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ABSTRACT

THE MONITORING OF THE PRIORITY AND PRIORITY HAZARDOUS METALS USING MODERN SPECTRAL TECHNIQUES IN THE MANAGEMENT OF WASTE

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I. OBJECTIVES OF THE THESIS AND ORIGINAL CONTRIBUTIONS

1.1. General frame

Knowing the impact of the storage of waste containing priority and priority hazardous substances over the environment which are unstable or capable of bioaccumulation is of great importance. These kinds of waste may contain organic compounds and priority or priority hazardous metals which often are released into the environment in gaseous or liquid phase as an issue of waste biodegradation. The key for understanding the potential threats to the environment of waste materials is the processes of degradation they are involved in. Beside the industrial waste there are huge quantities of municipal waste selectively collected or not, which are safely or unsafely stored, or they are reused or recycled. At a global scale every human being generates 250 kg waste yearly, which implies 2.3 Mtone of waste globaly in a year [1]. The major part of the municipal waste is stored, and a fraction less than 10% is reused or recycled.

Starting from the ’90s the policy of monitoring priority and priority hazardous metals present both in the municipal and industrial waste was introduced in legal norms with regard to the protection of the environment and was also treated in many scientific publications. Some metals are concidered priority waste, such as antimony, arsenic, barium, beryllium, boron, cobalt, chromium, copper, molybdenum, selenium, silver, tellurium, thallium, tin, titanium, uranium, vanadium and zinc. These metals represent a significant pollution risk to the aquatic environment and to humans through the water supplies. Beyond their toxicity, the metals concidered priority hazardous waste (cadmium, lead, mercury and nichel) are persistent in the environment and tend to bioaccumulate.

The classification of the metals in the two categories corresponds with the 2000/60/CE and 2008/105/CE Directives which support the policy framework for water resources [3, 4].

1.2. General and specific objectives

General objectives:

1. The monitoring of priority and priority hazardous metals using modern spectral techniques based on atomic emission spectroscopy and inductively coupled plasma mass spectrometry (ICP-AES and ICP-MS) in the process of integrated management of incinerated medical waste and in the study of the impact over the environment (water and air) of the waste stored in safe and unsafe municipal landfills. Both spectral methods are standardized for simultaneous multielemental analyses of water.

2. Validation of a modern method applied for the quantification and monitoring of metals considered priority and priority hazardous waste present in soils contaminated by industry and waste landfills using high-resolution continuous-source atomic absorption spectroscopy (HR-CS FAAS). This spectral method is recently commercially available. All the standardized methods based on atomic absorption use the low-resolution line-source atomic absorption spectroscopy (LR-LS AAS) characterized with low processing speed in the sequential system.

Specific objectives:

1. The current state of the management of waste in the European Union and Romania, and the stage of the implamantation of the integrated management of waste in Romania, focalizing on the 6 NV Region.
2. Evaluation of the material and chemical composition of waste and the stage of technological development with respect to the reuse and recycling of waste as secondary raw materials or as energy sources.
3. Monitoring of the metals categorized as priority (As, Co, Cr, Cu, Sb, Tl, V) and priority hazardous (Cd, Hg, Ni, Pb) waste present in the ash resulted from the incineration of hazardous medical waste processed in a Hoval Multizon type installation in Cluj-Napoca, using the ICP-MS analytical method.
4. Environmental contamination assessment of the soil and the air with metals categorized as priority and priority hazardous waste as a result of the incineration process by comparing the experimental results with the reference values given by the legislation in the field.
5. Environmental contamination assessment of the soil and the air caused by the released leachate resulted from the unsafe storage of solid municipal waste (MSW) at Pata Rât.
6. Comparative evaluation of the contamination risk of the soil with metals categorized as priority and priority hazardous waste (Cd, Cr, Cu, Ni, Pb, Zn) from the MSW stored in unsafe landfills in the 6 N-V Region. There were considered the following landfills being in post-closing monitoring phase: Pata Rât - Cluj-Napoca, Urbana - Bistriţa, Câmpia-Turzii, Dej, Gherla.
7. Evaluation of the contamination risk of the soil with metals (Cd, Cr, Cu, Ni, Pb, Zn) categorized as priority and priority hazardous waste present in the waste stored in some industrial landfills from the 6 N-V Region (Cesom - Dej, Someş - Dej, HCH -

Turda, Uzina Electrică - Zalău, Iaifo - Zalău, Silcotub - Zalău, Ario - Bistriţa, Dan Steel - Beclean).

8. Contamination risk comparison of the soil caused by solid municipal waste and by waste stored in industrial landfills considered in the study.
9. Contamination risk assessment of the water caused by the leachate of used battery waste and electrical and electronic equipment waste (WEEE).
10. Interpretation of results by multivariate statistical methods (Principal Component Analysis PCA and Cluster Analysis CA).
11. Validation of a new analytical method in the quantification of priority metals (Ag, Co, Cr, Cu, Zn) and priority hazardous metals (Cd, Ni şi Pb) from soil by high-resolution continuous-source atomic absorption spectroscopy (HR-CS FAAS) in fast sequential system.

1.3. The novelty and the contribution in the scientific field

Data from literature revealed the lack of complete informations about the nature and contribution of waste stored in safe and unsafe landfills, and their management on the aspect of polluting the soil and water in Romania with metals considered priority and priority hazardous waste. There is also a lack of systematic studies with regard to the concentration variation of these metals in the different layers of the depositied waste. These informations would provide a thorough knowledge about the fate of the metals in the environment.

The originality of the thesis consists in providing for the first time in Romania a complex and thorough study about the problem and monitoring of the priority and priority hazardous metal waste considering the different types of deposits and waste as potential soil and water contamination sources. Thus, the results obtained by carrying the PhD programme into execution enabled to support a well-set management of the different types of waste, and to evaluate the contaminaiton risk taking into account the present conditions.

1.3.1. Novelty items

The novelty items of the thesis which come from the performed research are:

- ⇨ Identification and quantification of the environmental impact caused by the priority and priority hazardous metal waste deriving from nonconforming municipal waste landfills and from medical waste incinerators;

- ⇨ Identification and quantification of the environmental impact caused by the priority and priority hazardous metal waste deriving from industrial waste landfills in comparison with municipal waste landfills;
- ⇨ Elaboration of economically and ecologically standing measures for the MSW management system;
- ⇨ Contamination risk assessment of soil with priority and priority hazardous metal waste (issuing from the municipal and industrial waste landfills and incineration ash) by modern methods which are based on the determination of contamination indices: enrichment factor, contamination factor and contamination degree in agreement with the Hakanson methodology [18];
- ⇨ Advanced interpretation of the analytical results obtained by the monitoring study of some municipal and industrial waste landfills using multivariate statistical methods (PCA şi CA);
- ⇨ Validation of a novel analytical method for the determination and monitoring of 8 elements classified as priority and priority hazardous metal waste from contaminated soils applying the HR-CS FAAS instrumental concept appeared recently on the market as an alternative to the standardized methods based on inductively coupled plasma atomic emission spectroscopy (ICP-AES) and low-resolution line-source flame atomic absorption spectroscopy (LR-LS FAAS).

1.3.2. Original contributions

Original contributions of the thesis carried out by research are the followings:

1. **Devise of a complex monitoring and information supplying system under the terms of environmental pollution with priority and priority hazardous metal waste** due to the incineration ash and municipal and industrial waste landfills, using the contamination indices methodology which enabled to set a prioritization of the contaminants and a classification of waste and landfills with the highest contamination capabilities, especially in regard to the soil
2. **Identification by performing the advanced method of Principal Component Analysis (PCA) of the sources of priority and priority hazardous contaminants, as well as their proportion in the municipal waste leachate and in the composition of the soil in the surroundings of the landfills.** The PCA enabled **identifying the chemical indicators of quality which have the highest influence over the leachate and soil contamination in the surroundings of landfills.**

3. Grouping of the chemical parameters and the studied landfills by carrying out the Cluster Analysis according to the contaminants origin from either common or different sources of waste.
4. **Extending the applicability of the new instrumental concept based on the high-resolution continuous-source flame atomic absorption spectroscopy (HR-CS FAAS) to the waste management field** as a monitoring and determination method for priority and priority hazardous metal waste in soil. The originality of this study was ascertained by the lack of published data in the literature with regard to the validation of analytical applicability of HR-CS FAAS in the foregoing field. This method excels in rapidity, multielemntal capability, easy handling for optimization and for overcoming the spectral interferences.

The results of the research presented in this thesis disseminated as follows: 5 articles published in ISI rated journals summing 6.422 impact factor, 16 articles published in BDI journals, 4 studies presented orally („Relaţia Mediu & Agricultură & Industrie: Conflict şi Sinergie”, "R"- Regenerare, Reabilitare şi Restaurare a Solului- de la Concept la Realizare, USAMV Cluj-Napoca, "Managementul deşeurilor municipale - O mare responsabilitate", Cluj-Napoca, Baia-Mare, "Gestionarea deseurilor menajere-provocari şi soluţii", Cluj-Napoca) and 5 studies presented as posters at national and international conferences in Romania and Slovacia.

II. STAGE OF REGULATIONS AND POLICIES OF INTEGRATED WASTE MANAGEMENT IN EUROPE AND ROMANIA

For about 20 years the European Union builds its environmental policy around the sustainable development concept. Through the problem of waste sustainable development primarily means the integrated management of waste encouraging selective collection at the source and especially their revaluation.

In the field of waste management the legislation of the European Union includes several directives, regulations and decisions which have as main objective the reduction of the negative effects caused by the production and management of waste on the environment and health.

The environmental protection policy in Romania is built since the 90s. Compliance with the EU policy on the management of waste started to be ensured since 2000 by suitable development of the legislation. All the principles, priorities, objectives and targets of directives in this field had been taken over and transposed in the Romanian legislation.

The main normative acts in the waste management field effectives in the EU and their corresponsives in Romania are presented in Table 2.2.

There are two important ways of waste management in Romania:

1. Storage – it is a classical method which necessitates major investments in order to work out safety waste landfills which would correspond with the effectual legislation. Recent data showed that the storage continually remains the main option of municipal waste management and that about 80% of functioning municipal landfills in Romania are not conformable, hereby they could be sources of environmental pollution [14].

2. Incineration – it is a modern method which enables the reduction of the waste amount, but there remains the ash which raises notable concern, since it may contain considerable amount of priority and priority hazardous metal waste. Nonetheless this technology is used for all kinds of waste in the European countries, in our country it is used only in the case of industrial and hazardous medical waste. The incineration ash is eliminated mainly in conformable and nonconforming municipal waste landfills and it may be a contamination risk through the leaching of priority and priority hazardous metal waste into the waters [14]. This is the case of the landfill at Pata Rât, where is stored the ash resulted from the incineration of hazardous medical waste at the Hoval Multizon from Cluj-Napoca.

The stage of the implementation of municipal waste management at the level of the year 2010 is presented in Tablel 2.3 [14].

There were visible progresses on the implementation of legistlation for waste management (from 2009 to 2010 there was an increase in the coverage degree of the sanitation services, which grew from 63% to 70%, there were realized and put in operation a number of 27 landfills conformable with the European standards and there were performed 91 facilities for treatment of waste). In 2010 Romania became one among those member states of the EU which have the largest share in the municipal waste storage (99% according CE Eurostat-2012, 95% according ANPM, 2011) [14,31].

The practice of incineration in Romania at first was applied to the medical waste carried out in the furnaces of the hospitals, which – in the best case – eliminated the coarse particles from the combustion gases. The strict regulations forced to equip the incinerators with modern feeding systems, advanced gas purifying devices, energy recovery boilers, controlling, recording and tracking systems of the parameters, operating conditions and concentrations of the pollutants. According with the new legislative criteria, in 2004 it began a multi-staged closing process of the installations unconformable with the requirements of the 2000/76/CE Directive [15] and a development of ecological technologies in the incinerating field.

Tabelul 2.2. The main normative acts in the waste management field effectives in the EU and in Romania implemented after the year 2000

European legislation	**Romanian legislation**	**Content**
The ***2008/98/CE*** Frame Directive on waste [2]	➢ ***The 211/2011*** law on waste management [33]	Establishes the legislative framework for the handling of all types of waste, including hazardous waste, refuse oils and medicals, the need for enhancing their efficiency of recycling and reducing the negative effects of their management.
Commission Decision 2001/118/CE on waste legislation [20]	➢ ***Governmental Decision 856/2002*** on keeping the record of the management of waste and approval of the list of waste, including hazardous waste [34]	Lists of the categories and types of waste which have encryptions according to the activities of generating waste and possibilities to keep their record.
Directive 1999/31/CE on waste disposal [10]	➢ ***Governmental Decision 349/2005*** on waste disposal [11] ➢ ***Decree 757/2004*** Technical normative on waste disposal [12]	Frame for waste disposal in consideration of creating landfills, exploration, monitoring, closing and after closing monitoring of both new and existing landfills managed in environmentally safe and health-protection conditions.
Council Decision 2003/33 on establishing criteria and procedures for the acceptance of waste at landfills [21]	➢ ***Decree 95/2005*** on establishing acceptance criteria and preliminary procedures of acceptance of waste for disposal on landfills and the national list of accepted waste in each kind of landfills. [35]	Criteria for accepting waste in the defferent kinf of landfills.
Directive 2000/76/CE on waste incineration [15]	➢ ***Governmental Decision 128/2002*** on waste incineration [16] ➢ ***Governmental Decision 268/2005*** for modifying and supplement the pentru modificarea şi completarea ***Governmental Decision*** 128/2002 on waste incineration [17] ➢ ***Decree 756/2004*** Technical normative on waste incineration [9]	Regulation of waste incineration and co-incineration activities, and measures for installation controlling and functioning. Time-table of the closing stages of old installations used for medical waste incineration (HG 268)

European legislation	**Romanian legislation**	**Content**
Directive 94/62/CE on packaging and packaging waste [22]	➢ ***Governmental Decision 621/2005*** on privind packaging and packaging waste management [36]	The Directive establishes measures, aims and objectives for limiting the production on packaging waste and the re-use, recycling and other forms of recovery of these waste. The reduction to the minimum of the hazardous metals (Cd, Cr, Hg, Pb) in the composition of packagies is provided, including as a first priority the production of reusable and recoverable packages.
Directive 2006/66/CE on batteries and accumulators and waste batteries and accumulators [23]	➢ ***Governmental Decision 1132/2008*** on batteries and accumulators and waste batteries and accumulators regime [37]	The primary objective of this Directive is to minimise the negative impact of batteries and accumulators and waste batteries and accumulators on the environment, by establishing limiting levels for cadmium, mercury and lead content of batteries and accumulators and setting out aims and objectives for collection, treatment, recycling and elimination of the waste.
Directive 2012/19/CE on waste electrical and electronic equipment (WEEE) [24]	➢ ***Governmental Decision 1037/2010*** on waste electrical and electronic equipment [38]	The Directive stipulates provisions on preventing the production of WEEE, in addition, the re-use, recycling and other forms of recovery of such waste so as to reduce the disposal of waste.
Directive 2011/65/UE on the restriction of the use of certain hazardous substances in electrical and electronic equipment [6]	➢ ***Governmental Decision 992/2005*** on the restriction of the use of certain hazardous substances in electrical and electronic equipment [39]	The Directive introduces restrictions to the Pb, Cd, Hg and Cr (VI) content of electrical and electronic equipments (EEE).

Table 2.3. Data concerning the implementation of municipal waste management in Romania, for the year 2010 [14]

Quantity of municipal waste (tone)	Quantity of valorized municipal waste (tone)	Quantity of stored municipal waste (tone)	Total number of landfills	Number of conformed landfills	Number of non-conformed landfills	Number of transfering or sorting installations	Number of composting installations
5823321	296000	6777280	133	27	106	70	21

III. WASTE, SOURCES OF RECYCLABLE MATERIALS AND POLLUTING

In this chapter it was realized a classification of waste into four main groups by their provenance and by their hazardous quotient based on the content of priority and priority hazardous leachable metals [21,35]. Likewise, there is given a characterization of the waste monitored in the PhD thesis (municipal and assimilable waste, electrical and electronic equipments, waste batteries and accumulators, incineration ash, landfill leachate) by the chemical composition, as recyclable and polluting materials.

The aim in the knowledge of the chemical composition of waste is joined with the proper management which should be applied in order to prevent the risk of pollution of the environment with priority and priority hazardous metal waste. This knowledge is important for the waste recycling point of view, because waste should be collected selectively, if possible, creating different categories by waste material (glass, plastic, wood, metals). If selective collection is impossible the waste should be sorted according to the categories previously named, or in a better way, according to subcategories.

The study of the chemical composition based on metals showed a heterogeneous character of waste. There was also observed an important contribution of the priority and priority hazardous metals to the flux of MSW, WEEE, batteries and accumulators, incineration ash and the leachate generated by the biodegradable part of MSW. Based on these data it can be emphasized the differences in the contamination risk of the environment of the various kinds of waste and of the waste with different content of priority and priority hazardous metals. For exemple, the bottom ash from the incineration process cannot be considered a hazardous waste; instead the fly ash is a hazardous waste. The waste of batteries and accumulators constitutes a higher contamination risk of the environment than the WEEE waste or the plastic materials issuing from them.

The evalution of the data on the waste management presented in literature indicated the development of an integrated management system and technologies based on (i) re-use, (ii) primary, mechanic and chemical (by pyrolysis, thermolysis and hydrolysis) recycling, (iii) energetic valorization by waste incineration, (iv) storage in safe conditions of original and residual waste, the later resulting from recycling or energy coversion.

IV. ENVIRONMENTAL CONTAMINATION RISK OF THE PRIORITY AND PRIORITY HAZARDOUS METAL WASTE

Evaluation of the potential environmental contamination risk of waste may be obtained either by comparing the parametric values of waste with the quality standards of environmental components, or by the use of relative contamination indices for metals present in waste resulted from the processing of different kinds of materials.

In order to evaluate the environmental contamination risk of priority and priority hazardous metals in waste there were developed three methods:

Quality standards method:

✓ For soils (O 756/1997) [120], applied for the results of the incineration ash samples, the soil being from the area of landfills under study.

✓ For surface/underground/waste waters (O 161/2005; L 458/2002; HG 352/2005) [19,121,143], applied for water samples collected from the Zapodie stream and the leachate from Pata Rât landfill.

Relative contamination indices method:

✓ Enrichment factor (EF) [128,129] was applied for the evaluation of the anthropogenic enrichment of the incineration ash with priority and priority hazardous metals. It was calculated as a ratio of the metal concentration related to the concentration of a reference element present in the sample and the concentration of the metal and the reference element present in the geochemical background of the surface rocks [126].

✓ Contamination factor (CF), intoduced by Hakanson [18], is calculated as the ratio of the concentrations of the contaminant in the sample and in the background rock [126] and it was applied to the incineration ash and soil samples;

✓ Contamination degree (CD) [18], is calculated by the summing of the contamination factors and it was applied for the evaluation of the contamination level of the soil in the area of the studied landfills and of the incineration ash, respectively.

The use of the contamination indices previously presented is helpfull in setting up a priority order (hierarchy) of the contaminants and in the classification of the contaminated sites. With the help of this hierarchy the most contaminated sites and the sites characterized with the most elevated contamination risk to the soil and the sediments can be easily distinguished.

Multivariate statistical method:

✓ Principal Component Analysis (PCA). This advanced approach was applied for the evaluation and interpretation of experimental data in order to highlight the origin of the contaminants and the share they have in the description of the variability in composition of the leachate and the soil by the Varimax method.

✓ Cluster Analysis (CA) is a chemometric technique for the classification of the objects of a system in some categories, named as clusters, on their closeness or similarity bases, without a prior assumption.

PCA and CA proved their usefullness in the interpretation of the results of the environmental by highlighting the natural or anthropogenic origin of some contaminants in the environmental samples (soil, water, sediment, ash) [119,244–252].

The statistical evaluation was applied for the leachate of the Pata Rât landfill and for the soil sapmles from the MSW and industrial waste landfills studied in this thesis.This advanced approach of the interpretation of results enabled to obtain suplimentary data concerning the origin of the priority and priority hazardous components of a MSW leachate, and the grouping by Cluster Analysis of the chemical quality indices with the major influence over the chemical composition variability of the leachate, the soil and the landfills.

V. MODERN SPECTRAL TECHNIQUES FOR THE MONITORING OF THE PRIORITY AND PRIORITY HAZARDOUS METALS IN WASTE

The monitoring of the metals in waste present in low concentrations necessitates highly sensitive spectral techniques which enable the determination of metal concentration in the range of $\mu g\ mL^{-1}$ or as low as $ng\ mL^{-1}$.

Thus for the determination of mercury the cold vapour atomic fluorescence spectroscopy (CV-AFS) was used, and for the determination of arsenic the hydride generation-Quartz furnace atomic absorption spectroscopy (HG-QFAAS) was applied, which is described in the references [233,234]. The other metals were determined by modern spectral techniques based on atomic emission spectroscopy, inductively coupled plasma-mass spectrometry (ICP-AES şi ICP-MS), flame atomic absorption spectroscopy (FAAS) and graphite furnace atomic absorption spectroscopy (GFAAS).

A classification of the spectral techniques used in the monitoring of metals in waste is presented in Figure 5.1.

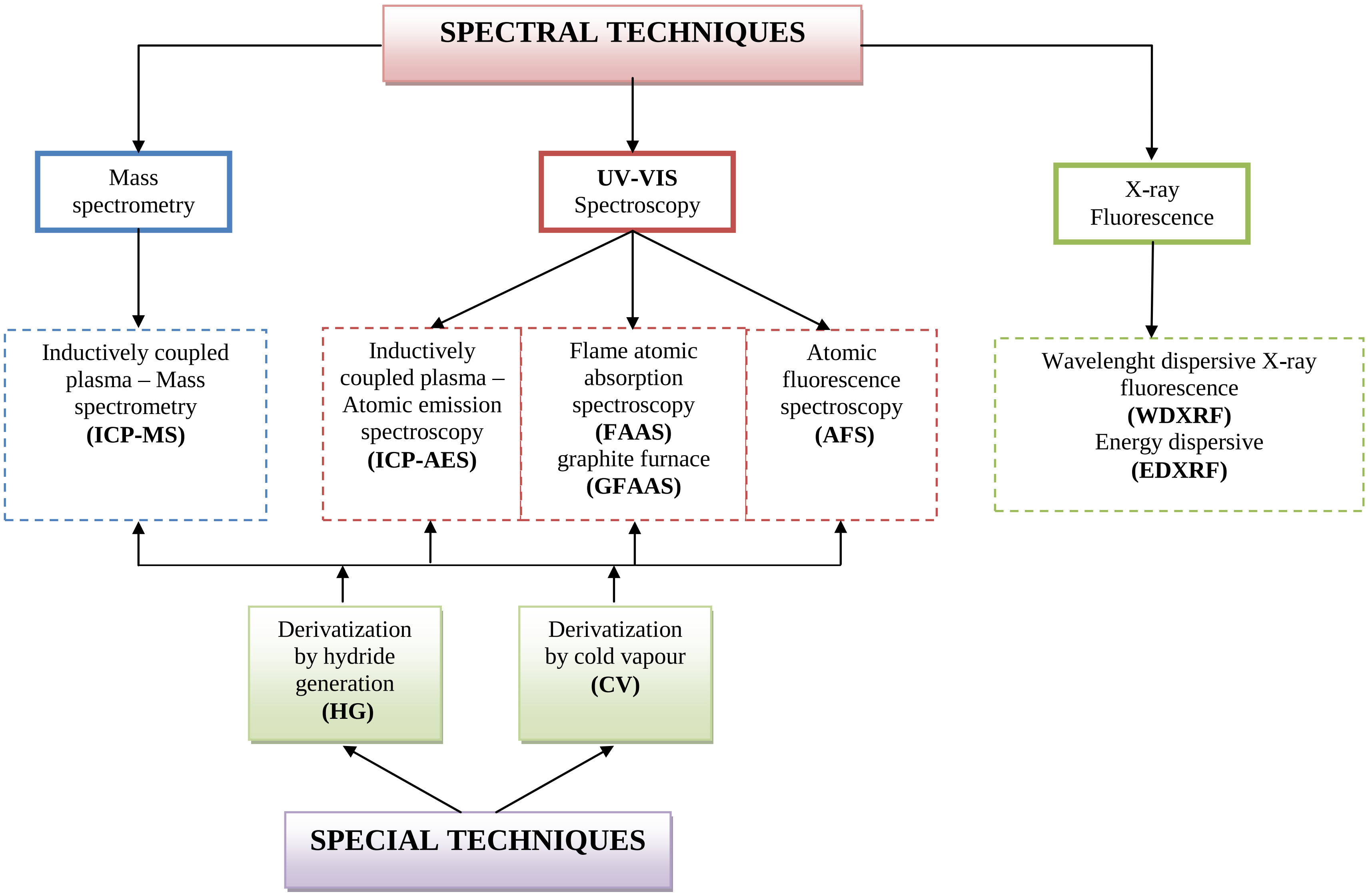


Figure 5.1. Classification of spectral techniques for the monitoring of metals from waste

6.2.1. Description of the waste incineration installation Hoval Multizon GG 24, Cluj-Napoca

Monitoring study of concentration of priority metals (As, Co, Cr, Cu, Sb, Tl, V) and priority hazardous metals (Cd, Hg, Ni, Pb) from the incineration ash of hazardous medical waste was realized at the Hoval Multizon GG 24 (made by Hoval AG, Switzerland) from Cluj-Napoca in the period of 2009–2012. This incineration installation (put in operation in 2005) is the only one in Transylvania and mainly incinerates medical waste from hospitals from Cluj-Napoca and other Transylvanian hospitals.

The schematic diagram of the operating incineration is presented in Figure 6.3.

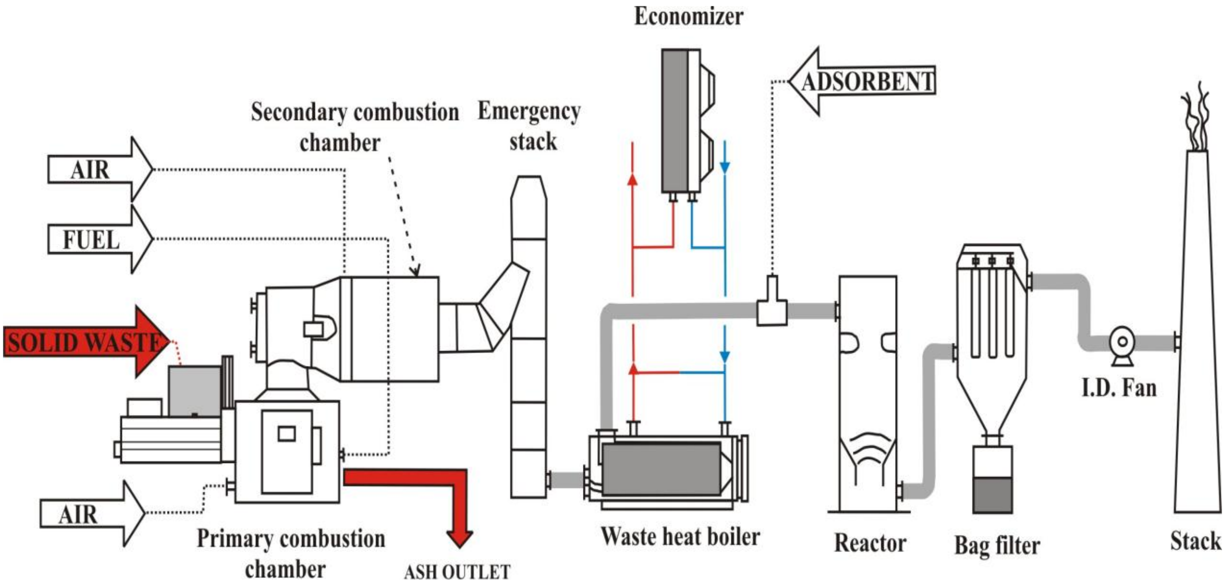


Figure 6.3. Schematic diagram of the Hoval Multizon GG 24 incinerator [200,205]

The incineration technology is characterized by high efficiency in combustion and in recovery of combustion gases heat by vapour generation in five stages [200]:

i. Primary (elementary) combustion at a temperature between 800–900 °C;
ii. Secondary (complete) combustion at a temperature of 1000–1400 °C;
iii. Combustion gas heat recovery by vapour generation;
iv. Chemical purifying of combustion gases with lime;
v. Physical purifying of combustion gases by filtration.

6.2.2. Characteristics and management of incinerated waste and of the residual waste following the incineration process

The waste resulting from the incineration technology consist of the bottom ash stored at the Pata Rât landfill, of the fly ash retained on the filters and of the recycled waste absorbed by the lime.The evolution of the quantities of the incinerated waste by the Hoval Multizon GG 24 installation, by categories, and of the quantity of the bottom ash is presented in Figure 6.4.

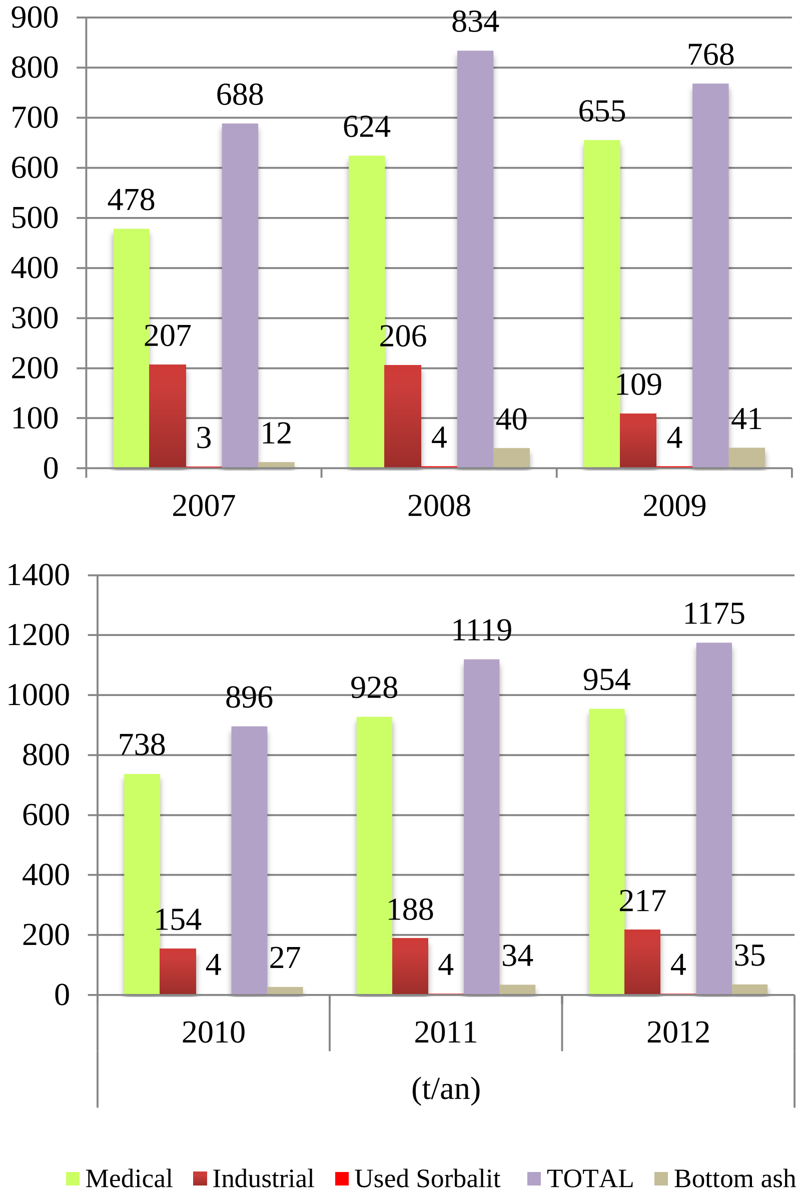


Figure 6.4. Evolution of the quantities of the incinerated waste by the Hoval Multizon GG 24 installation, by categories (2007–2009); reference values [206]; (2010–2012) – personal informations obtained from the owner of the installation

6.4. Evaluation of priority and priority hazardous metal content of the incineration ash from the Hoval Multizon installation, Cluj-Napoca

The priority and priority hazardous metal distribution in the bottom ash, in the fly ash retained by the dust-control equipment for the combustion gases and in the fly ash released in the atmosphere was studied. In order to monitorize the metal content in the bottom ash and in the fly ash retained by the dust-control equipment from the combustion gases there were collected five samples in the year of 2009. In order to evaluate the contamination risk of the fly ash released in the atmosphere through the chimney there were collected two samples in each year in the period of 2007–2012.

An inductively coupled plasma mass spectrometer, Perkin-Elmer SCIEX (ELAN DRC II model, Toronto, Canada) was used for the determination of Cd, Co, Cr, Cu, Ni, Pb, Sb, Mn, V, Tl and As in all kinds of ashes. The CV-AFS Hydra-F, Teledyne (Leeman Instruments, USA) was used for the determinatin of Hg.

The validation of the analyses by ICP-MS and CV-AFS was carried out by the optimization of the operating parameters using CRM materials. The differences between the obtained and certified values were not significants at a confidance level of 95%.

The results obtained are presented in Table 6.9. The same table presents the average concentration of 4 soil samples collected in 2009 in the area of Pata Rât landfill, where municipal waste and bottom ash waste are stored. The values are compared with the normal, alert and intervention levels for sensible soils according to the Decree 756/1997 [120].

Accoring to the data of analyses presented in Tabelul 6.9, the metal concentrations in the bottom ash does not exceed the normal level given for soils. Thus the bottom ash in included in the first group of waste, which means it is not polluted, and it can be stored in a municipal waste landfill without any risk of environmental pollution.

With regard to the soil of the Pata Rât landfill, some metal concentrations of the samples exceeded the normal values in the case of Hg, As, Cu, Ni, and the alert value in the case of Pb, for the sensible soils. In conclusion there can be affirmed that the elevated concentrations of some metals in the soil near Pata Rât cannot be attributed to the bottom ash stored in this landfill.

With regard to the metal content of the fly ash retained by the dust-control equipment, in each sample the values for each studied metal exceeded all the normative values (normal, alert and intervention levels). Thus the fly ash is included in the third group of waste meaning that it is a strongly polluted waste.

Table 6.9. Concentration of elements in the bottom ash, in the fly ash retained by the dust-control equipment for the combustion gases and soil collected from the area of municipal waste disposal from Pata Rât, compared with the reference values for sensible soils [206].

Categories of elements	**Element**	**Bottom ash**		**Fly ash retained by filters**				**Soil collected from Pata Rât**		**Reference values [120] (mg kg^{-1})**		
		Concentration (mg kg^{-1})^{a}	Ratio normal v. for soil	Concentration (mg kg^{-1})^{b}	Ratio normal v. for soil	Ratio alert v. for soil	Ratio intervention v. for soil	Concentration (mg kg^{-1})^{c}	Ratio normal v. for soil	Normal value	Alert limit	Intervention limit
Priority hazardous	**Cd**	0.02	0.02	9.82	9.82	3.27	1.96	0.37	0.37	1	3	5
	Hg	0.08	0.80	2.33	23.30	2.33	1.17	0.8	8.00	0.1	1	2
	Ni	2.80	0.14	2200	110.00	29.33	14.67	20.8	1.04	20	75	150
	Pb	1.18	0.05	2200	88.00	44.00	22.00	61.1	2.44	25	50	100
Priority	**As**	4.8	0.96	18.1	3.62	1.21	0.72	14.8	2.96	5	15	25
	Co	1.25	0.08	200	13.33	6.67	4.00	5.45	0.36	15	30	50
	Cr	2.75	0.09	2400	80.00	24.00	8.00	11.3	0.38	30	100	300
	Cu	2.20	0.11	3500	175.00	35.00	17.50	25.2	1.26	20	100	200
	Sb	4.85	0.97	40.9	8.18	3.27	2.05	4.5	0.90	5	12.5	20
	Tl	0.05	0.50	1.7	17.00	3.40	0.85	0.08	0.80	0.1	0.5	2
	V	3.32	0.07	170	3.40	1.70	0.85	40.8	0.82	50	100	200
	Mn	1.95	0.00	380	0,42	0,25	0,15	870	0,97	900	1500	2500

^{a} – Values determined in bottom ash (n=5)
^{b} – Values determined in fly ash retained in the gas filters (n=5)
^{c} – Values determined in soils collected in the area of Pata Rât (n=4)

According to the ratios of the concentration values in the ash and the reference values given for sensible soils, shares to the contamination risk of the priority and priority hazardous metals presents in the two types of ashes were calculated and are represented in Figure 6.10.

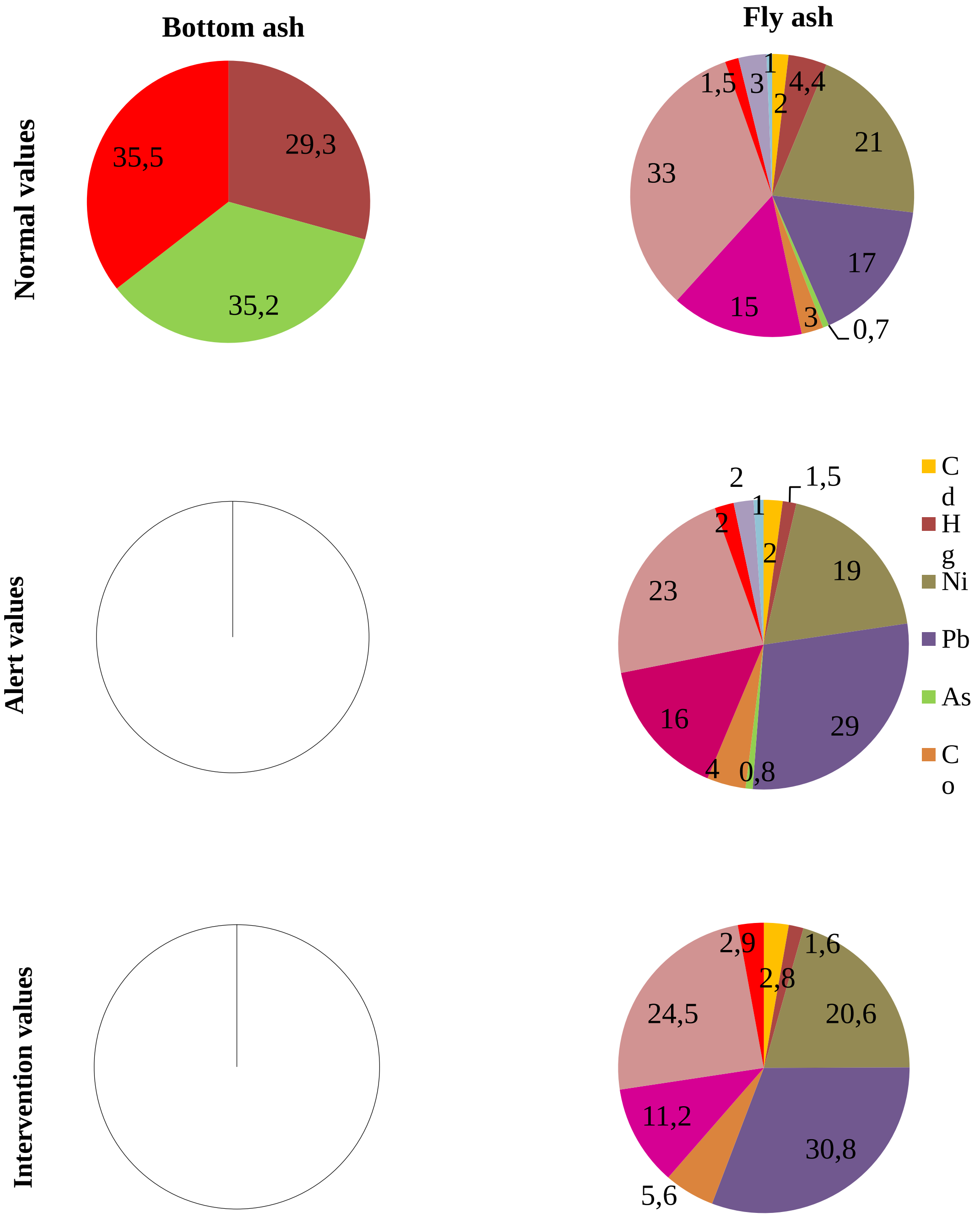


Figure 6.10. Contribution (%) to the contamination risk of the sensible soils of priority and priority hazardous elements in the bottom ash and fly ash retained by gas filters from the Hoval Multizon installation

The excesively high concentrations of the metals in the fly ash retained by filters is primarily due to Pb, Cu, Ni şi Cr, the shares of these elements to the contamination risk of soils relating to the intervention values are: Pb (30.8%) > Cu (24.5%) > Ni (20.6%) > Cr (11.2%).

As Figure 6.10 showes, unlike the fly ash in which Pb, Cu, Ni şi Cr are concentrated, the bottom ash contains high levels of Sb, As and Hg. The shares of these elements to the contamination risk of soil relating to the normal values are: 35.5% for Sb, 35.2% for As and 29.3% for Hg.

6.5. Evaluation of enrichment factors, contamination factors and contamination degree of ashes with priority and priority hazardous metals

There was performed a comparison between the enrichment factors (EF) of the metals in the bottom ash and fly ash retained by filters with respect to the Sakan and Buat - Menard report [128, 129], considering the Mn concentration as reference value. The contamination factor (CF) and the contamination degree (CD) were calculated in concordance with Hakanson [18]. The results are presented in Table 6.10.

The enrichment order of the priority and priority hazardous metals from moderate to extremely sever in the bottom ash is the following: sever (V<Pb<Tl<Cr) < very sever (Cu<Co<Ni) < extremely sever (Cd<Hg<As<Sb). In the fly ash retained by filters the enrichment factor varies as follows: moderate (Tl<V) < sever (Hg<As) < very sever (Co) < extremely sever (Cr<Cd<Ni<Pb<Cu<Sb). It is notable that 6 elements (Cr, Cd, Ni, Pb, Cu, Sb) determines an extremely sever contamination risk for the fly ash, against 4 elemens (Cd, Hg, As, Sb) in the bottom ash. The highest enrichment was found for Sb in both categories of ashes.

If the contamination factors and contamination degrees are considered, significant differences can be observed in the priority order of ashes. Thus, the order of contamination factors from the lowest to the highest is: low (V<Pb<Tl<Cr<Cu<Co<Ni<Cd<Hg) < considerable (As) < very high (Sb). In the case of fly ash the order of the contamination factors is: moderate (Tl<V) < very high (Hg<As<Co<Cr<Cd<Pb<Ni<Cu<Sb).

As showed previously the fly ash exhibits a very high contamination degree, the shares of the elements in its case being 8.8% Cr < 12.9% Cd < 14.1% Pb < 18% Cu < 26.2% Sb. In comparison with the fly ash, the bottom ash exhibits only a considerable contamination, especially due to Sb, which has a share of 88% and to As which has a share of 12%.

The shares of the metal contaminants in the fly ash and bottom ash are represented in Figure 6.11.

Table 6.10. Enrichment factors, contamination factors and contamination degree of ashes with priority and priority hazardous metals

Enrichment factor (EF)[a]

Type of ash	No	Minor	Moderate	Moderately sever	Sever	Very sever	Extremely sever
	0 < EF ≤ 1	1 < EF ≤ 3	3 < EF ≤ 5	5 < EF ≤ 10	10 < EF ≤ 25	24 < EF ≤ 50	EF > 50
bottom					V(17.5)<Pb(18.5) <Tl(20.5)<Cr(24.2)	Cu(27.1)<Co(38.5)<Ni(43.1)	Cd(62.8)<Hg(98.5)<As(984)<Sb(7461)
fly			Tl(3.6)<V(4.5)		Hg(14.1)<As(19.1)	Co(31.6)	Cr(108)<Cd(158)Ni(173)≤Pb(173)<Cu(221) <Sb(323)

Contamination factor (CF)[b]

Type of ash	Low	Moderate	Considerable	Very high
	CF<1	1 < CF≤ 3	3 < CF ≤ 6	CF > 6
bottom	V(0.06)<Pb(0.06)<Tl(0.07)<Cr(0.08)<Cu(0.09) <Co(0.13)<Ni(0.14)<Cd(0.20)<Hg(0.32)		As(3.2)	Sb(24.3)
fly		Tl(2.3)<V(2.8)		Hg(9.3)<As(12.1)<Co(20)<Cr(69)<Cd(100)<Pb(110)< Ni(110)<Cu(140)<Sb(205)

Contamination degree (CD)[b]

Type of ash	Low	Moderate	Considerable	Very high
	CD < 8	8 < CD ≤ 16	16 <CD≤ 32	CD > 32
bottom			27.5 (especially due to Sb)	
fly				780 (especially due to Cr <Cd <Pb<Ni<Cu <Sb)

[a] Calculated in agreement with Sakan şi Buat- Menard [128, 129] against the background levles in the superficial crust [126, 127] – Mn as reference element

[b] Calculated in concordance with Hakanson [18] against the background levles in the superficial crust [126, 127]

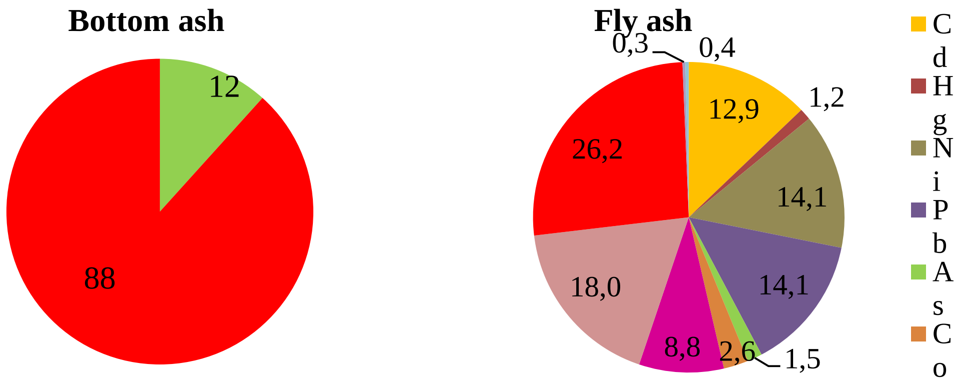


Figure 6.11. Shares of the priority and priority hazardous metals to the contamination potential of the bottom ash and fly ash from the Hoval Multizon installation.

6.6. Evaluation of the priority and priority hazardous metal content of the fly ash particles released in the air from the Hoval Multizon Cluj-Napoca

There were evaluated the contents of Hg, of Σ(Cd, Tl) and of Σ(Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V) of the fly ash released in the atmosphere together with the emission of gases after filtration. The results of the monitoring study in the period of 2007–2012 compared with the limit values of emissions set by the HG 128/2002 on waste incineration [16] are presented in Table 6.11. The sample collection time was of 30 minutes [206].

Table 6.13 Evolution of average yearly of the priority and priority hazardous metals in the emission gases [206]

	Hg (mg m^{-3})	Σ(Cd, Tl) (mg m^{-3})	Σ(Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V) (mg m^{-3})
LVE[a]	0.05	0.05	0.5
2007	0.001	0.02	0.41
2008	0.001	0.002	0.48
2009	0.003	0.006	0.09
2010	0.0006	0.005	0.14
2011	0.0008	0.005	0.24
2012	0.001	0.01	0.36
Average	**0.0010**	**0.008**	**0.29**
Standard deviation	0.0009	0.006	0.15

[a].- Limit value of emission measured at 30 minutes, in agreement with HG 128/2002 [16]

In accordance with Table 6.11 it results that in the overall period of monitoring the limit values of emission were not exceeded. This is a strong proof to the safety of the incineration technology, which doesn't exhibit contamination risk of the air in normal operating conditions.

Thus the studied hazardous medical waste incineration installation is based on a safe technology, it doesn't show contamination risk with priority and priority hazardous metals neither of the soil by the bottom ash, nor of the air by the release of incineration gases.

VII. EVALUATION OF THE ENVIRONMENTAL CONTAMINATION RISK OF THE MUNICIPAL AND INDUSTRIAL WASTE STORED IN NONCONFORMING LANDFILLS IN THE 6 NV AREA OF ROMANIA

Evaluation of the environmental contamination risk of the municipal and industrial waste stored in nonconforming landfills in the 6 NV area of Romania was carried out. In this study out of 35 landfills there were considered the followings: Pata Rât Cluj-Napoca, Gherla, Câmpia Turzii, Dej and Bistriţa. The waste storage was suspended in the period of 2005–2012, in order to carry out the ecologization and/or after-closing monitoring. In the case of industrial landfills there were studied the next ones: Ario-Bistriţa, Daniel Steel Beclean, Cesom Dej and Someş Dej, Uzina Electrică, Iaifo and Silocotub Zalău, finally the late HCH landfill in Turda. In all the counties from the 6 NV Area some Integrated Waste Management Systems/Centres (IWMS and IWMC) started to be realized, the first conformed landfill being put in operation in Oradea in 2005. In Cluj county the IWMC working started in 2012.

7.3. Evaluation of the contamination risk of the water and of the soil caused by the nonconforming municipal waste landfill of Pata Rât, Cluj-Napoca

7.3.1. Site description and sampling

The municipal waste landfill of Pata Rât is situated at a distance of 15 km from Cluj - Napoca, in the beltway area of the city. At the eastern part the landfill is bounded not farther than 2–10 m by the Zapodie stream, a tributary of the Someşul Mic river. The landfill was set in operation in 1973 and it was projected for a capacity of 3,5 million tones of municipal waste, having an area of 9 hectares and an operating duration of 30 years. However, the exploitation duration of the landfill was expanded to 37 years. At the present time the landfill has an area of 18 hectares. The current municipal waste quantity stored without a preliminary separation or pre-treatment is about 8–10 million tones, its projected capacity being surpassed by far. In the year of 2010 the municipal waste storage was stopped and ecologization works were started. At the present the landfill is partially ecologized, and the leachate resulting from the breakdown of biodegradable waste is collected through a 1720 m long drain [213-216].

In order to evaluation of the contamination risk of the water and of the soil caused by the nonconforming municipal waste landfill of Pata Rât, Cluj-Napoca, there were collected 4 soil samples from the Pata Rât area in 2009, and yearly 4 samples from the leachate in the period of 2007–2011. In the meantime two samples were collected from the Zapodie, upstream and downstream from the landfill.

In the soil samples from Pata Rât there were determined the concentrations of Cd, Cr, Cu, Ni, Pb and Zn by FAAS. The same metals were determined from the leachate samples by GFAAS, the concentrations of As by HG-QFAAS and the concentrations of Hg by CV-AFS. From the leachate there were also determined the following ions: ammonium, chloride, nitrite, nitrate, phosphate, sulphate, extractable substances in petroleum ether, pH and electrical conductivity, chemical oxygen demand by titration with $K_2Cr_2O_7$ and the total dissolved solids, respectively. Beside the metals, the knowledge of the suplimentary parameter values were important so as to highlight the role of the breakdown process of the biodegradable waste materials in the pollution of the leachate, the Zapodie stream, the soil and the groundwater.

7.3.2. Monitoring of the leachate quality, generated by the waste stored in the Pata Rât landfill

The results of the leachate quality monitoring influenced by the waste stored in the landfill of Pata Rât are presented in Table 7.16. For the purpose of evaluation of contamination risk the results were compared with reference values given in HG 352/2005 for the waste water quality, which is to be released into the aquatic environment [19], as well as with those corresponding with quality (V) – a poor quality for the surface waters given in Decree 161/2006 [121], respectively with the alert limits for groundwater in agreement with the law 458/2002 [143].

According to Table 7.16 the contamination of the leachate is determined only by Cu and Cr among the priority and priority hazardous metals, taking into account the alert limit for the waste water quality which is to be released into the aquatic environment. These results can be explained by the formation of water soluble complex compounds by the two metals with organic matter, which is stable in a large interval of pH, even at values less than 5 [238, 239].

Against the priority and priority hazardous metal contamination, the leachate exhibits a high load with hardly oxidable anorganic and organic compounds, which is revealed by the elevated values of COD-Cr and it is an impediment in the process of autoxidation. However, there were determined high concentration values, exceeding the limits given by law, for all the anions (chloride, nitrite, nitrate, sulphate) and the ammonium ion, as well as in the case of extractable compounds in the petroleum ether.

Table 7.16. Chemical quality indicators for the period of 2007–2011 of the leachate originating from the waste storing landfill of Pata Rât, Cluj-Napoca, in comparison with waste water quality, which is to be released into the aquatic environment, as well as with the alert limits for groundwater [218]

Annual average values[a]																		
Year	pH	CCO-Cr (mg L^{-1} O_2)	TDS[a] (mg L^{-1})	Cl^{-1} (mg L^{-1})	NO_2^-- N (mg L^{-1})	NO_3^-- N (mg L^{-1})	PO_4^{3-} - P (mg L^{-1})	P total (mg L^{-1})	SO_4^{2-} (mg L^{-1})	NH_4^+ - N (mg L^{-1})	Pb (μg L^{-1})	Cr (μg L^{-1})	As (μg L^{-1})	Ni (μg L^{-1})	Cd (μg L^{-1})	Cu (μg L^{-1})	Hg (μg L^{-1})	Petrol ether extract (mg L^{-1})
2007	7.64	1718	15720	6629	0.21	12.3	0.16	0.20	1534	110.4	43	1490	13	235	77	324	2.9	27
2008	7.31	970	2932	1448	0.45	10.7	0.07	0.14	1731	151.3	60	1970	8	73	18	144	3.0	30
2009	7.88	1250	1953	876	0.50	16.8	0.06	0.15	392	108	50	500	3	20	15	110	3.0	50
2010	8.90	2036	4991	862	1.00	24.0	0.05	0.06	666	49.4	50	1200	3	20	17	140	3.1	44
2011	7.89	1156	7593	2770	0.56	51.1	0.07	0.14	653	48.3	100	700	3	130	70	141	3.1	47
Average	**7.92**	**1426**	**6638**	**2517**	**0.54**	**23.0**	**0.08**	**0.14**	**995**	**93.5**	**61**	**1172**	**6**	**96**	**39**	**172**	**3.0**	**40**
Standard deviation	0.59	439	5518	2426	0.29	16.5	0.04	0.05	596	44	23	594	4	90	31	86	0.08	10
Ref. values for waste water[b]	-	125	2000	500	0.3	5.6	-	1	600	2	200	1000	100	500	200	100	50	20
Reported[b]	-	11.4	0	5.0	1.8	4.1	-		1.7	46.7		1.2	0	0	0	1.7	0	2.0
Ref.values for water (V)[c]	-	>125	>1300	>300	>0.3	>11.2	>0.9	>1.2	>300	>3.2	>50	>250	>100	>100	>5	>100	>1	-
Reported[c]	-	11.4	0	8.4	1.8	2.1	0	-	3.3	29.2	1.22	4.7	0	1.0	7.8	1.7	3	-
Ref. values for groundwater[d]	-	-	-	250	0.15	11.2	0.5	-	250	0.5	10	50	10	20	5	100	1	-
Reported[d]	-	-	-	10.1	3.6	2.1	0	-	4.0	187	6.1	23.4	0	4.8	7.8	1.7	3	-

[a] Annual average values obtained by the trimestral analyses

[b] Reference values according to HG 352/2005 [19] on waste water release into the aquatic environment

[c] - Reference values according to Decree 161/2006 [121] on surface water quality conditions, reference values for water quality (V) - poor

[d] – Reference values for potable water according to law 458/2002 [143]; Reference alert limits for groundwater

According to the results the share was calculated for each contaminant present in the leachate with regard the contamination risk of the Zapodie stream by the escape of the uncollected leachate. The share of a contaminant was calculated as the ratio of the experimental average value and of the reference value for waste water, surface water and groundwater. There were not taken into account those quality parameters whose ratio was subunitary (phosphate and total phosphorus), metals (Pb, As, Ni, Cd, Hg), and do not present contamination risk in accordance with HG 352/2005 [19]. Likewise, there were omitted from the calculations the values of the total dissolved solids because it refers to a group of substances instead of a specific contaminant. The share of the pollutants with contamination risk for the Zapodie stream in comparison with the reference values given by the 3 standards are presented in Figures 7.12, 7.13, 7.14.

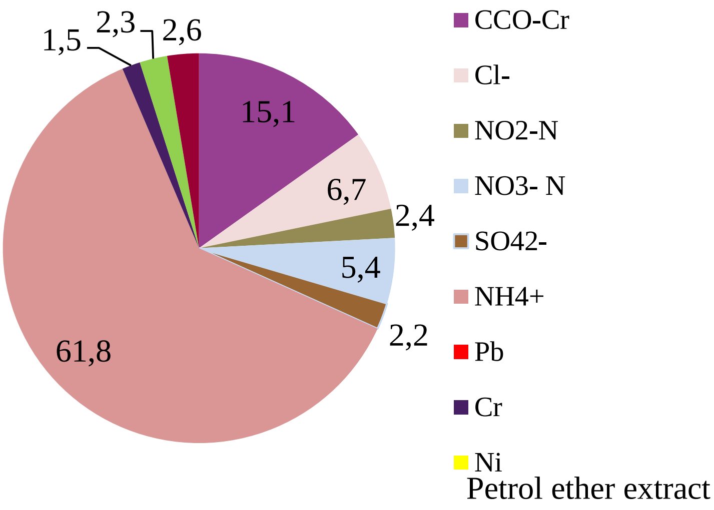


Figure 7.12. The share of the pollutants with contamination risk for the Zapodie stream due to the leachate of the waste stored in the landfill of Pata Rât. Reference values for waste waters in accordance with HG 352/2005 [19].

In agreement with Figure 7.12, the highest contamination risk of the Zapodie stream is due to the ammonium ion (61.8%), and to the oxidable substances with $K_2Cr_2O_7$ (15.1%), chloride (6.7%), nitrite (5.4%), nitrate (2.4%) and sulphate (2.2%). The extractable organic substances with petroleum ether, which are not eliminated by the process of autopurification, have a share of 2.6% in the contamination risk. As for the metals, the share for the contamination risk are the followings: Cr (1.5%) < Cu (2.3%). The values were calculated choosing the reference limit values given in HG 352/2005 [19].

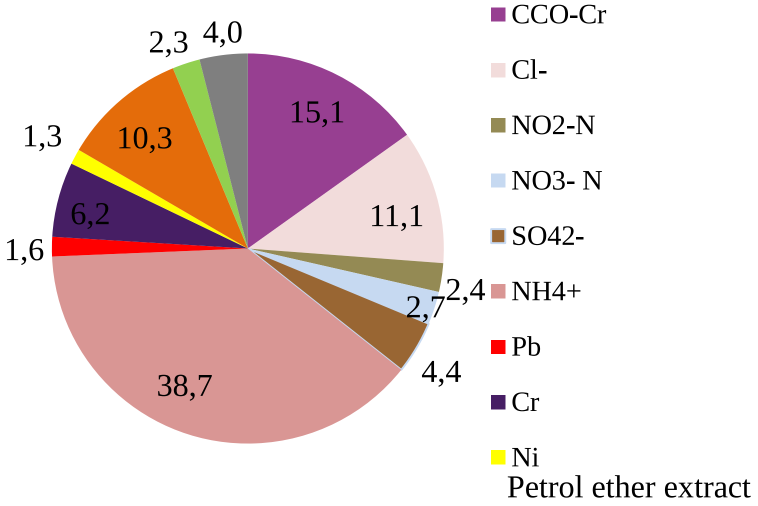


Figure 7.13 The share of the pollutants with contamination risk for the Zapodie stream due to the leachate of the waste stored in the landfill of Pata Rât. Reference values taken for the quality of surface waters; ecological quality – poor [121].

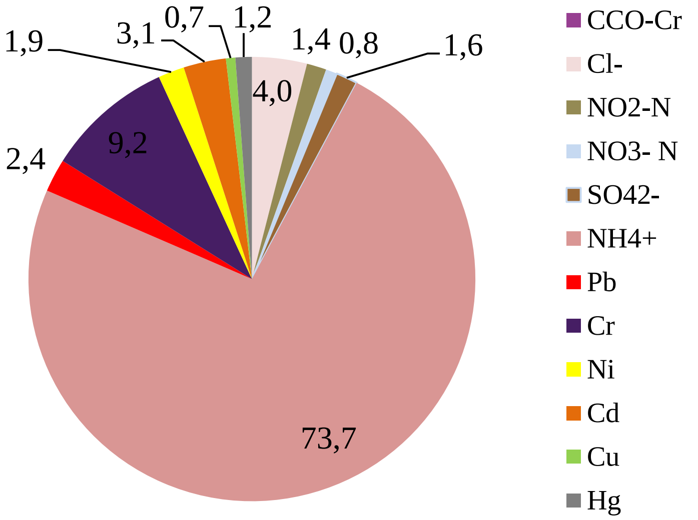


Figure 7.14. The share of contaminants to the potential contamination risk of the groundwater due to the leachate of the waste stored in the landfill of Pata Rât [141, 142].

In accordance with Figure 7.13, the concentrations of all metals in the leachate, except As, exceed the reference limit values. Thus, the share of priority and priority hazardous metals in the leachate to the contamination risk of the Zapodie stream is about 26%, mainly due to hazardous priority metals: Cd (10.3%), Cr (6.2%) and Hg (4%). There was observed a significant share to the contamination risk of the ammonium ion (38.7%), of chloride (11.1%), and of the oxidable substances expressed by the COD-Cr (15.1%), respectively.

Regarding the possibility of groundwater contamination by infiltration of the leachate (Figure 7.14.), it was found that the ammonium ions have an overwhelming share (73,7%), along with a possible contamination with Cr (9.2%) and Cd (3.1%). There was found a less probable contamination of groundwater with nitrite, nitrate, sulphate, chloride and metals as Pb, Ni, Cu and Hg.

7.3.3. Water quality monitoring of the Zapodie stream

Table 7.17 presents the chemical and biochemical parameters determined in 2 samples of water collected from the Zapodie stream, upstream and downstream to the landfill of Pata Rât. In comparison are presented the reference values for surface waters exhibited in 5 quality groups according to law 161/2006 [121]. The metal content was determined by graphite furnace atomic absorption spectroscopy (GFAAS), the arsenic content by HG-QFAAS and the mercury by CV-AFS.

The data presented in Table 7.17 show a degradation of the quality of Zapodie stream possibly due to the escape of leachate, which is not collected from the landfill of Pata Rât. Thus, due to the ammonium ion, the upstream is classifiable in the IVth quality ecological state (poor). The downstream is qualified as a Vth group water due to ammonium ion, total dissolved solids, COD-Cr, BOD_5, nitrite, nitrate and total phosphorus.

The share of the contaminants driven by the leachate into the stream, which determine the degradation of the water of Zapodie stream, is presented in Figure 7.15.

The share of a given contaminant was considered to be proportionate with the difference of its concentration in the downstream and upstream divided by the reference limit value. This reference value is chosen according to the classification group in which the water sample can be set. In the present case this is the Vth quality group. The graphical representation shows that the degradation of the water quality in the Zapodie stream is caused in about 60% and 30% by the ammonium ion and by the oxidable substances which deplete the physically dissolved oxygen in the water. Likewise, a negative influence of the nitrite, nitrate and phosphorus ion on the water quality of the stream can be set forth. The influence of the prmary and priority hazardous metals is insignificant.

Table 7.17. The values of chemical and biochemical parameters for the water samples collected from the Zapodie, upstream and downstream to the landfill of Pata Rât [218].

	Parameters[a]														
	pH	TDS (mg L^{-1})	COD-Cr (mg L^{-1} O_2)	BOD_5 (mg L^{-1} O_2)	NO_2^- - N (mg L^{-1})	NO_3^- - N (mg L^{-1})	total P (mg L^{-1})	NH_4^+ - N (mg L^{-1})	Pb (μg L^{-1})	Cr (μg L^{-1})	As (μg L^{-1})	Ni (μg L^{-1})	Cd (μg L^{-1})	Cu (μg L^{-1})	Hg (μg L^{-1})
Upstream	8.13	2290	20.4	5.3	0.03	1.7	0.17	1.7	2.1	40.8	12.2	13.8	0.10	23	0.12
Downstream	8.9	6690	1210	50.0	0.37	21.3	1.3	65	3.1	43.0	14.5	17.6	0.50	24	0.14
I[b]	6.5-8.5	500	10	-	0.01	1	0.15	0.4	5	25	10	10	0.5	20	0.1
II[b]		750	25	-	0.03	3	0.4	0.8	10	50	20	25	1	30	0.3
III[b]		1000	50	-	0.06	5.6	0.75	1.2	25	100	50	50	2	50	0.5
IV[b]		1300	125	-	0.3	11.2	1.2	3.2	50	250	100	100	5	100	1
V[b]		>1300	>125	-	>0.3	>11.2	>1.2	>3.2	>50	>250	>100	>100	>5	>100	>1
Difference[c]	0.77	4400	1190	44.7	0.34	19.6	1.33	63.3	1	2.2	2.3	3.8	0.4	1	0.02
Reports[d]		0	9.5	0	1.1	1.8	1.1	19.8	0	0	0	0	0	0	0

[a] – Average of 5 successive measurements.
[b] – Reference values according to Decree 161/2006 [121] on surface water quality.
[c] – Concetration difference between downstream – upstream (C_{down}-C_{up}).
[d] – Report (C_{down}-C_{up})/$C_{ref\ (V)}$. Ecological quality reference (V) – poor [121].

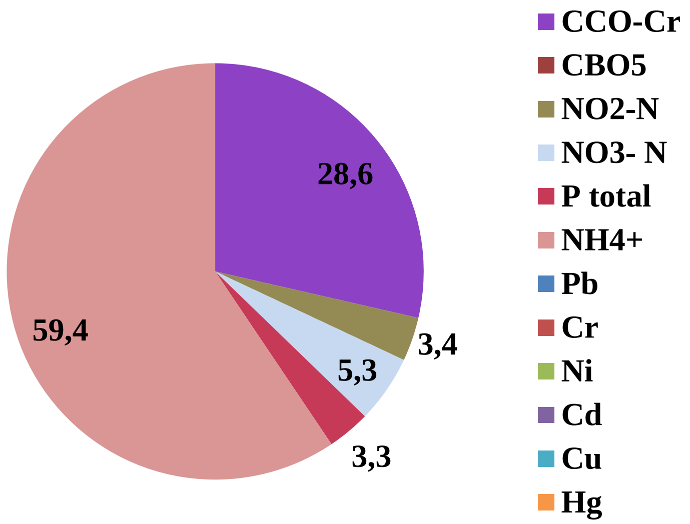


Figure 7.15. Entrance share of the leachate contaminants escaped from the landfill of Pata Rât into the Zapodie stream. The share was calculated as follows: $P = (C_{down}-C_{up})/C_{ref\ (V)}$.

7.3.4. Soil quality monitoring in the area of Pata Rât landfill

In Table 7.18 are presented the results obtained for Cd, Cr, Cu, Ni, Pb, Zn from soil samples collected in the area of Pata Rât landfill and analyzed by FAAS. The results are the average of 5 successive measurements performed in the case of each sample.

Table7.18. Results obtained at the determination of Cd, Cr, Cu, Ni, Pb, Zn from soil samples collected in the area of Pata Rât landfill [216,218].

Sample	Average metal content (mg kg^{-1})[a]					
	Cd	Cr	Cu	Ni	Pb	Zn
Average	**0.37**	**11.3**	**25.2**	**20.8**	**61.1**	**86.4**
Standard deviation	0.12	3.2	8.9	6.4	24.9	18.7
NV[c]	1	30	20	20	20	100
Reference values for sensible soils[b]						
AV[d]	3	100	100	75	50	300
IV[e]	5	300	200	150	100	600
Reference values for less sensible soils[b]						
AV[d]	5	300	250	200	250	700
IV[e]	10	500	500	500	1000	1500
Concentration in the superficial crust[f]	0,098	35	25	20	20	71

[a] – Average values obtained on the bases of 5 successive measurements for each sample

[b] – Reference values according to law 756/1997 [120].

[c] – Normal values (NV) according to the Decree 756/1997[120].

[d] – Alert values in accordance with the Decree 756/1997[120].
[e] – Intervention values in accordance with the Decree 756/1997[120].
[f] – Concentrations of the superficial crust according to Tylor [126].

Among the 6 studied elements only in the case of Pb was found an elevated concentration level exceeding the alert limit for sensible soils. In the case of Cu and Ni it was observed only an exceeding of the normal background values for soils. Relying on this study it can be stated that the highest contamination risk of soil is determined by the Pb present in the waste, probably due to the batteries, accumulators, electrical and electronic equipments of large dimensions (televisions, monitors, etc.), stored at the landfill of Pata Rât.

The contamination factors of the soil relying on the studied priority and priority hazardous metals and the average contamination degree of the soil calculated in accordance with the Hakanson methodology [18] are presented in Table 7.19, this time considering as reference values the concentrations in the superficial crust according to Tylor [126].

Table 7.19. Average contamination factors (CF) of the soil with metals and the average contamination degree of the soil from themunicipal waste landfill of Pata Rât.

Contamination factor (CF)[a]			
Small	**Moderate**	**Considerable**	**Very high**
$CF<1$	$1 < CF \leq 3$	$3 < CF \leq 6$	$CF > 6$
Cr (0,33), Cu (1.0)	Ni (1.1) Zn (1.2)	Pb(3.1) Cd (3.8)	
Contamination degree (CD)[a]			
Small	**Moderate**	**Considerable**	**Very high**
$CD < 8$	$8 < CD \leq 16$	$16 < CD \leq 32$	$CD > 32$
	10.4		

[a] – Average values obtained on the bases of 4 samples. Reference: concentration in the superficial crust according to Tylor [126], Table 4.4, Chapter 4.

According to the data presented in Table 7.19, the contamination factor of the soil in the area of Pata Rât obtained for Pb and Cd is considerably high, it is moderate for Ni and Zn, respectively moderate to small for Cu, and small in the case of Cr. In accordance with these factors the soil from the area of the municipal waste landfill of Pata Rât is classified in the moderate degree contamination category (CD = 10.4). The share of the priority and priority hazardous metals to the soil contamination in the studied area according to the Hakanson methodology [18], is the following: Cd(33.3) > Pb(32.0%) > Zn(12.5 %) > Ni(11.0%) > Cu(8.8%) > Cr(3.0%).

Finally it can be concluded that beside the contamination risk of the soil from Pata Rât with Pb, Ni and Cu, cadmium should be considered, too.

7.4. Principal Component Analysis and Cluster Analysis for the leachate from the landfill of Pata Rât

Analiza statistică multivariată, Principal Component Analysis (PCA) and Cluster Analysis (CA) was applied for the evaluation and interpretation of experimental data in order to highlight the origin of the contaminants and of their share in the description of the leachate composition variability.

The PCA analysis was carried out using normalized data, as a consequence of the differences in the measuring units of the determined chemical parameters and of the large variances of the concentration ranges. The normalization of data in the PCA tends to increase the influence of the variables with small variance (in our case the priority and priority hazardous metals) and to reduce the influence of the variables with high influence..

According to Kaiser Criterion only those principal components (PCs) were preserved and subjected to the varimax rotaion whose value was greater than 1.0. The influence factors for different parameters used for evidencing the relative importance of a variable in comparison with other variables in a PC were classified as having “powerful”, “moderate” and “weak” correlation, corresponding to some influence factors with values of > 0.75; 0.50-0.75 and 0.30-0.50 [253, 254].

The influence of the parameters over 4 PCs, considering as variables the components determined in the leachate are presented in Table 7.20. The 4 principal components presented in Table 7.20 describe 80% of the variability of the leachate composition.

The first factor (PC1) which describes 32.2% of the total variance was attributed to the dissolved anorganic substances in the leachate (chlorides and phosphates). These substances are the result of the biodegradation of waste containing them in high concentrations as remains of food and biodegradable plastic materials. Ni, Cd and Cu are included in this factor with a high influence, thus PC may show the share of priority metals in the variability of the leachate composition. The strong correlation between chloride, phosphate and TDS, shows that the majority of the dissolved anorganic salts are in the form of chlorides and phosphates. There is found a moderate positive influence of As and total P, and a negative influence of the nitrite. This factor shows that Ni, Cd and Cu are usually present in the solution as chlorides. A possible source for Ni, Cd and Cu in this factor could be attributed among other things to the electrical and electronic waste of small dimensions (Ni-Cd batteries), and the main source of Cu could be the pesticides (for example the copper oxychloride). This statement is in agreement with the positive correlation between Cu and total P, which can also come from the pesticides.

Table 7.20. The share of 4 principal components, which describe the variability of the leachate composition.

Parameter	PC1	PC2	PC3	PC4
pH	-0.193	0.040	0.829**	-0.271
CCO-Cr	0.263	-0.279	0.806**	-0.054
TDS	0.878**	-0.012	0.118	0.125
Cl^-	0.875**	-0.071	-0.091	0.143
NO_2^-	-0.537*	0.187	0.684*	-0.093
NO_3^-	0.047	0.821**	0.131	-0.327
PO_4^3-	0.825**	-0.257	-0.144	0.182
P total	0.602*	-0.185	-0.634*	-0.042
SO_4^{2-}	0.284	-0.180	-0.274	0.782**
NH_4^+	-0.074	-0.502*	-0.618*	0.402
Pb	-0.043	0.866**	-0.191	-0.106
Cr	0.058	-0.203	-0.039	0.868**
As	0.622*	-0.361	-0.215	0.485
Ni	0.847**	0.087	-0.177	0.208
Cd	0.814**	0.360	-0.086	-0.021
Cu	0.817**	-0.259	0.034	0.252
Hg	-0.347	0.666*	0.298	-0.384
SE	-0.422	0.278	0.162	-0.720*
Variability (%)	32.2	15.7	16.5	15.6

** Strong influence over the factor > 0.75;
* Moderate influence over the factor > (0.50-0.75)

The second principal component (PC2) with a contribution of 15.7% was equally attributed to the biodegradation of waste which leads to the formation of nitrogen containing compounds (ammonium ion and nitrate). This factor can be attributed mainly to the textile, foodstuff and gardening waste. There are evidenced by this factor the priority hazardous metals (Pb and Hg) which come from electrical and electronic waste of small dimensions. The presence of Pb and Hg, showing a positive correlation between them, may be the consequence of the biodegradation of some waste (biodegradable food packages made of oxo polyethylene or starch). Another possible source of these priority hazardous elements could be the leachate generated by lead-based accumulators and mercury-based batteries. The positive correlation between Pb, Hg and nitrate shows that these metals are present in the leachate as nitrates. There can be revealed in this factor a negative correlation between the ammonium ion and the nitrate. This is attributed to the oxidation process of the ammonium ion to nitrate.

The third principal component (PC3) with a variability of 16.5% was attributed to the oxidable substances in the leachate, asserted by the strong influence of the COD-Cr parameter. The presence of the nitrogen-based compounds (ammonium ion and nitrite) shows that this factor can be attributed to the biodegradable waste with nitrogen content (textiles, food remains, gardening waste). The positive moderate correlation between the COD-Cr and the nitrite, meantime the the lack of COD-Cr correlation with the extractible organic compounds with petroleum ether, shows that the O_2 is consumed in the process of the nitrite oxidation instead of the oxidation of organic compounds. In accordance with the influence factor, these later compounds are resistant to the oxidation with $K_2Cr_2O_7$. The average negative influence factor of the ammonium in this factor comparing with the influence factor of the nitrite highlitghs that ammonium ion can be oxidized to nitrite along with the increase of pH, the idea being asserted by the positive correlation of the nitrite with the pH.

The fourth factor (PC4) with a variability of 15.6 % was attributed to the biodegradation of sulphur containing waste (paper, textiles, tires, leather). This fact is asserted by the strong influence of the sulphate which is the result of the activity of sulphur metabolizing microorganisms. The presence of Cr with an elevated factor in PC4 shows that the Cr and the S have the same origin. The main source of Cr is the leather-based waste, especially shoes and clothes. In the tanning process of the leather chromium salts are used. The negative factor (-0.72) of the extractible substances in petroleum ether in contrast with the positive factor of the Cr shows that the former substances are oxidized the most probably by the chromium salts which are present in the leachate.

The results obtained in PCA were confirmed by the grouping of chemical parameters of the leachate in three clusters as follows: breakdown of the nitrogen-based biodegradable waste (clothes and food waste), degradation of sulphur-containing waste (clothes and shoes), and the third cluster containing the phosphorus-based and chloride-based waste (food remains, insecticides, pesticides, plastic materials) which groups the most metallic contaminants (Cd, Ni, Cu and As).

In Figure 7.17 is presented the dendrogram of the clusters of chemical parameters presents in the leachate from Pata Rât.

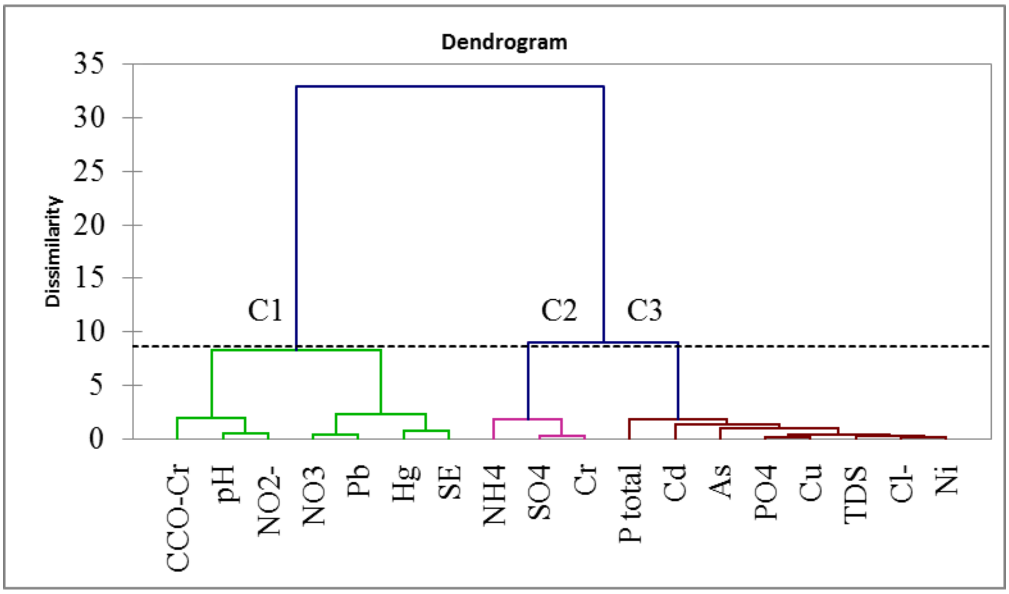


Figure 7.17. Dendrogram of chemical parameters clusters of the leachate from Pata Rât

7.5. Comparative study on the priority and priority hazardous metals monitoring in the municipal and industrial waste in the 6 NV Region

The aim of this study was to own comparative data on soil contamination with priority and priority hazardous metals originating in municipal and industrial waste landfills.

With regard to the soil contamination with metals from household waste there were found elevated levels for Cu, Ni, Pb andi Cd, Cr, Zn. The concentration of Cu was higher than the normal background level in the case of landfills from Pata Rât, Gherla, Câmpia Turzii and Bistriţa, and in one case of the landfill from Gherla the alert limit was exceeded. The concentration of Ni exceeded the normal background level at the landfills from Pata Rât and Câmpia-Turzii, and lead concentration exceeded both normal background and alert limits at the landfills from Pata Rât, Gherla, and Bistriţa. In the case of Cd, Cr şi Zn there was exceeded the normal background levels only at the landfill from Gherla. In one case, the landfill from Dej, neither limit was exceeded.

The lead contamination of the soil due to industrial waste exceeded the normal background level at 6 landfills, and the alert limit in the case of the landfill from Uzina Electrică Zalău. The increasing order of the exceeding values is the following: Cesom Dej < Someş Dej < Silcotub Zalău < Turda (HCH) < Ario Bistriţa < Uzina Electrică Zalău. Likewise, the increasing order of the exceeding values for Cu is the following: Beclean < Someş Dej < Uzina Electrică Zalău < Turda (HCH) < Iaifo Zalău. The Ni concentrations exceeded the normal background levels at 3 landfills: Ario Bistriţa < Silcotub Zalău < Iaifo Zalău. Two landfills exhibited contamination of soil with Cr: Uzina Electrică Zalău < Silcotub Zalău. Three landfills in the case of Zn: Uzina Electrică Zalău < Iaifo Zalău < Beclean exhibited elevated concentration levels, and in the case of Silcotub Zalău landfill the alert limit for the less sensible soils was exceeded as well. In the case of Cd the concentration levels were beyond the alert limit for sensible soils at two landfills (Uzina Electrică Zalău and Beclean), and beyond the intervention limit for less sensible soils in the case of slag landfill from Iaifo Zalău.

The share to the soil contamination risk was calculated for Cd, Cr, Cu, Ni, Pb and Zn, as the ratio between experimentally determined values and both normal levels in the soil and alert limits for sensible soils. There were not considered those metals whose concentrations did not exceed the limit values.

Graphical reprezentations of the share to the soil contamination risk calculated as the ratio between experimentally determined values and both normal levels in the soil and alert limits for sensible soils revealed important contributions of Pb, Cu and Ni presents in the municipal waste and of Cd, Zn, Pb and Cu presents in the industrial waste.

Average contamination factors of the metals and average contamination degree of the soil calculated for soils collected from municipal and industrial waste landfills in function of Cd, Cr, Cu, Ni, Pb and Zn, in accordance with the Hakanson methodology [18], the concentration values in the superficial crust after Taylor considering as reference values [126] have determined a hierarchy between the two types of landfills:

- Dej (5.1-small) < Bistriţa (8.6-moderate) < Pata Rât (10.0-moderate) < Câmpia Turzii (10.7-moderate) < Gherla (43.2-very high). Cd, Pb and Cu are the key metals in the determination of the hierarchy and the contamination degree, respectively.

- Cesom Dej (6.7-small) < Turda HCH (8.5-moderate) < Someş Dej (10.9-moderate) < Ario Bistriţa (10.9-moderate) < Dan Steel Beclean (17.1-considerable) < Uzina Electrică Zalău (20.4-considerable) < Silcotub Zalău (25.4-considerable) < Iaifo Zalău (166-very high). The soils

The considerable and very high contamination of the soils in the area of industrial waste landfills is caused mainly by Cd and Pb, and the moderate contamination is due to Pb, Cu, Ni and Zn.

If the municipal waste landfills contribute, for the most part, to a moderate contamination of the soil, three of the industrial waste landfills contribute to a considerable contamination of the soil, and finally there is one industrial waste landfill with a very high contamination degree.

7.6. Principal Component Analysis and Cluster Analysis for municipal and industrial waste landfills

The PCA evidenced that 78% of the metal content variability in the soil is determined by two principal factors: the first factor in 45% was determined by Cu, Pb and Zn, and the second one in 33% was determined mainly by chromium, and to a lesser extent to the Cd and Ni. In the area of the industrial waste landfills the variability is described by three principal factors, altogether in proportions of 80% (30.8% due to Cd and Cu, 29% mainly due to Zn, Ni and Cr, and 20.9% mainly due to Pb). Thus, the influence of metals on the soil composition variability for the municipal waste landfills decreases in the next way: Pb > Cu > Zn > Cr > Cd > Ni, and for the industrial waste landfills decreases in the order of: Cd > Cu > Zn > Pb > Ni > Cr. There could be established a clear influence of the two types of stored waste on the soil contamination risk. Through the cluster analysis a classification of the municipal waste landfills into 3 groups was performed, as follows: (C1) Pata Rât and Bistriţa, (C2) Dej and Câmpia Turzii, and finally (C3) Gherla. There could not be realized a classification into clusters of the industrial waste landfills, probably due to the significant differences in the types of waste stored in these landfills.

The dendrogram representing the clusters of the municipal waste landfills, based on the priority and priority hazardous metal content of the soil, is presented in Figure 7.26.

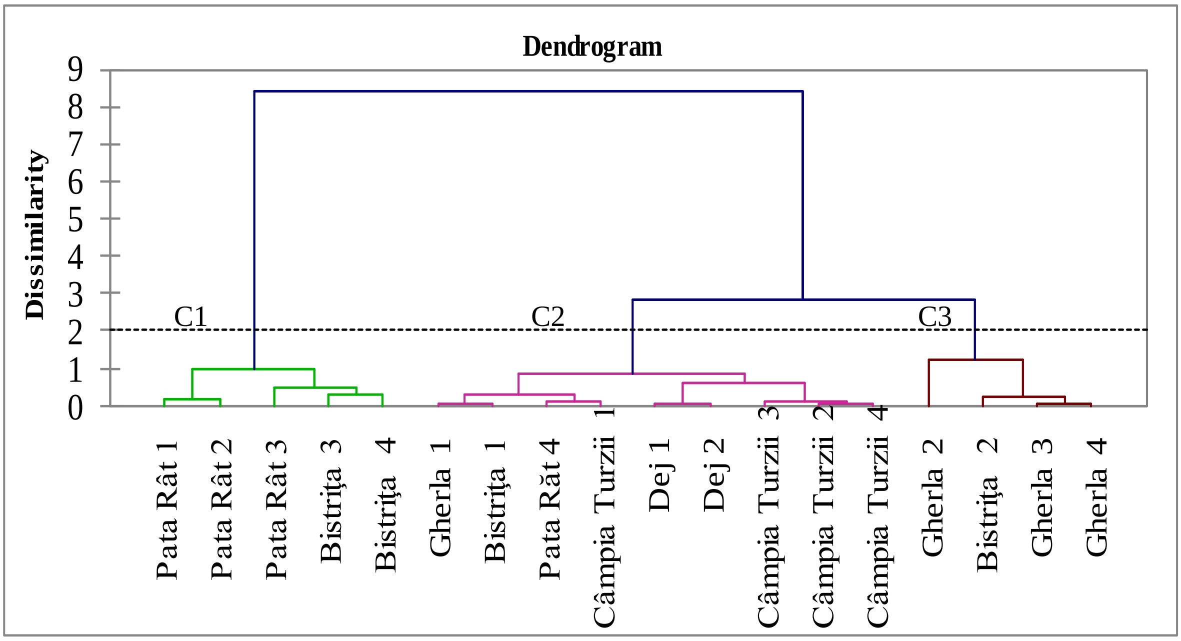


Figure 7.26. The dendrogram representing the clusters of the municipal waste landfills, based on the priority and priority hazardous metal content of the soil

8.2.3. Evaluation of the waste batteries leachate composition

The priority and priority hazardous metal content of two leachate samples, generated by waste batteries, was determined in comparison with the leachate generated by non-selectively collected biodegradable municipal waste. The shares of the metals to the contamination risk of waters when the leachate escapes in the environment were calculated based on the ratios between the concentration of metals in the leachate and the reference values for waste waters releasable in emissaries in agreement with the HG 352/2005 [19]. The ratios were calculated only for the metals with concentrations exceeding the reference values.

The results showed that the leachate generated by waste batteries are far more contaminated, firstly with priority hazardous metals (Hg, Pb and Ni), in comparison with non-selectively collected municipal waste which led to exceeds for two priority metals, namely Cu and Cr concentrations in the leachate. (Figure 8.4) [257].

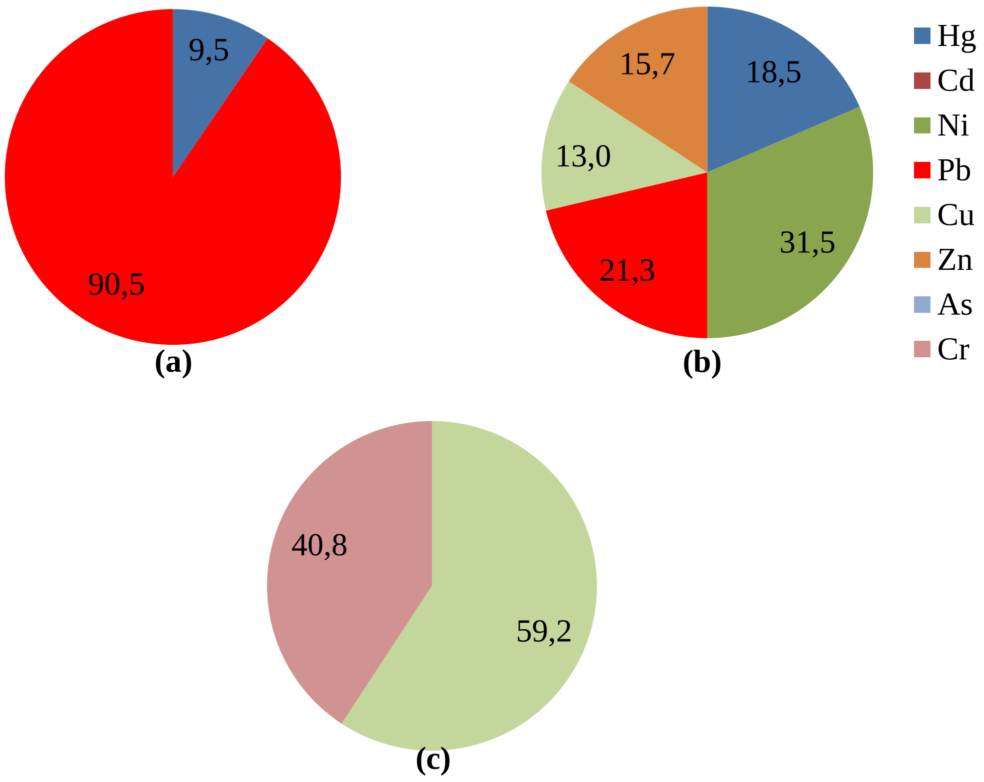


Figure 8.4. The share of metals on water contamination risk in the case of emissaries by escape of the leachate. (a), (b) batteries generated leachate, (c) municipal waste generated leachate [257]

The waste batteries and accumulators should be collected selectively and stored in landfills conformed to the European normatives until a possible technological recycling by recovery of metals.

8.2.4. The leaching of lead from the CRT monitors

In Table 8.6 [267] is presented the Pb content of the screen glass and glass funnel of CRT monitors.

Table 8.6. Pb content (mg kg^{-1}) in the leachate of CRT monitors [267]

Screen glass	Glass funnel
0.2[a]	1.4[a]

[a]- mean of 5 indipendent measurements

The results obtained in a leachate with the composition of solid:water of 1:10 [72], in agreement with the Table 8.6 show that the glass of the funnel exhibits a higher Pb contamination risk, because in this case the limit value of the inert waste (0.5 mg kg^{-1}) is exceeded in comparison with the screen glass, which is also considered an inert waste.

The higher leaching results for Pb in the case of the funnel than of the screen are explicable on the one hand with the higher Pb concentration in the funnel than in the screen itself, on the other hand by the lower pH of the leachate (7.88 in the case of the funnel in comparison with 9.77 in the case of the screen itself).

There is evident the need to avoid the contact of the CRT monitors from the precipitation. They represent a potential contamination risk of the water by the leaching of lead. Likewise, it is important to separate the funnel from the screen, since the lead content of the funnel is higher than that of the screen.

IX. VALIDATION OF AN ANALYTICAL METHOD BASED ON HIGH-RESOLUTION CONTINUOUS-SOURCE ATOMIC ABSORPTION SPECTROSCOPY FOR THE FAST, SEQUENTIAL DETERMINATION OF PRIORITY AND PRIORITY HAZARDOUS METALS IN SOIL

In this chapter the validation of an analytical method for the fast and sequential determination of priority and priority hazardous metals (Ag, Cd, Cr, Cu, Ni, Pb and Zn) is presented based on HR-CS AAS.

The importance of this study for the analytical practice has the following reasons:

- ❑ Standardized methods for the soil analysis by low-resolution atomic absorption spectroscopy with line-source (LR-LS FAAS/GFAAS) are monoelental, slow methods, instead the inductively coupled plasma atomic emission spectroscopy (ICP-AES) is a fast, multielemental method, but implying high costs.

- ISO/IEC 17025-2005 standard [324] requires validation before the use of a new technique/method for a special intended purpose.
- The recently introduced novel instrumental concept based on high-resolution ccontinuous source atomic absorption spectroscopy (HR-CS FAAS) on the market.
- The lack of published data in literature related to the applicability of HR-CS FAAS method for priority and priority hazardous metal determination in soil samples.

The statistical method Bland & Altman [326, 327] was used for the concordance between the proposed method and ICP-AES, as a standardized multielemental method for the determination of metals in soil [182].

The FAAS measurements were carried out on a flame atomic absorption spectroscope with high-resolution and ContrAA 300 continuous source (Analytik Jena AG, Jena, Germania), the unique producer of this kind of instrument at the moment.

The schematic set-up of the HR-CS AAS ContrAA 300 spectroscope is presented in Figure 9.1.

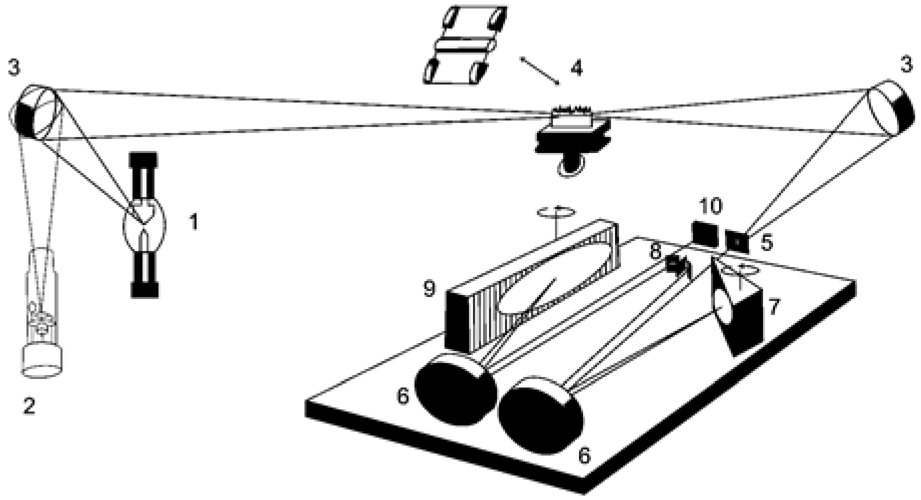


Figure 9.1. The schematic set-up of the ContrAA 300 spectroscope (1 xenon lamp with short arc, 2 chatode lamp, 3 elliptical mirrors, 4 nebulizer, 5 entrance slot, 6 parabolic mirrors, 7 prism, 8 radial mirror, 9 echelle grating, 10 CCD detector)

The ContrAA 300 spectroscope is equipped with a short arc xenon lamp XBO 301 (GLE, Berlin, Germania), in order to ensure the continuous spectrum adequate for all the elements.

In order to carry out comparative determinations a simultaneous ICP-AES spectroscope SPECTRO CIROS^{CCD} was used with axial view of the plasma (Spectro Analytical Instruments, Kleve, Germania), presented in Figure 9.3.

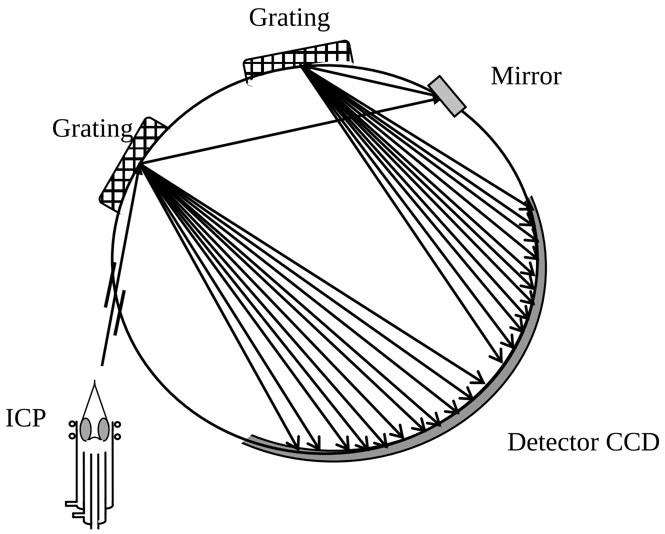


Figura 9.3. Schematic set-up of the ICP-AES SPECTRO CIROS^{CCD} spectroscope

The validation was carried out based on a performance study of the new method (detection limit, determination limit, precision and accuracy [322,323].

The detection and determination limits found for HR-CS FAAS and ICP-AES, în acord cu according to the 3σ criterion are presented in Table 9.4 [325]. There were found better limits of detection for Cr, Cu, Ni and Pb by HR-CS FAAS than by ICP-AES.

Table 9.4. The limits of detection (3σ criterion) and limits of determination (mg kg^{-1}) in soil [325].

	HR-CS-AAS			ICP-AES			Aplicability limits for LR-LS-FAAS[C]
	λ (nm)	LOD[a]	LOQ[b]	λ (nm)	LOD[a]	LOQ[b]	
Ag	328.068	0.18	0.54	328.068	0.12	0.36	-
Cd	228.802	0.14	0.42	214.438	0.05	0.15	>2
Co	240.206	0.36	1.08	228.615	0.15	0.45	>12
Cr	357.869	0.25	0.75	267.716	1.4	4.2	>12
Cu	324.754	0.09	0.27	324.754	0.15	0.45	>5
Ni	232.003	1.0	3.0	305.082	2.5	7.5	>12
Pb	217.000	1.4	4.2	220.351	2.5	7.5	>15
Zn	213.856	0.18	0.54	213.856	0.04	0.12	>2

[a] – LOD calculated for 1.000 g soil mineralized and diluted to 100 ml solution.
[b] – LOQ calculated as 3 times the LOD.
[c] – In agreement with [223].

The accuracy of the analytical method based on HR-CS FAAS was verified by four certified reference materials. The results, in comparison with ICP-AES results, are presented in Table 9.5 [325]. According to these results, the analytical method based on HR-CS FAAS exhibitied recoveries between 94–106% showing a good accuary, similar to the values obtained by ICP-AES (97–103%). At the same time, the precision determined by a repetability study on 51 soil samples showed similar results in the case of both methods.

The validation study of the method based on HR-CS FAAS applied for the determination of the elements on a large concentration range, was determined by the Bland & Altman test, considering the ICP-AES as reference method.

According with this statistical methodology the differences between methods are plotted against the mean concentration values obtained with both methods. The lines representing the systematic errors and the confidence intervals for 95% are showed in the graphic.

The Bland and Altman test revealed no systematic error between the two methods as the differences between the results obtained with the two methods fall between the confidence limits, and the confidence interval of the mean difference contains the zero value. Furthermore, the confidence interval of the upper and lower limits must be reasonably narrow, which is the case of a large number of samples.

The Bland and Altman plots are presented in Figure 9.4, in the meantime the statistical description for a confidence interval of 95% is given in Table 9.7.

Three of eight studied elements (Cu, Pb and Zn) had concentrations in a very large range, with individual values grouped in subdomains. Thus, in the case of Cu, the samples were devided into two groups, one with concentrations lower than 1000 mg kg^{-1} (34 samples) and the second with a concentration range of 1000–22000 mg kg^{-1} (16 samples). The distribution of Pb concentrations imposed the formation of three groups: less than 1000 mg kg^{-1} (28 samples), the range of 1000–10000 mg kg^{-1} (14 samples) and the range of 10000–60000 mg kg^{-1} (13 samples). The samples were devided into two groups with regard the Zn concentration: less than 1000 mg kg^{-1} (30 samples) and over 1000 mg kg^{-1} (20 samples). The use of some narrower concentration ranges asserted a better verification of the accuracy of the results obtained by HR-CS FAAS and ICP-AES.

The representations in Figure 9.4 and the data in Table 9.7 prove a good concordance between methods at a significance level of 95%, the lack of systematic errors and good analytical performances determined by the limits of detection and of determination, precision and accuracy in comparison with ICP-AES.

Table 9.5. The values found by analysis (m=3 indipendent samples) in the CRM samples for soils in comparison with the certified values (mg kg^{-1}) [325]

	BCR 025-050[a]			LGC 6135[a]			LGC 6141[a]			NCSDC			Recovery[b] (%)	
	Found		Certified	Found		Certified	Found		Certified	Found		Certified	ICP-AES	HR-CS FAAS
	ICP-AES	HR-CS FAAS		ICP-AES	HR-CS FAAS		ICP-AES	HR-CS FAAS		ICP-AES	HR-CS FAAS			
Cd	340±45	383±76	369±46.3	-		-	-	-	-	2.50±0.5	2.40±0.2	2.45±0.3	97±17	101±15
Co	4.00±0.8	3.98±0.8	4.07±0.93	19±3	16±4	20±4	-	-	-	17.1±1.5	17.0±2.0	16.5±1.8	99±16	94±20
Cr	448±41	403±34	441±50.1	349±12	344±30	336±28	120±20	115±20	130±31	88±5	105±6	90±8	99±10	100±11
Cu	8.35±1.68	9.62±1.60	7.76±1.68	100±5	102±11	105±5	52.2±0.8	52.3±7.5	51.1±13	54±5	51±2	53±6	102±14	105±12
Ni	12.0±3.25	12.9±1.80	12.2±3.54	240±16	275±27	227±13	50±5	50±5	49±13	34±6	30±3	32	103±17	106±11
Pb	1448±108	1454±188	1447±203	400±21	395±10	391±16	75.1±12	74.1±10	75.8±16	78±5	75±5	79±12	100±10	99±10
Zn	55.0±8.14	60.6±11.0	51.8±8.29	316±18	339±26	316±41	167±30	168±30	169±39	248±38	245±24	251	101±14	105±14

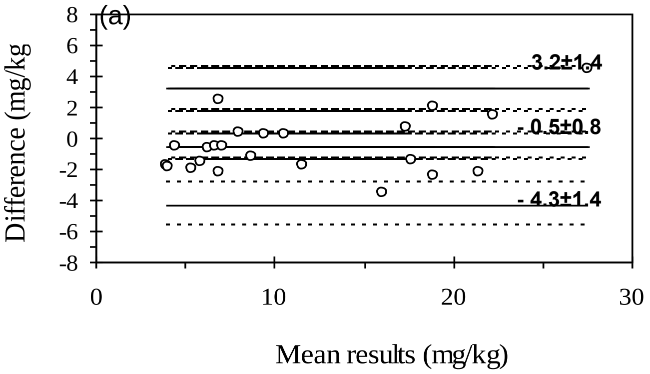
[a] – mean ± U (U – uncertainty for a confidence coefficient of 95%)

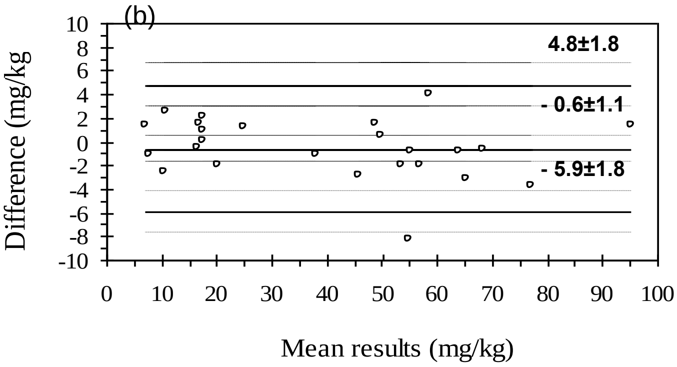
[b] – mean recovery for a confidence coefficient of 95%

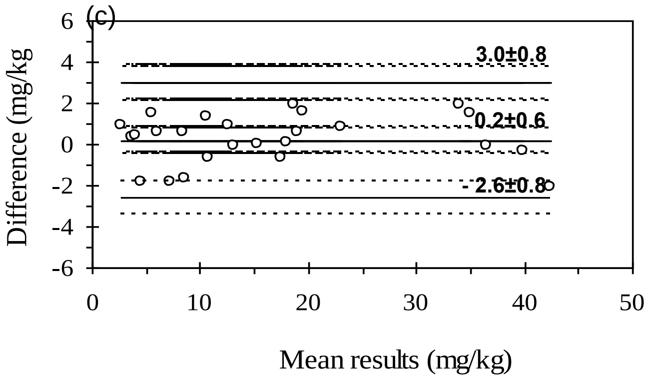
Table 9.7. Description for the Bland & Altman statistical test (confidence coefficient of 95%, m=3 indipendent samples) [325].

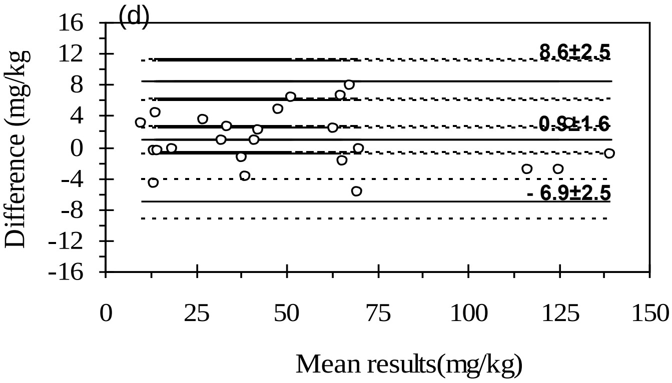
Element	Standard deviation of the method (mg kg^{-1})		Standard deviation between methods (s_B) (mg kg^{-1})	Confidence intervals systematic error $\bar{\Delta} \pm t\frac{s_B}{\sqrt{n}}$ (mg kg^{-1})	Confidence intervals confidence limits $\bar{\Delta} \pm 1.96 s_B \pm t \cdot s_{LL,UL}$ (mg kg^{-1})
	ICP-AES	HR-CS-FAAS			
Ag (n=25)	0.4	0.3	1.8	-0.5±0.8	-4.1±1.3 3.1±1.3
Cd (n=25)	1.0	0.8	2.7	-0.6±1.1	-5.9±1.8 4.8±1.8
Co (n=25)	0.7	0.7	1.4	0.2±0.6	-2.6±0.8 3.0±0.8
Cr (n=25)	1.3	1.4	3.9	0.9±1.6	-6.9±2.5 8.6±2.5
Cu (n=34) (<1000)[a]	30.1	18.7	33.4	4.8±11.7	-60.8±14.0 70.3±14.0
Cu (n=16) (1000-22000)[a]	260	246	390	-57±208	-821±258 707±258
Ni (n=25)	0.9	1.9	2.5	-0.4±1.0	-5.3±1.3 4.5±1.3
Pb (n=28) (<1000)[a]	29.6	22.9	42.5	4.9±16.5	78.3±20.8 88.2±20.8
Pb (n=14) (1000-10000)[a]	174	56	214	-36±123	-455±162 383±162
Pb (n=13) (10000-60000)[a]	712	494	1477	-243±893	-3138±1343 2652±1343
Zn (n=30) (< 1000)[a]	7.5	5.2	13.2	-3.3±4.9	-29.1±6.9 22.6±6.9
Zn (n=20) (> 1000)[a]	122	90	169	13±79	-319±100 345±100

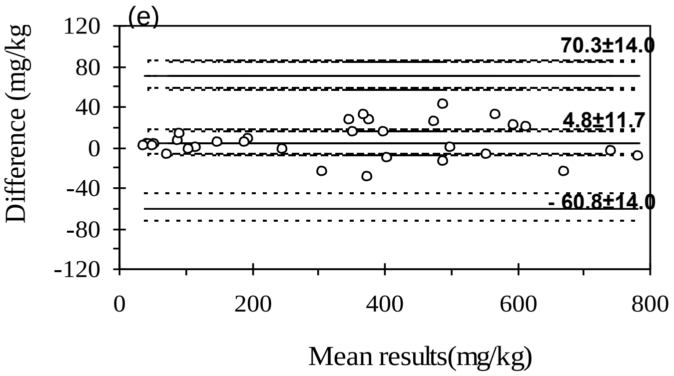
[a] – concentration range in mg kg^{-1}; n – number of samples

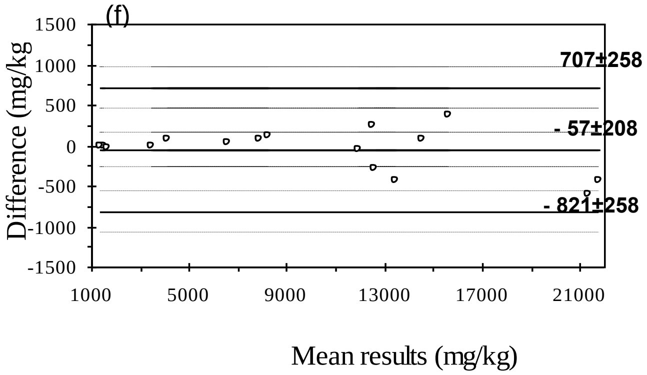

(a)
Difference (mg/kg
8
6
4
2
0
-2
-4
-6
-8
3.2±1.4
- 0.5±0.8
- 4.3±1.4
0
10
20
30
Mean results (mg/kg)

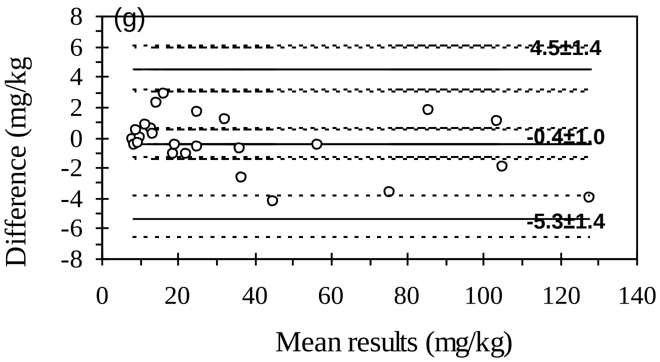

(b)
Difference (mg/kg
10
8
6
4
2
0
-2
-4
-6
-8
-10
4.8±1.8
- 0.6±1.1
- 5.9±1.8
0
10
20
30
40
50
60
70
80
90
100
Mean results (mg/kg)

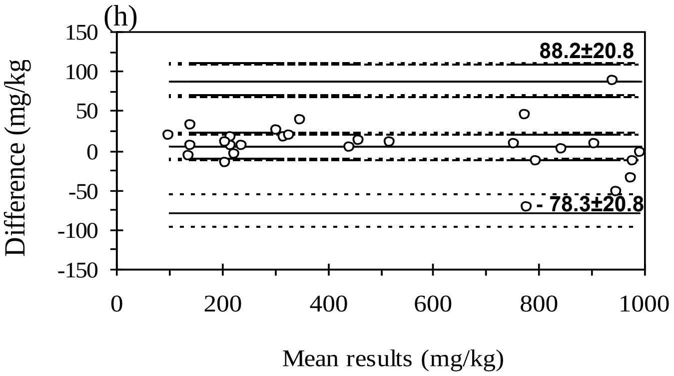

(c)
Difference (mg/kg
6
4
2
0
-2
-4
-6
3.0±0.8
0.2±0.6
- 2.6±0.8
0
10
20
30
40
50
Mean results (mg/kg)


(d)
Difference (mg/kg
16
12
8
4
0
-4
-8
-12
-16
8.6±2.5
0.9±1.6
- 6.9±2.5
0
25
50
75
100
125
150
Mean results(mg/kg)


(e)
120
80
40
0
-40
-80
-120
Difference (mg/kg
70.3±14.0
4.8±11.7
- 60.8±14.0
0
200
400
600
800
Mean results(mg/kg)


(f)
1500
1000
500
0
-500
-1000
-1500
Difference (mg/kg
707±258
- 57±208
- 821±258
1000
5000
9000
13000
17000
21000
Mean results (mg/kg)


(g)
8
6
4
2
0
-2
-4
-6
-8
Difference (mg/kg
4.5±1.4
-0.4±1.0
-5.3±1.4
0
20
40
60
80
100
120
140
Mean results (mg/kg)


(h)
150
100
50
0
-50
-100
-150
Difference (mg/kg
88.2±20.8
- 78.3±20.8
0
200
400
600
800
1000
Mean results (mg/kg)

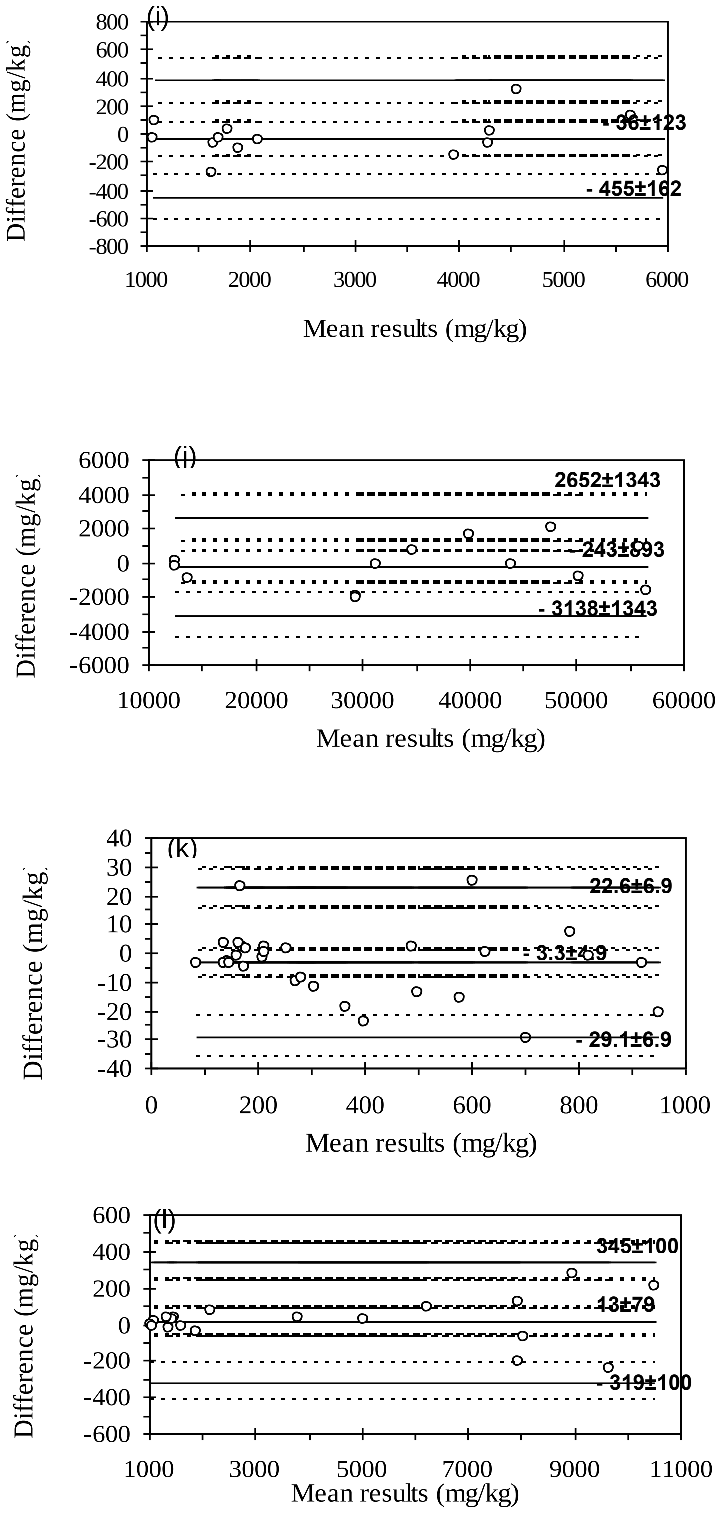


Figure 9.4. Bland and Altman reprezentations: (a) Ag (n=25); (b) Cd (n=25); (c) Co (n=25); (d) Cr (n=25); e) Cu (n=34 < 1000 mg kg^{-1}); (f) Cu (n=16 > 1000 mg kg^{-1}); (g) Ni (n=25); (h) Pb (n=28 < 1000 mg kg^{-1}); (i) Pb (n=12 între 1000-10000 mg kg^{-1}); (j) Pb (n=13 > 10000 mg kg^{-1}); (k) Zn (n=30 < 1000 mg kg^{-1}); (l) Zn (n=20 > 1000 mg kg^{-1}). n– number of samples [325].

In these circumstances is obvious that the new instrumental concept based on HR-CS FAAS, can be successfully applied for the determination of priority and priority hazardous metals in soil, with similar performances of ICP-AES.

X. RESULTS, NOVELTY AND CONCLUSIONS. RESEARCH PERSPECTIVES

As it was shown in the first chapter of this thesis, 2 main objectives and 11 specific objectives were named. The achieved results and the conclusions issuing from these objectives are the followings:

- The waste management monitoring showed the implementation of some integrated waste management system both for municipal and special (WEEE, waste batteries and accumulators, medicals) waste. The activity in the major part of the non-conforming landfills was stopped, at the moment thay are in different post-closing ecologizing and monitoring stages. All the hospital crematoriums were closed. In 2005 in the NV6 Region the first municipal waste landfill was opened at Oradea, and the first conforming incinerator for hazardous medical waste was put in operation at Cluj-Napoca, and in the year 2012 the first integrated waste management center was started to build in Cluj County.
- The evaluation of chemical and material composition of waste revealed a heterogeneous composition and concentrations varying in a large range for the studied indicators. The solid municipal waste, WEEE, batteries and accumulators proved to be important sources of raw material and of energy. An integrated waste management programme relies on five pillars: (i) reducing the waste quantity at the source, (ii) reuse, (iii) priority, mechanical and chemical recycling of waste, (iv) energetic valorification of waste, (v) safe storage of original or processed waste.
- Evaluation of the priority and priority hazardous metal contents of ash resulted from the pharmaceutal and hazardous industrial waste incineration at the Hoval Multizon installation at Cluj-Napoca led to the categorization of the bottom ash as inert waste, and the fly ash retained in filters of the dust-control equipment as hazardous waste being highly polluted with Pb, Cu, Ni, Cr, Co, Sb, Cd and Hg. The fly ash released into the atmosphere as suspensed particles do not represent contamination risk to the air.
- The evaluation of contamination risk of surface water and groundwater by the leachate escaped from the MSW stored in the Pata Rât landfill revealed the exceedings in the case of Cu and Cr of the quality standards for waste waters which are allowed to be released

into the aquqtic environment. The highest contamination risk of the surface waters and groundwater is mainly attributed to the ammonium ion, chloride, nitrate, nitrite and sulphate.

- The Zapodie stream situated next to the Pata Rât landfill is potencially contaminated with ammonium ions originating from the leachate which escapes from the landfill and reaches the stream. The quality of the stream water is poor, and is categorized in the Vth quality group.
- The soil in the area of non-conforming landfill from Pata Rât is principally contaminated with Pb, whose concentration values exceeded the alert limits for sensible soils, followed by Cu and Ni whose concentrations exceeded the normal background levels. In agreement with the Hakanson methodology Cd and Zn should be equally considered.
- The comparative study of the contamination risk of the soil in the area of municipal waste landfills revealed exceedings of the normal, alert and intervention limits for sensible soils in the case of Pb, Cu, Ni, Zn, according to the landfills. The highest shares to the contamination risk related to the alert limit were obtained for Pb (100% in the case of Pata Rât and Bistriţa landfills, 53% for the landfill from Gherla, the remaining 47% being determined by Cu).
- The comparative evaluation of the contamination risk of the soil by the waste stored in industrial landfills resulted in the evidence of much more elevated concentration levels of metals against the municipal waste landfills. Shares as high as 100% against the alert limits were found for Pb (at the Uzina Electrică Zalău), Zn (at the Ario Bistriţa) and Cd (at the Dan Steel Beclean).
- In agreement with the Hakanson methodology, the MSW landfills exhibited, as usual, a moderate contamination degree with priority and priority hazardous metals, as for the industrial waste landfills exhibited a considerable contamination degree (Beclean, Uzina Electrică Zalău and Silcotub Zalău), and a very high contamination degree (Iaifo Zalău), due mainly to Cd.
- The contamination risk of water by the leachate generated by used batteries is attributed to the priority hazardous metals (Hg, Pb and Ni), and by the municipal waste is attributed to priority metals, namely Cu and Cr.
- Evaluation of contamination risk with Pb by the leachate generated from the CRT monitors stated that the funnel glass constitutes a higher risk, than the screen, which can be considered an inert waste.
- The interpretation of the multivariate statistical results (PCA şi CA) enabled to identify the sources of the priority and priority hazardous components of the leachate, to

categorize the chemical quality indicators which have the highest influence over the variability of chemical composition of the leachate and of the soil, and to group the chemical indicators and the landfills by Claster Analysis.

- The Bland and Altman statistical test was used for the validation of the high-resolution continuous-source flame atomic absorption spectroscopy (HR-CS FAAS). This method contributed to the extension of the applicability of this concept as an alternative to ICP-AES for the analysis of priority and priority hazardous metals (Ag, Cd, Co, Cr, Cu, Ni, Pb and Zn) in soil, due to its attractiveness such as the fast determinations, multielemental analysis, easy operation in the correction of spectral interferences.

PERSPECTIVES OF THE RESEARCH

1. To obtain supplementary data by advanced elemental speciation methods, which rely on metal fractionation in the soil, and in the biodegradable residue of waste.
2. To carry out comparative studies on the bases of elemental speciation with regard to the metal distribution in the soil in the area of municipal and industrial waste landfills and to establish factors that influence the mobility of metals from the waste to the deeper layers of the soil.
3. To carry out elemental speciation study in order to fractionate the priority and priority hazardous metals in the ashes from the incinerators and in the compost produced in mechanical-biological treatment station to find out a possible influence on the soil and on the water.
4. Studies related to the implementation of some technologies for the recovery of useful metals from WEEE and CRT monitors, which imply both elemental analyses and non-distructive speciation analyses using X-ray diffraction and methods of elemental imagistic analyses of surfaces of metters.

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