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HEAVY METAL CONTAMINATION ASSESSMENT AND ITS ENVIRONMENTAL IMPACT IN THE AREA OF RURAL WASTE DISPOSALS IN CLUJ COUNTY, ROMANIA

G. POPIȚA[1,✉], I. VARGA[1], C. MODOI[1], R. HAȚEGAN[1], A. POPOVICI[2]

[1]Babes Bolyai University, Faculty of Environmental Science, Department of Environmental Science, 30 Fântânele Street, 400294, Cluj-Napoca, ROMANIA
[✉]E-mail: gabi.popita@yahoo.com
[2]Regional Environmental Protection Agency, 99 Dorobanților Street, 400609, Cluj-Napoca, ROMANIA

This study aims at to investigate the environmental impact caused by heavy metal contamination from the waste disposal facilities in rural areas and depending on soil pollution, the possible future uses of these lands. In addition, we have studied the heavy metal contamination of the surface waters from the vicinity of these disposal facilities. The heavy metals influence was investigated by analyzing various water and soil samples collected from two county areas where more rural disposal facilities were functioned. ZeEnit 700 atomic absorption spectrometer was used for the analysis of metals and the collected soil samples were mineralized according to ISO 11466, by extraction with aqua regia (3 parts HCl: 1 part HNO_3). The evaluation of the soil analysis results from the area No. 1 proves that there is no potential impact, because the studied metals concentrations are below the alert threshold. Water analysis results from area No. 1, shows a quality class V for lead and nickel, which indicate a high pollution originating from these metals. In the area No. 2, lead has exceeded the intervention thresholds for sensitive and less sensitive use of land and it is considered that there is an environmental impact on the soil. Regarding the water quality, it can be concluded that the area No. 2 exhibits the greatest pollution impact stemming from heavy metals.

Keywords: heavy metals, soil pollution, water pollution, waste.

Introduction

Recently, in Romania, the closure of legally non-complying municipal landfills is on increase. This action was implemented also in the rural areas, with the final objective: land rehabilitation (July 16, 2009) by cleaning up and rehabilitation/re-entry into the natural ecocycles or by closure.

In the past, approximately 80 storage facilities were in operation in Cluj County and the most of them were declared to be closed, cleaned and/or rehabilitated.

For further utilization/use of these waste disposal sites the assessment of the soil pollution and underground waters were taken into consideration depending on the use and classification of the land (sensitive or less sensitive use) and the contamination levels/classification under the threshold regarding the type of use.

In terms of the legislation, the sensitive use of land is considered in case of residential, recreational, agricultural utilization/purposes, as protected areas or sanitary areas with restriction regime, while less sensitive use of land includes all industrial and commercial uses.

The heavy metals content was investigated by analyzing various water and soil samples collected from two county areas *(Fig. 1)*, where several rural disposal facilities were functioned:

- *area No. 1* is situated in the NW of the Cluj County with six waste disposal facilities*:* Tog site from Turea village, Cariera site from Corneşti village and four waste storage facilities in: Ticu village, Ticu Colonie village, Arghişu village and Dâncu village *(Fig. 2)*;
- *area No. 2* is situated in the E of the Cluj County with four waste disposal facilities: Sojba site from Mociu village, Sub Deal site from Chesău village, Ciscut site from Aruncuta village and Dâmburile site from Dâmburile village *(Fig. 3)*.

The soil samples were taken from the surface of the waste disposal facilities and the surface water samples were taken from the immediate vicinity of these facilities, because the most of them were located at the sides of different streams.

Figure 1: The location of the sampling points in the areas No. 1 and No. 2, Cluj County, Romania

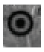
 – drinking water sampling point,  – surface water sampling points,  – soil sampling points

Figure 2: Waste disposal facility in rural area No. 1

Figure 3: Waste disposal facility in rural area No. 2

Materials and Methods

The soil is a rich and fragile ecosystem which can be found on the surface of the Earth crust with a thickness of about 1.5 m. It is a dynamic layer in which several complex physical, chemical and biological processes are taken place continuously. The soil pollutions stems from human activity that causes an imbalance in the normal functioning of the soil as an element of the environment. It is manifested in physical, chemical or biological degradation.

The analyses that can be carried out to assess the soil pollution are as follows:

- Physical methods: resistance of penetration, conductivity, etc.
- Chemical methods: pH, humus content, total N, mobile P, mobile K, soluble salts, heavy metals, pesticides, etc. [1].

The soil sampling was carried out in plastic bags with a plastic spatula. Before sampling, the vegetal top layer was removed on an area of 15x20 cm. The samples were taken from a depth of 10–15 cm.

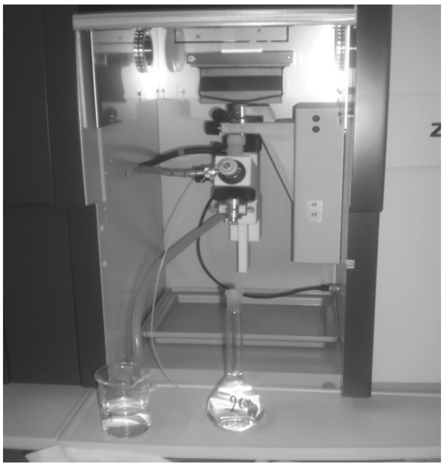


Figure 4: Atomic absorption spectrometer ZeEnit 700

In order to determine the concentration of heavy metals, the atomic absorption spectrometer ZeEnit 700. was used *(Fig. 4)*. The collected soil samples were mineralized according to ISO 11466, by extraction with aqua regia (3 parts HCl : 1 part HNO_3). Water samples collected for heavy metal analysis were acidified with HNO_3 65%, at site, to a pH of about 2-3 to prevent the precipitation of the heavy metal ions and the retention of these on the vessel wall.

Results and Discussions

Soil samples

The metals from the soil can be strongly bounded or complexed. The sum of total forms represents the total metal content in the soil. The forms under which the metal can be founded depends on the nature of the soil, pH and on the presence of the humic matter content [2].

The soil is characterized by the existing heavy metals, which depends on soil type and its composition and by soil contamination with these metals provided by human activity [3].

Table 1: The heavy metals concentration in the soil samples from area No. 1

	mg/kg						
Sample	**Cd**	**Cr**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**
Ss1	0.043	0	7.78	1340.60	6.08	21.80*	22.64
Ss2	0.073	4.73	6.93	1477.27	7.58	20.47*	33.49
Ss3	0.089	4.73	7.85	1422.27	24.82*	19.80	37.79
Ss4	0.093	13.79	8.83	1456.93	24.92*	22.80*	29.29
Ss5	0.080	15.26	11.30	1436.93	24.52*	24.13*	39.82
Ss6	0.086	12.56	9.26	1381.93	14.20	21.80*	28.42
Ss7	0.090	5.11	3.36	1147.93	4.57	11.80	9.13
Ss8	0.006	10.61	12.38	1296.27	20.33*	35.80*	40.49
Note							
NV	**1**	**30**	**20**	**-**	**20**	**20**	**100**
AT	**3**	**100**	**100**	**-**	**75**	**50**	**300**
IT	**5**	**300**	**200**	**-**	**150**	**100**	**600**

Ss – soil sample, NV – normal value, AT – alert threshold,
IT – intervention threshold, according to the Decree No 756 of the Government of November 3 of 1997,
*the heavy metals concentrations that are higher than NV

The household waste contains heavy metals, especially stemming from: batteries, metal alloys, plastic, paper, cardboard and glass.

In *Table 1* the heavy metals concentrations from the analyzed soil samples are given from the area No. 1.

For the area No. 1, samples were taken from two sites from the waste disposals: Ticu Colonie village and Dâncu village *(Fig. 5)*.

The soil samples were taken from all the waste disposal sites including surface, from both areas, and the sampling points were fixed as shown in *Fig. 6.*

For the area No. 2, samples were taken from two sites from the waste disposals: Sojba site from Mociu village, Sub Deal site from Chesău village, Ciscut site from Aruncuta village and Dâmburile site from Dâmburile village *(Fig. 7).*

Figure 5: Selection of the soil sampling points in area No. 1
– soil sample point

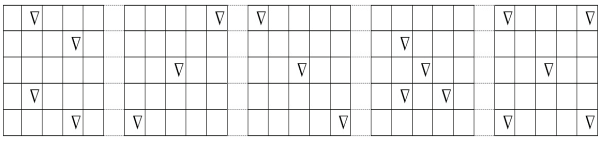


Figure 6: Selection of the sampling points

Figure 7: Selection of the soil sampling points in area No. 2
 – soil sample points

After sampling, the samples were good homogenized and the final soil samples obtained were numbered from Ss_1 to Ss_8.

For area No. 1 the homogenous soil samples belongs to each waste disposal as follows: Ss_1 – waste disposal Ticu Colonie; Ss_2 – waste disposal Ticu Colonie; Ss_3 – waste disposal Ticu sat; Ss_4 – waste disposal Dâncu; Ss_5 – waste disposal Dâncu; Ss_6 – waste disposal Arghisu; Ss_7 – waste disposal Cornesti; Ss_8 – waste disposal Turea.

For area No. 2 the homogenous soil samples belongs to each waste disposal as follows: Ss_1 – waste disposal Sojba, Mociu; Ss_2 – waste disposal Sojba, Mociu; Ss_3 – waste disposal Sub Deal, Mociu; Ss_4 – waste disposal Sub Deal, Mociu; Ss_5 – waste disposal Ciscut, Aruncuta; Ss_6 – waste disposal Ciscut, Aruncuta; Ss_7 – waste disposal Dâmburile; Ss_8 – waste disposal Dâmburile.

The disposed waste, from both areas, comes from the village houses: plastic, paper, glass, hazardous waste, metals, WEEE, construction waste, demolition waste, etc, but unfortunately there is no inventory on the quantities of the disposed waste.

Fig. 8 shows the cumulative results of the heavy metals concentrations from the soil samples from the area No. 1.

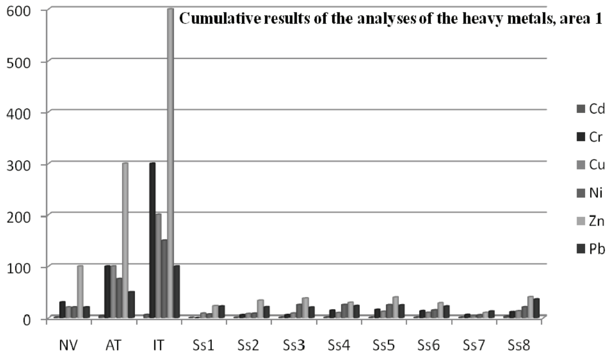


Figure 8: Cumulative results of the heavy metals concentrations in the area No. 1

The heavy metals concentrations in the soil of the area No. 1, are as follows:

- Cd, Zn, Fe, Cu, Cr – the samples concentrations are lower than the normal values
- Ni – the concentrations of the samples no. 3, 4, 5 and 8 are higher than the normal values
- Pb – the concentrations of the samples no. 1, 2, 4, 5, 6 and 8 are higher than the normal values

The results proved that in the soil from the area No. 1, the lead and nickel exhibit the highest concentrations, more than the normal values specified in the national legislation but those are under the alert threshold, compared with cadmium, copper, zinc and chromium, whose concentrations are below the normal values.

In *Table 2* the heavy metals concentrations are given from the analyzed soil samples from area No. 2.

Fig. 9 shows the cumulative results of the heavy metals concentrations from the soil samples taken from area No. 2.

The heavy metals concentrations in the soil of the area No. 2, are as follows:

- Cu – the concentration of the sample No. 4 is higher than the normal values, but under the alert threshold
- Cd, Zn, Fe, Cr – the concentrations of the samples are below than the normal values
- Ni – the concentrations of the sample No 1 is higher than the normal values but under the alert threshold
- Pb – the concentrations of the samples No 1, 3, 5, 6, 7 and 8 are higher than the normal values; the concentration of the sample No. 4 is higher than the alert threshold and the concentration of the sample No. 2 is higher than the intervention threshold.

In the soil of area No. 2, lead has exceeded the intervention threshold set forth by the legislation and nickel and copper have exceeded the normal values comparing with cadmium, zinc, iron and chromium whose concentrations are below the normal values.

Table 2: The heavy metals concentration in the soil samples from area No. 2

Sample	mg/kg						
	Cd	**Cr**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**
Ss1	0.006	16.83	16.67	4553.33	20.93*	40.33**	31.13
Ss2	0.006	12.82	13.15	4493.33	18.40	154.67^{+}	22.98
Ss3	0.006	14.93	13.38	4436.67	18.70	28.00**	19.64
Ss4	0.032	21.94	29.07*	4253.33	16.08	60.00^{+}	38.37
Ss5	0.006	8.11	15.17	3923.33	17.06	39.00**	27.13
Ss6	0.006	11.68	14.54	3823.33	15.55	41.67**	29.87
Ss7	0.006	6.97	14.30	3780.00	17.35	34.33**	19.47
Ss8	0.006	6.94	14.10	3563.33	17.81	35.33**	19.91
Note							
NV	**1**	**30**	**20**	**-**	**20**	**20**	**100**
AT	**3**	**100**	**100**	**-**	**75**	**50**	**300**
IT	**5**	**300**	**200**	**-**	**150**	**100**	**600**

Ss – soil sample, NV – normal value, AT – alert threshold,
IT – intervention threshold, according to the Decree No 756 of the Government of November 3 of 1997,
*the heavy metals concentrations that are higher than NV
**the heavy metals concentrations that are higher than AT
$^{+}$the heavy metals concentrations that are higher than IT

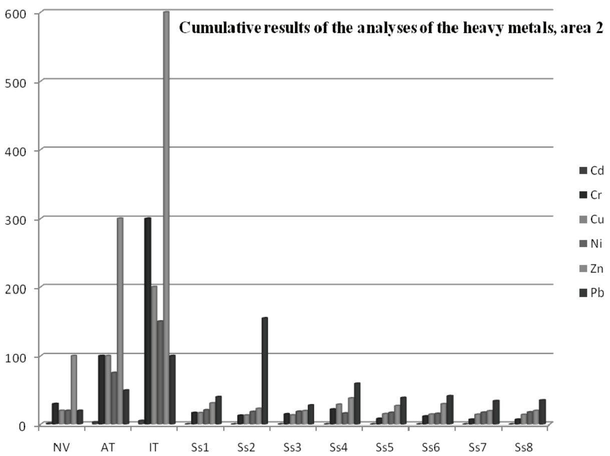


Figure 9: Cumulative results of the heavy metals concentrations in the area No 2

Water samples

The following physical and chemical parameters: pH, conductivity, salinity, total dissolved solids, redox potential and temperature were determined using WTW Multiparameter InoLab 720 series at site *(Fig. 10)*.

Figure 10: The WTW Multiparameter InoLab 720 series

According to the results for TDS, high conductivity and salinity, indicates a high load of dissolved salts. The national law doesn't provide normative figures for the conductivity, TDS and salinity in wastewater and natural waters, although an increase in the growth of the TDS level may indicate higher water pollution.

The main sources of the water pollution with heavy metals are as follows:

- Geological sources (natural), mining and metal processing;
- Industrial use of the heavy metal salts (chromium from tanneries, manganese from paints, dyes, batteries, fertilizers, herbicides, cadmium from electroplating process, Ni-Cd/Pb batteries, pigments, mercury from fungicides, the salt water electrolysis, lead from the ore processing);
- The infiltration from the waste disposal sites [4].

Among the analyzed metals, the most frequently identified water pollutants are as follows: iron, cadmium and mercury. The heavy metals are toxic in different valence states, except mercury which is toxic in the elemental form [5].

Regarding the classification of the land use, the transfer of heavy metal pollution was studied into the surface water. It can be given that the water quality classes are as follows: I – very good, II – good, III – moderate, IV – weak, V – bad, according to the Decree No 161 of the Government of February 16 of 2006. It is used for the assessment and classification of the surface waters to determine the ecological status of the water.

From the streams of the area No. 1 samples were taken and analyzed at the follow points: Sw_1, Sw_2, Sw_3, Sw_4 and Sw_5 *(Fig. 11)*.

Table 3 presents the metals concentrations in the surface water from the streams in the area No. 1.

Table 4 presents the water quality classes according to the Decree No 161 of the Government of February 16 of 2006.

Table 5 presents the clasification of the streams from the area No. 1 regarding the ecological status, from the point of view of the metal contaminations.

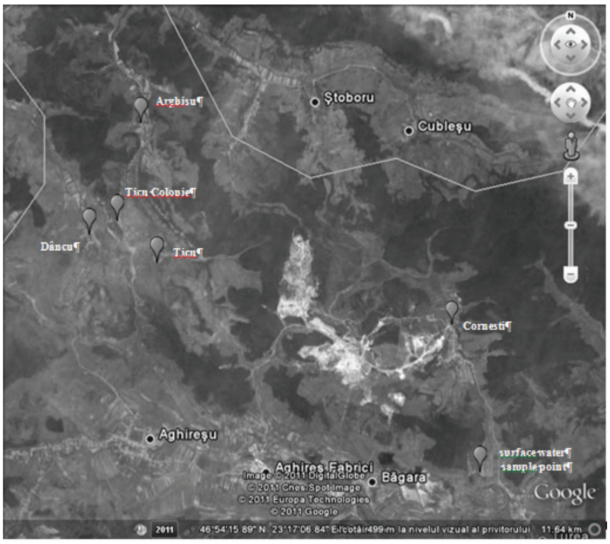


Figure 11: Selection of the surface water sampling points in the area No. 1

 – surface water sample points

Table 3: The metals concentration in the surface water from the streams in the area No. 1

Sample	**Cd µg/l**	**Cr µg/l**	**Cu µg/l**	**Fe mg/l**	**Ni µg/l**	**Zn µg/l**	**Pb µg/l**
Sw_1	0.03	110.0	35.5	0.1949	307.5	21.7	96.0
Sw_2	0.03	116.0	26.0	0.1449	311.6	90.5	108.0
Sw_3	0.03	112.0	49.8	0.1278	317.2	0	103.0
Sw_4	0.05	0	44.6	0.2231	317.9	0	109.0
Sw_5	0.03	0	50.1	0.1872	314.7	0	98.0

Sw– water sample

Table 4: The water quality classes according to the Decree No. 161/2006

	Quality class (conc. µg/l)				
metal	Class I very good	Class II good	Class III moderate	Class IV weak	Class V bad
Cr	25	50	100	250	>250
Cu	20	30	50	100	>100
Zn	100	200	500	1000	>1000
Pb	5	10	25	50	>50
Cd	0.5	1	2	5	>5
Ni	10	25	50	100	>100
	mg/l				
Fe	0.3	0.5	1	2	>2

Table 5: Clasification of the streams from the area No. 1 regarding the ecological status, according to the the analyzed metal content, Sw_1 (*), Sw_2 (+), Sw_3 (◊), Sw_4 (○), Sw_5 (□)

No.	Metal	Class I very good	Class II good	Class III moderate	Class IV weak	Class V bad
1	Cd	*+◊○□				
2	Cr	○□			*+◊	
3	Cu		+	*◊○	□	
4	Fe	*+◊○□				
5	Ni					*+◊○□
6	Zn	*+◊○□				
7	Pb					*+◊○□

Water analysis results from area No. 1, shows a quality class V for nickel and lead, which indicate a high pollution of these metals, and a quality class IV for chromium. For cadmium, iron and zinc the results support a quality class I.

From the streams of the area No. 2 were taken and analyzed samples from the following points: Sw_1 and Sw_2 *(Fig. 12)*.

Table 6 presents the metals concentration in the surface water from the streams in the area No. 2.

Table 7 presents the clasification of the streams from the area No. 2 regarding the ecological status, from the point of view of the analyzed metals.

For the area No. 2, the water analysis results show a V quality classes for lead and nickel regarding the pollution. For cadmium, copper, iron and zinc, the results support a quality class I.

Also samples were taken from the groundwater from wells situated in area No 2, in the villages, near to the waste disposal facilities. The concentration of the heavy metals is presented in the *Table 8*.

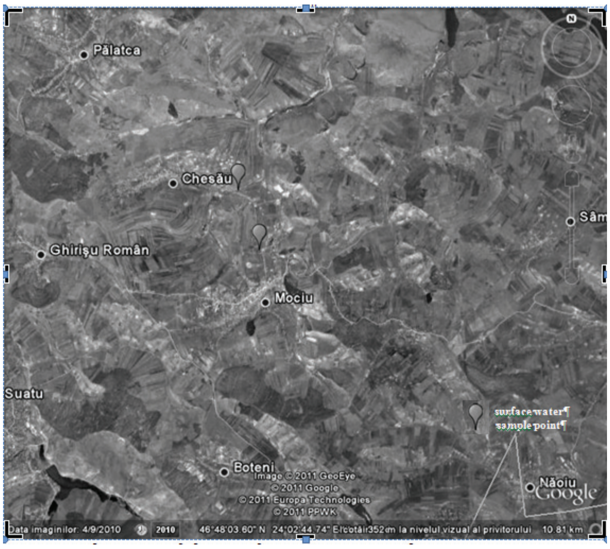


Figure 12: Selection of the surface water sampling points in area No. 2

 – surface water sample points

Table 6: The metal concentrations in the surface water from the streams in the area No. 2

Sample	**Cd µg/l**	**Cr µg/l**	**Cu µg/l**	**Fe mg/l**	**Ni µg/l**	**Zn µg/l**	**Pb µg/l**
Sw_1	0.04	41.7	5.9	0.2000	253.1	30.5	118.0
Sw_2	0.01	31.8	4.6	0.2200	244.5	16.9	116.0

Sw– water sample

Table 7: Classification of the streams from the area No. 2 regarding the ecological status according to the analyzed metal contents, Sw_1 (■), Sw_2 (●)

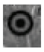
No.	Metal	Class I very good	Class II good	Class III moderate	Class IV weak	Class V bad
1	Cd	■●				
2	Cr		■●			
3	Cu	■●				
4	Fe	■●				
5	Ni					■●
6	Zn	■●				
7	Pb					■●

Table 8: The concentration of the heavy metals from the water of wells, in the area No 2

Sample	**Cd µg/l**	**Cr µg/l**	**Cu µg/l**	**Fe mg/l**	**Ni µg/l**	**Zn µg/l**	**Pb µg/l**
Sdw_1	0.03	34.4	7.0	0.230	244.2	20.6	103.0
Sdw_2	0.02	33.6	6.6	0.190	238.0	22.8	122.0
Sdw_3	0.01	34.5	6.8	0.249	260.3	18.9	116.0

Sdw – drinking water sample

Figure 13: Selection of the drinking water sampling points in the area No. 2

 – drinking water sample points

The analysis show similarities between the heavy metal concentrations of the water samples taken from wells and from the surface water.

Conclusions

The waste disposal facilities in rural areas had been declared to be closed down in 2009, but those failed to be cleaned and rehabilitated. This study was made in order to establish, depending on soil pollution, the possible future utilization/uses of these lands.

The evaluation of the soil analysis results from the area No. 1 proves that there is no potential impact, because the studied metal concentrations are below the alert threshold, however, higher than normal values. However, the ecological measures are necessary to be implemented in order to fit the sensitive use of the land.

In the area No. 2 due to the lead concentration which exceeds the intervention thresholds for sensitive and less sensitive use of land, it is to be noted that there is a significant environmental impact on the soil. According to the Decree No 756 of the Government, when the concentrations of one or more pollutants in soils exceed the intervention threshold, the competent authorities should enforce a risk assessment study and mitigation measures should be done to reduce the concentration of the pollutants in discharges.

Additionally, analyses were made on the surface water from the streams situated near to the waste disposal areas, and for the area No. 2, water samples were taken from wells situated in the villages near to the waste disposal areas.

Water analysis results from area No. 1 and 2 shows a quality class V for nickel and lead, which indicate a high pollution with these metals. Regarding the water quality, it was found, as in the case of soil pollution with heavy metals, that the surface waters, in both areas have exhibited serious impact of heavy metal pollution.

The results of the analyses of the wells in area No. 2, shows that the concentrations of the heavy metals are similar to that of the surface water streams.

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REFERENCES

1. V. CIOBOTARU, A. M. SOCOLESCU: Priorities of the environmental management, Publishing House Meteor Press, 2006 Bucharest
2. C. ROȘU: The basis of the environmental chemistry, theoretical elements and practical applications, Publishing House Casa Cărții de Știință, 2006 Cluj-Napoca
3. C. DRĂGHICI, D. PERNIU: The pollution and the environmental monitoring, Publishing House Universității Transilvania, 2002 Braşov
4. G. BURTICĂ, D. MICU, A. NEGREA, C. ORHA: The pollutants and the environment, Publishing House Politehnica, 2005 Timişoara
5. A. X. LUPEA, A. GHARIBEH BRANIC, A. ARDELEAN, D. ARDELEAN: The basis of the environmental chemistry, Publishing House Didactică şi Pedagogică, 2008 Bucureşti