low nitrogen content and a high carbon content. The loss of basic elements, especially calcium, from the colloidal complex, under the conditions of low organic matter contents, causes soil structure deterioration, what is evident on all locations under investigation. Soil degradation decreases the productivity of the land, and presents the threath of chronic intoxication by heavy metals, when such soil is used as arable land.

Intake of heavy metals by plant, a bioindicator, indicates the level of contamination and its possible way to enter the food chain. For these reasons it is necessary to improve the technology of the thermal-power plant by: reducing the emissions of gases and solid particles, implementing the coal-pretreatment technologies as well as to avoid the agricultural activities in the vicinity of thermal power plant.

Contaminated soil should be subjected to the decontamination or recultivation treatments alongside with the necessary technological improvements.

CONCLUSIONS

Production of electrical energy in the Thermal power plant Tuzla presents the most imoportant industrial activity in the region of Tuzla canton. Monitoring of the emissions showed that the values are still above the international norms and that the measures already undertaken should be improved. The emission of gases and solid particles resulted in degradation of soil in the surrounding area. Since heavy metals present high environmental risk due to known toxicity and persistence, the monitoring of the possible contamination is a permanent task. Bioavailability of heavy metals depends on complex chemical interactions between the metal and other parametres. The investigations showed that the acidity of soil is increased in the vicinity of the thermal power plant and that the pollution with heavy metals is more intensive due to the traffic pollution. The fact that emission influences the agricultural soil resulted in increased concentrations of heavy metals above maximum tolerable content. The voltammetric method was applied in experimental investigations, and the results obtained were accurate and reproducible. The investigations showed that the technology of electrical production from coal should be improved to meet the international standards, and that the measures of soil remediation should be implemented in agricultural locations.

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