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MONITORING TECHNIQUES FOR INORGANIC AND ORGANIC POLLUTANTS IN SOILS AROUND AN INTEGRATED IRON AND STEEL PLANT*

Antoaneta ENE[1], Alina (BOSNEAGA) SION[1], Lucian P. GEORGESCU[1], Oleg BOGDEVICH[2]

[1]"Dunarea de Jos" University of Galati, Faculty of Sciences and Environment, Department of Chemistry, Physics and Environment, Romania
[2] Institute of Geology and Seismology, Laboratory of Geochemistry, Moldova

ABSTRACT

In this paper the analytical techniques of X-Ray Fluorescence (XRF) and Gas Chromatography with Electron Capture Detection (GC-ECD) and coupled with Mass Spectrometry (GC-MS) are used in order to assess the level of industrial and agricultural pollution of soils. The soil samples were collected from Galati County, near an industrial plant and near cultivated areas. In this study, it is investigated the way in which the anthropic activities influence the quality of the environment, due to the contribution of inorganic and organic elements enrichments.

KEYWORDS: XRF, GC-ECD, GC-MS, organic and inorganic pollutants, soil pollution

1. Introduction

The extent of anthropogenic environmental pollution did affect the quality of the environment, and also the human life. Polycyclic aromatic hydrocarbons, commonly referred to as PAHs, are classified as organic compounds of two or more fused aromatic rings of carbon and hydrogen [1].

One of the most important sources of PAHs is the incomplete and/or inefficient combustion of fossil fuels. The steel production is involving either the refining of molten iron made from ore or the refining of recycled scrap steel. The first way is involving a high consumption of energy, by burning fossil fuels, being a contributor to PAHs discharge into the environment.

The second way of production is more electric furnace dependent, discharging a much smaller amount of PAH into the environment [1].

In other studies, there have been used zucchini (*Cucurbita pepo L.*) and spinach (*Spinacia oleracea*) as bioaccumulators for persistent organic pollutants (POPs) and heavy metals [2].

The potential for negative impacts of these elements and compounds on humans and the environment is of major concern. The aim of this work is the determination of some heavy metals and POPs in soils from selected regions in Romania using the analytical techniques of X-Ray Fluorescence (XRF) and Gas Chromatography with electron capture detection (GC-ECD) and coupled with Mass Spectrometry (GC-MS).

2. Experimental results

2.1. Sample collection

Six representative locations were chosen for sample collection of the soils, in Galati and Constanta counties, Romania, including industrial suburban and rural zones. Usually the texture of the soil samples was a mixture of sand and clays. The soil was collected with proper instruments, labelled and stored before sample preparation and analysis. The samples were collected from different depths according to the characteristics of the sample locations presented in Table 1.

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Table 1. *Characteristics of the sample locations*

Sample No.	Depth (cm)	Sample location (global position)		Other characteristics
		N:	W:	
1	5 20	45°56′23.14″	28^{0}06′54.91″	Oancea commune, Galati county, close to a cultivated zone, at 0.01 km from the Prut River
2	5 15	45°44′36. 3″	28^{0}04′37.73″	Foltesti commune, Galati county, near a stable, and a cultivated area, at 5.99 km from the Prut River and at 35 km from the industrial plant
3	5 30	44°5′56.5″	27°25′48.3″	Bugeac village, Ostrov commune, South of Romania (Dobruja region), Constanta county, unpolluted site, far from traffic
4	5 30	45°25′50.6″	27°55′24.3″	Sendreni commune, Galati county, near a cultivated zone, at 1 km from the steel complex of Galati
5	5 30	45°24′31.3″	27°58′36.3″	Movileni village, Sendreni commune, near the South gate of the steel complex of Galati
6	5 30	45°27′19.4″	27°58′22.5″	Smardan commune, near the North gate of the steel complex of Galati
7	5 30	46°01′27.90″	27°43′45.55″	Adam village, Draguseni commune, Galati county, unpolluted site

2.2. Sample preparation

For the XRF analysis, the soil samples were dried, the foreign objects were removed, and then the samples were crushed into a fine powder using a mortar and pestle. The soil was encapsulated in specially made capsules to be used for the quantitative and qualitative determination of 20-22 elements.

For GC-ECD and GC-MS determination, 1 g of soil sample is used, treated consequently with internal standard solutions and a mixture of hexane-acetone. This procedure is named Soxlet method [2].

2.3. Instrumentation

The XRF determinations were performed using a Niton XLT analyzer from 700 series. It is a portable device that offers reliable results, at low costs, in a short time, according to a non-destructive method, and a very simple sample preparation. These analyses were done at the European Center of Excellence, from the Faculty of Sciences, "Dunarea de Jos" University of Galati, Romania.

GC is an established and well accepted analytical method for trace organic compounds [3].

The GC-ECD and GC-MS were employed for the determination of pesticides and PAHs.

The determination of pesticides is accomplished using an Agilent 6890 gas chromatograph equipped with ^{63}Ni μECD detector and PAHs concentrations were obtained by using an Agilent 6890 gas chromatograph equipped with Agilent 5973 Network mass spectrometer (GC/MS 6890/5973).

These analyses were performed at Institute of Geology and Seismology, Laboratory of Geochemistry (GEOLAB) from Chisinau, Moldova.

3. Results and discussion

3.1. XRF results

For the XRF results, the soil sample is measured for five times, only the average value is in Table 2. The results indicate that the elements such as As, Cr and Ni are in all the cases above the normal values. For Pb, the normal values were exceeded at site 3, 5 and 6. In the case of sites 5 and 6, the values are indicating an anthropic pollution.

Zinc is an element that did not exceed in any place the normal values established by the Romanian legislation [4].

3.2. GC-ECD and GC-MS results

The concentrations of the organic pollutants are presented in Table 3. Phenanthrene in this case is representing 94.69%, from the PAHs concentration. In the case of pesticides b_BHC is representing 47% from the entire concentration. According to the Romanian legal norms [4] under normal conditions the total amount of PAHs should not exceed 0.1 mg kg^{-1}.

In this case the total amount is 3.831 mg kg^{-1}, value found between the normal values and the alert threshold for sensitive areas.

Table 2. *Heavy metals concentration obtained by the XRF technique*

Sample No.	As (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})	Ni (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})
1 /5 cm	9.9	90.09	29.7	60.71	17.22	73.11
1/20 cm	10.51	83.4	26.63	51.25	15.3	65.38
2/5 cm	5.99	57.1	19.34	38.05	15.21	52.29
2/ 15 cm	8.01	55.13	17.04	41.7	12.16	42.58
3/5 cm	9.62	102.34	22.66	59.11	20.67	68.546
3/30 cm	11.06	124.72	n.d.	58.15	23.82	82.03
4/5 cm	9.5	83.728	23.68	51.64	18.9	51.404
4/30 cm	10.29	73.01	27.47	63.86	16.51	46.397
5/5 cm	10.3	52.906	29.89	65.55	30.37	71.484
5/30 cm	10.21	71.43	34.2	63.73	29.74	77.168
6/5 cm	9.813	99.194	25.13	62.67	25.63	61.62
6/30 cm	10.55	83.752	24.82	59.45	21.4	61.19
7/5 cm	7.19	69.322	18.38	44.71	11.02	34.072
7/30 cm	6.24	96.155	n.d.	36	11.15	19.51

Table 3. *Organic compounds concentration obtained by GC and GC-MS technique*

Sample No.	**PAHs** (mg kg^{-1})				**Pesticides** (mg kg^{-1})			
	Naphtalene	Fluorene	Phenanthrene	Antracene	a_BHC	b_BHC	Heptachlor	Trifluralin
1 /5 cm	0.001	0.007	0.027	<0.001	<0.002	<0.002	<0.003	<0.002
1/20 cm	0.002	0.021	0.045	0.002	<0.002	<0.002	<0.003	<0.002
2/5 cm	<0.004	0.033	1.345	0.194	0.027	0.019	0.108	0.231
2/ 15 cm	<0.004	0.023	0.876	0.125	<0.002	<0.002	<0.003	<0.002
3/5 cm	0.001	0.007	0.067	0.004	<0.002	<0.002	0.346	<0.002
3/30 cm	<0.004	<0.001	0.029	<0.001	<0.002	<0.002	<0.003	<0.002
4/5 cm	<0.004	<0.001	0.006	<0.001	2.159	4.273	<0.003	0.152
4/30 cm	<0.004	<0.001	<0.001	<0.001	0.065	0.053	0.260	<0.002
5/5 cm	0.001	0.006	<0.001	0.043	<0.002	<0.002	0.524	<0.002
5/30 cm	<0.004	0.010	<0.001	0.038	0.062	<0.002	<0.003	<0.002
6/5 cm	0.010	0.008	0.008	0.010	0.022	<0.002	<0.003	<0.002
6/30 cm	<0.004	<0.001	<0.001	0.004	0.373	0.203	0.333	<0.002
7/5 cm	0.007	0.006	0.044	<0.001	0.074	<0.002	<0.003	<0.002
7/30 cm	<0.004	<0.001	<0.001	<0.001	<0.002	<0.002	<0.003	<0.002

4. Conclusions

The highest concentration of pesticides is found at location 4, which is an agricultural area.

The highest concentration of PAH is found for location 2, which is close to a stable and to an agricultural area.

The high amount of PAHs can be explained by the waste incineration and also by its closeness to a main industrial point.

The heavy metal concentration is maximum at site 3 and minimum at site 2. Site 3 exhibits the highest amounts of Cr.

This metal is also found in pesticides and this can be the most probable source, because the site is close to a cultivated area.

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