

ATOMIC AND NUCLEAR SPECTROMETRIC METHODS WITH HIGH SENSITIVITY APPLIED IN THE STUDY OF ENVIRONMENTAL POLLUTION WITH HEAVY METALS: SYNTHESIS

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Abstract. *The paper contains a synthesis of results obtained in the study of environmental pollution with heavy metals by application of Atomic and Nuclear Analysis Methods (MAN) in combination with the biomonitoring technique using bioindicators: mosses and lichens, edible wild mushrooms and their substrate and surface waters. Samples were collected from different geographic areas of Romania. Analyses of heavy metals (Cr, Mn, Fe, Ni, Cu, Zn, Cd, Se, Pb) by MAN from the samples of moss and lichens, edible wild mushrooms (and their substrate) and surface waters were performed. Concentration values of heavy metals in moss and lichens, determined by MAN, were statistically interpreted and distribution maps were made. Analysis of edible wild mushrooms samples are resulted in a higher accumulation of Fe, Cu and Zn in the their substrate. In order to characterize the quality of surface waters (Olt and Potop Rivers), quality indicators (pH, electrical conductivity, salinity, turbidity and TDS) were determined. The statistical interpretation led to a linear correlation between TDS and conductivity and total hardness and conductivity. Concentrations of heavy metals in surface water samples obtained by MAN were compared to the maximum permissible limits.*

Keywords: environmental pollution, methods, heavy metals, moss, lichens, wild mushrooms, water

1. Introduction.

Atomic and Nuclear Analytical Methods (ANM) are based on techniques in which use is made of the properties of the atoms (like X-ray fluorescence spectrometry in all variants) and nuclei (like activation analysis nuclear reactions) [1 – 24].

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The basic characteristics of NAMs such as high precision and sensitivity in the identification and quantitative determination of several chemical elements are the result of the linearity of the calibration function covering a range of concentrations of several orders of magnitude. Because some NAMs require expensive installations (nuclear reactors, particle accelerators, atomic spectrometers and so on) and their availability is limited to a small number of appropriately equipped institutes.

The researches based on advanced analysis methods and techniques of high and ultra-high sensitivity using electromagnetic radiations and accelerated particle beams have been imposed for the solving of some necessities with interdisciplinary character, in many fields like the environment, biology, life science, archaeology, material science and so on.

So far, in Multidisciplinary Research Institute of Science and Technology of Valahia University of Targoviste (ICSTM-UVT), have been implemented a variety of elemental analysis methods, with high sensibility applied in different research domains . At the same time UVT have partnership agreements for using experimental facilities with National Institute for Physics and Nuclear Engineering Horia Hulubei (IFIN-HH) from Bucharest and Joint Institute for Nuclear Research from Dubna-Rusia(JINR-Dubna). These methods are based on charged particle beams, electromagnetic radiations and neutrons flux provided by a nuclear reactor [1, 2].

Spectrometric techniques are based on the data delivered by characteristic energy transfers between radiations and matter[1,2]. They provide information about the nature and concentration of elements in either crystallized or non-chrySTALLIZED materials, in any type of material. To some degree, they provide additional information about chemical bonds. Energy transfers during interaction with high-energy radiations can be expressed in two complementary ways: alteration of matter and alteration of radiation, the total energy being preserved. This results in the following complementary effects which are exploitable for spectrometry:

- Excitation-de-excitation processes of atomic levels leading to characteristic emission of radiations (like X-Rays, electron emission),

- Characteristic absorbtion processes,

- Gamma Ray emission in neutrons activation method and nuclear reactions.

Those three types of effects provide data which are theoretically identical and can both be used for analytical purposes, leading, respectively, to two groups of techniques:

- absorption spectroscopy wich is including atomic absorption spectrometry (AAS),

-emission spectroscopy which includes Induced Coupled Plasma (ICP), etc.

-secondary emission spectrometry which including X-ray fluorescence analysis (XRF), Particle Induced X_Rays Emmission (PIXE).

The data provided by any spectrometric methods are expressed in terms of a spectrum processing which depends on the basic physical effect.

Qualitative analysis requires us to identify a given element by means of one or several characteristic emission lines or absorption lines. Identifying of the major elements is mostly straightforward. Analysing the minor elements or the trace elements is determined by the sensitivity of the method; it may vary over a large range, depending on the physical process involved, on the atomic number and on the instrumental characteristics. The main parameter in qualitative and quantitative analysis is the detection limit of elements. For a given analytical method, the detection limit depend on the element to be analysed and on the chemical element which contain it. The aim of quantitative analysis methods is to determine the mass fraction of any detectable elements in a specimen. For a given element should be measured the intensity of a characteristic emission lines. The intensity measurement provided by a atomic spectrometer depends on three kinds of parameters: physical parameters characterising the nature and the concentration of the element to be analysed; physical parameters due to any other elements in the specimen (matrix effects); and instrumental parameters.

2. Experimental methods

In this synthesis are shown the following analytical methods and their applications in analysis of minor and trace elements including heavy metal in bioindicators for the study of environmental pollution and certain specific biological samples: Atomic Absorption Spectrometry (AAS) Atomic absorption spectrometry (AAS) in variants: with flame (Flame AAS) and with graphite tube (Graphyte Flame AAS)[3,4,5,6,7,8,9,10]; Atomic Emission Spectrometry (AES) in the variants: Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) [8,9,10,11,12,13,14]; X-Ray Fluorescence Spectrometry(XRF) in three variants: Energy Dispersive X-Ray Fluorescence (EDXRF), Wave Dispersive X-Ray Fluorescence (WDXRF))[16,17,18,19,20,21] and Particle Induced X-Ray Emission Spectrometry (PIXE) [22, 23, 24, 25,26, 27]. A nuclear method is Neutron Activation Analysis Spectrometry (NAA)[28, 29, 30,31,32,33,34,35], which is based on the nuclear process of neutron capture by the atomic nucleus, to determine the concentrations of the elements in a vast amount of materials.

As bioindicators we used the following samples: mosses, lichens, soils, vegetables and fruits, surface water and deep waters.

2.1. Atomic Absorption Spectrometry (AAS)

Atomic Absorption Spectrometry (AAS) [3 - 10] is an analytical method for the quantitative determination of trace elements using the absorption of optical radiation (light) by free atoms in the gaseous state. AAS can be used to determine over 70 different elements in solution or in solid samples (processed in liquid form) contained in the large spectrum of samples: environmental, biological, metallurgical, archaeological, pharmaceutical and so on. AAS is based on the exponential Lambert-Beer law [10]. The law Lambert-Beer is rigorously respected only for a monochromatic radiation. The intensity of a beam of radiation transmitted through the atomic vapor cloud sinks decreases exponentially with the thickness of the layer of substance permeated. The Lambert-Beer is usually written as: $A = a(\lambda) \times b \times c$, where A is the measured absorbance, $a(\lambda)$ is a wavelength-dependent absorptivity coefficient, b is the path length, and c is the analyte concentration. Data are frequently reported in absorbance $A = \ln(I/I_0)$, where I is the light intensity after it passes through the sample and I_0 is the initial light intensity. Experimental measurements are usually made in terms of transmittance T , which is defined as: $T = I / I_0$. The relation between A and T is: $A = -\ln T = -\ln(I/I_0)$. Modern absorption instruments can usually display the data as either transmittance, %-transmittance, or absorbance. An unknown concentration of an analyte can be determined by measuring the amount of light that a sample absorbs and applying Lambert-Beer law [10].

In the last time, atomic absorption spectrometer (AAS) are selective detectors for elemental concentrations, and some of the spectrometer also show multielement analysis capability [24]. There are flame (FAAS) and graphite furnace (GFAAS) systems. In comparison with FAAS, GFAAS requires only a few microliters of sample and provides low detection limits, between 0.1 - 5 ppm. AAS method, in two technical variants, applies only in relative measurements.. It is a method of analysis monoelement. Sensitivity of the method is in the range, ppb–ppm.

2.2. Atomic Emission Spectrometry. ICP (Induced Coupled Plasma)

Atomic emission spectrometry (AES)[8 - 15] is an analysis technique of chemical elements, minor and trace elements, that uses the intensity of light emitted from a flame, plasma, arc, or spark at a particular wavelength to determine the elemental concentration in a sample. The wavelength of the atomic spectral line gives the identity of the element while the intensity of the emitted light is proportional to the number of atoms of the element (the concentration).

A sample of a material (analyte) is brought into the flame as a gas, sprayed solution, or directly inserted into the flame by use of a small loop of wire, usually platinum. The heat from the flame evaporates the solvent and breaks chemical

bonds to create free atoms. The thermal energy also excites the atoms into excited electronic states that subsequently emit light when they return to the ground electronic state. Each element emits light at a characteristic wavelength, which is dispersed by a prism and detected in the spectrometer. ICP analysis spectrometry is applied in two versions: Inductively Coupled Plasma- Emission Spectrometry (ICP-AES) or Inductively Coupled Plasma- Optical Spectrometry (ICP-OES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Through these techniques, both qualitative (identification of elements in sample) and quantitative (concentrations of elements in sample) elemental analyzes are performed. It is a qualitative, and in the same time quantitative analysis method.

2.2.1 Inductively coupled plasma atomic emission spectrometry (ICP-AES), uses an inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of any chemical element in sample [3,6,8,10-12]. The plasma torch confines the plasma to a diameter of about 18 -20 mm. Plasma is generated using a radiofrequency generator at 40.68 MHz. Atoms and ions produced in the plasma are excited and emit light. The intensity of light emitted at wavelengths characteristic of the chemical element of interest is measured and related to the concentration of each element from sample. ICP-AES spectrometer use argon gas and the argon plasma is sustained in a quartz torch. The detection system used is a sequential monochromator with a wavelengths range (160-800) nm. The emission spectra are recorded using a personal computer. ICP-AES is a multi-element analysis method of high sensitivity. Advantages of ICP-AES [7] are excellent limit of detection and linear dynamic range, multi-element analysis, low chemical interference and a stable and reproducible signal. Disadvantages are spectral interferences (many emission lines), cost and operating expense and the fact that samples typically must be in a liquid solution. The detection limits for a large spectrum of elements are in the range of concentrations (1 ppb - 1 ppt).

2.2.2. Inductively coupled plasma mass spectrometry (ICP-MS) [3, 13, 14], it is a high sensitivity and high precision analysis technique, has greater speed in analyses, due to the coupling of the atomic emission spectrometer using inductively coupled plasma (ICP) with a mass spectrometer (MS) which is capable of detecting chemical elements at very low concentrations (part per billion, ppb, up to quadrillion, ppq) on low-background isotopes. This is achieved by ionizing the sample with inductively coupled plasma and then using a mass spectrometer to separate and quantify those ions. For coupling to mass spectrometry, the ions from the plasma are extracted through a series of cones into a mass spectrometer, usually a quadrupole. The ions are separated on the basis of their mass-to-charge ratio and a detector receives an ion signal proportional to the concentration, recording in a computer.

The concentration of a sample can be determined through calibration with certified reference material such as single or multi-element reference standards. ICP-MS also lends itself to quantitative determinations through isotope dilution, a single point method based on an isotopically enriched standard. The variety of applications exceeds that of inductively coupled plasma atomic emission spectroscopy (ICP-AES) and includes isotopic analyses. ICP-MS has many advantages over other elemental analysis techniques, including: detection limits for most elements equal to or better than those obtained by AAS and XRF methods; the ability to handle both simple and complex matrices with a minimum of matrix interferences due to the high-temperature of the ICP source; superior detection capability to ICP-MS with the same sample throughput; the ability to obtain isotopic information. ICP-MS has a large spectrum of applications including in nuclear technologies.

2.3.X-Ray fluorescence Spectrometry

X-Ray Fluorescence (XRF)[15,16,17,18,19,20] consist in emission of characteristic X- rays of the atoms, from a material, that have been excited by bombarding with high energy X-rays (emitted by a X-Ray tube) , gamma rays (emitted by a radioactive source) or accelerated charged particles (proton, alfa, heavy ions) using an particle accelerator [21 - 24]. X-Ray fluorescence spectrometry is widely used for elemental analysis heavy metals (for instance in the investigation of environmental samples collected from different gheographycal zone considered polluted), biologicaly samples, archaeological, etc. XRF spectrometry can be applied in following experimental arrangements: Energy Dispersive X-Ray Fluorescence (EDXRF), Wave Dispersive X-Ray Fluorescence (WDXRF) and Particle Induced X-Ray Emission (PIXE).

2.3.1.Energy dispersive X-ray fluorescence (EDXRF)

The EDXRF[15 - 20] analyzer uses an primary X-ray source (X-ray tube, radioactive gamma ray source) to excite the sample and it may be configured in one of two ways: the first way is direct excitation, where the X-ray beam is pointed directly at the sample. Can be used also a filter made of various elements may be placed between the source and sample to increase the excitation of the element of interest or reduce the background in the region of interest. The second way uses a secondary target, where the source points at the target, the target element is excited and fluoresces, and then the target fluorescence is used to excite the sample. A detector is positioned to measure the fluorescent and scattered x-rays (characteristic X-ray emission) from the sample and a multichannel analyzer and software assigns each detector pulse an energy value thus producing a spectrum. The sensitivity of this analysis method can be is in the range 1 ppm up to 10 ppm.

2.3.2. Wave Dispersive X-ray fluorescence (WDXRF)

The WDXRF [15 – 20] spectrometer uses a X-ray source (X ray tube) to excite atoms contained in the sample. X-rays that have wavelengths that are characteristic to the elements within the sample are emitted and they along with the scattered source X-rays go in all directions. A crystal or other diffraction device is placed in the way of the X-rays coming off the sample. A X-ray detector is positioned where it can detect the X-rays that are diffracted and scattered off the crystal (Bragg law). Depending on the spacing between the atoms of the crystal lattice (diffractive device) and its angle in relation to the sample and detector, specific wavelengths directed at detector can be controlled. The angle can be changed in order to measure elements sequentially, or multiple crystals and detectors may be arrayed around a sample for simultaneous analysis. Sensitivity at a lower level 1 ppm.

2.3.3. Particle Induced X-ray Emission (PIXE)

Particle-Induced X-Ray Emission (PIXE)[21 - 24] is a technique also used in the determining of the elemental concentrations from a large spectrum of materials. When a material is exposed to an ion beam (proton, alpha-particle, heavy ions) provided by an accelerator, atomic interactions occur that give of electromagnetic radiation of wavelengths in the X-ray part of the electromagnetic spectrum specific to an element. PIXE is a powerful non-destructive elemental analysis technique now used routinely in a large spectrum of scientific fields. The technique was first proposed in 1970 by Sven Johansson of Lund University, Sweden [21,22] and developed over the next years in many countries, including in Romania, at Institute for Physics and Nuclear Engineering (IFIN HH). A recent extension of PIXE using highly focused beams (down to 1 μm) gives the additional capability of microscopic analysis. This technique, called microPIXE, can be used to determine the distribution of trace elements in a wide range of samples. In PIXE elemental analysis method the In PIXE elemental analysis method the sensitivity is in the ppm range.

2.4. Nuclear Activation Analysis (NAA)

Neutron Activation Analysis (NAA) [29 - 34] is a sensitive multi-element analytical technique used for both qualitative and quantitative analysis of major, minor, trace and rare elements from any samples: for determining the concentrations of elements in a materials (environmental, metallic and nonmetallic, historical artifacts, etc.). NAA method is based on neutron capture reaction of nuclei. Therefore the NAA spectrometry requires a source of neutrons- nuclear reactor with high neutron flux, about 10-14 n/cm²s .The sample is bombarded with neutrons, causing the elements to form radioactive isotopes. The radioactive emission and radioactive decay paths for each element are well known. Using this information, it is possible to study spectra of the gamma emissions of the radioactive sample, and determine the concentrations of

the elements within it. NAA can also be used to determine the activity of a radioactive sample. By NAA method may be analyzed a wide spectrum of different chemical elements contained in sample: from F up to U. Over 62 chemical elements can be analyzed with NAA. But is relatively expensive to be used this nuclear analysis technique because can be applied only at a nuclear reactor. Until the introduction of the ICP-MS and PIXE analysis techniques, NAA was the standard analytical method for performing multi-element analyses with minimum detection limits in the ppm -ppt range.

3. Experimental results

3.1.Sources and effects of heavy metals

Heavy metals [7, 32, 34,35], are emitted mainly as a results of various combustion processes and industrial activities like metals works and smelters. The contribution of various sources to emissions of heavy metals across Europe has changed in recent decades. The most important emission sectors include:

Metals industry (Al, As, Cd, Cr, Cu, Fe, Pb, Zn); Other manufacturing industries and construction (As, Cd, Cr, Hg, Ni, Pb); Electricity and heat production (Cd, Hg, Ni); Road transportation (Cu and Sb from brake wear, Pb, V, Zn from tires); Petroleum refining (Ni, V); Phosphate fertilisers in agricultural areas (Cd).

As well as polluting the air, heavy metals are deposited on terrestrial or water surfaces and subsequently build up in soils or sediments. Heavy metals are persistent in the environment and may bioaccumulate in food chains. Atmospheric deposition of metals has a direct effect on the contamination of crops used for animal and human consumption. In particular, leafy vegetables and fodder crops can accumulate heavy metals. Washing leafy vegetables before consumption reduces the risk of exposure by humans considerably.

Up to now we analysed heavy metals concentrations in many bioindicators: mosses, lichens, soils, vegetables and fruits, surface water and deep waters.

3.2.Mosses and lichens analysis as bioindicators

The heavy metals in mosses biomonitoring network was originally established as a Swedish initiative[34]. The idea of using mosses to measure atmospheric heavy metal deposition is based on the fact that carpet forming, ectohydric mosses obtain most trace elements and nutrients directly from precipitation and dry deposition; there is little uptake of metals from the substrate. The technique of moss analysis provides a time-integrated measure of heavy metal deposition from the atmosphere to terrestrial systems. It is easier and cheaper than conventional precipitation analysis as it avoids the need for deploying large numbers of precipitation collectors with an associated long-term programme of routine

sample collection and analysis. In recent decades, mosses have been applied successfully as biomonitors of heavy metal deposition across Europe. Heavy metal concentrations in moss provide a complementary, time-integrated measure of the spatial patterns and temporal trends of heavy metal deposition from the atmosphere to terrestrial systems, at least for the metals Cd and Pb [34].

The aim of this study was to assess the air quality in Romania using terrestrial moss, to reveal highly polluted critical regions in the country in order to permanently survey the degree of atmospheric pollution and to contribute to the European moss survey 2010/11 conducted under the auspices of the UNECE ICP Vegetation covering some “white areas” in the map of atmospheric deposition of heavy metals in Europe [34]. Within the bilateral project JINR- Romania, “Nuclear and related analytical techniques for Environmental and Life Sciences”, moss samples were collected during the summer/autumn of 2010 at 330 sites in Romania: in the Carpathian Mountains, Transylvanian plateau, and Moldavia province, following internationally accepted guidelines. Nuclear analytical technique Neutron Activation Analysis (NAA, JINR-Dubna, Russia) and Atomic Absorption Spectroscopy (AAS-Valahia University of Targoviste, Romania) were used to determine the concentration of minor and trace elements in moss samples collected in 2010 from Romania. The results for mean, median and geometric mean are compared with those previously obtained in 1990, 1995 and 2000 campaigns and the maps of the distribution of heavy metals were realized. A total of 42 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Ag, Cd, In, Sb, I, Cs, Ba, La, Ce, Sm, Eu, Tb, Hf, Ta, W, Au, Hg, Pb, Th, and U) were determined by NAA (JINR-Dubna) of which three of them (Cu, Cd, Pb) were determined by AAS (Valahia University of Targoviste) Romania [34].

The moss biomonitoring technique was employed to study the atmospheric deposition in Dambovita County Romania (in the period 2010-2015) together with complementary nuclear and atomic analytical methods: Neutron Activation Analysis (NAA), Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). These high sensitivity analysis methods were used to determine the elemental composition of some samples of moss placed in different vision areas with different pollution industrial sources. The concentrations of Cr, Fe, Mn, Ni and Zn were determined. The concentration of Fe from the same samples was determined using all these methods and we obtained a very good agreement, in statistical limits, which demonstrate the capability of these analytical methods to be applied on a large spectrum of environmental samples with the same results [34 - 43].

As bioindicators were used, *Sphagnum* species of moss have been considered especially suitable for monitoring heavy metal pollution due to the high caption-

exchange capacity of their cell walls. Very useful results have been obtained with this type of moss in flat and spherical moss-bags. In order to optimize the assessment of atmospheric pollution in an industrial area using active biomonitoring a novel sampling design was introduced, and transplants the moss *Sphagnum girgensohnii* were deployed in parallel in order to study the uptake of a series of trace chemical elements from the air over a defined time period. The site selected for this experiment was Dambovita County, Romania.

Three moss-bags were hung in parallel by means of a T-shaped support system made of wood. Moss *Sphagnum girgensohnii* was hanged in bags at 17 different locations (table 1), in February 2006, and analyzed by NAA, AAS and ICP-AES methods, respectively, after 1, 2 and 3 months of exposure to precipitation and wind.

Table 1. Zones of localization samples

<i>Samples code</i>	<i>Zones of localization samples</i>
1	Moroieni
2	Fieni
3	Pucioasa
4	Voineşti
5	Gheboieni
6	Moreni
7	Doiceşti
8	Viforâta
9	Teiş
10	Târgovişte N-V
11	Târgovişte V
12	Târgovişte E
13	Adâncă
14	Ulmi
15	Picior de Munte
16	Morteni
17	Tărtăşeşti

3.2.1 Experimental.

NAA (Neutron Activation Analyses) were performed at the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia. AAS and ICP-AES methods were applied in Multidisciplinary Research Institute for Science and Technology of Valahia University Targoviste (ICSTM-UVT), respectively..

In IUCN Dubna, conventional and epithermal NAA at the IBR-2 pulsed fast reactor FLNP JINR Dubna, Russia (Frontasyeva and Pavlov, 2000,[42]) were used to determine concentrations of following elements: Cr, Mn, Ni, Fe, Zn.

The Atomic Absorption Spectrometer used by us is an AAS-AVANTA GBC with hollow cathode lamp (HCL). Measurements were made separately for each element of interest from sample using the calibration curve – absorbance versus concentration.

ICP-AES (Inductively Coupled Plasma- Atomic Emission Spectrometry) method used is based on the fact that the atoms and ions produced in the plasma are excited and emit light. The intensity of light emitted at wavelengths characteristic of the particular elements of interest is measured and related to the concentration of each element from samples.

The ICP-AES spectrometer used was Baird ICP2070 - Sequential Plasma Spectrometer.

The AAS and ICP-AES techniques were applied in the determination of elemental concentration in the same sample of moss *Sphagnum girgensohnii*.

For the AAS and ICP-AES analysis, portions of about 0.4 g moss were decomposed with 4mL of concentrated nitric acid in a microwave oven. The extracts were then filtered and distilled water was added to a total volume of 25 mL. The presence of possible contaminants during the digestion process was controlled using blanks. Accuracy was checked by analysis of three replicates of references material IAEA 336, lichen.

3.2.2. Results and discussion

The analytical performance was checked by the regular analyses of the standard reference materials (SRM IAEA-336, lichen and moss) issued by the International Atomic Energy Agency.

The concentration values obtained in our study are presented in Tables 2 and 3, together with the concentration values of elements in SRM IAEA-336. In the next diagrams (figs. 6, 7) are presented the comparison between the values concentrations in moss obtained by us and the concentration from standard reference material [35,43].

Table 2. The mean values of elemental concentration (mg/kg) determined in mosses by NAA

<i>Samples code</i>	<i>Cr</i>	<i>Mn</i>	<i>Ni</i>	<i>Zn</i>
1	0.95±0.25	198.67±9.87	1.80±0.22	19.00±0.70
2	1.60±0.53	202.37±10.05	2.30±0.48	66.59±2.51
3	2.04±0.29	157.23±8.28	2.28±0.25	110.38±3.57
4	1.54±0.56	177.40±8.81	2.19±0.41	21.20±0.93
5	1.85±0.54	155.37±8.13	2.63±0.40	21.75±0.94
6	0.73±0.63	179.15±8.33	2.76±0.58	352.62±13.75
7	3.06±0.76	178.70±9.35	1.93±0.47	51.19±2.25
8	1.66±2.29	859.93±44.43	2.06±1.03	32.52±2.35
9	2.49±0.29	148.00±7.75	2.04±0.21	24.98±0.88
10	7.08±1.72	182.97±9.58	1.97±0.63	33.02±2.03
11	26.17±1.97	164.83±8.24	5.62±0.84	121.93±5.12
12	13.08±1.47	274.97±13.66	3.61±0.57	63.31±2.66
13	1.76±0.79	188.23±9.35	2.07±0.54	43.60±2.03
14	8.64±0.81	157.70±8.04	2.80±0.25	40.22±1.35
15	3.69±1.01	608.50±31.64	3.31±0.93	97.98±5.16
16	1.12±0.97	184.33±9.65	1.20±0.55	23.53±1.47
17	1.09±2.33	189.13±9.46	0.94±0.55	48.84±2.62
SRM -336, [10]	1.06±0.092	246±2.9	3.5±0.35	30.4±1.4

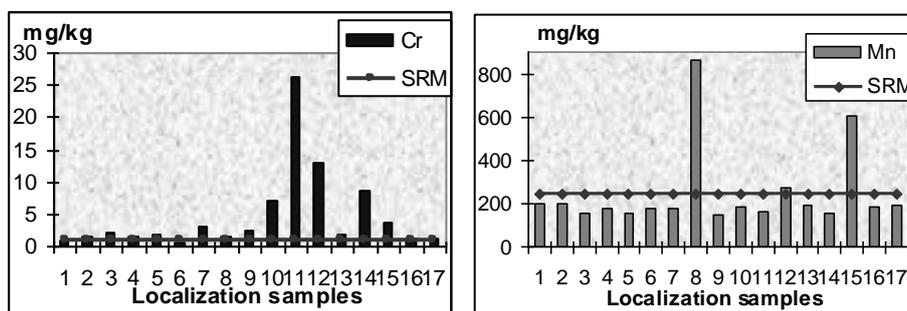


Fig. 6. The comparison between the Cr and Mn concentrations from moss determinate by NAA and their concentration from standard reference material.

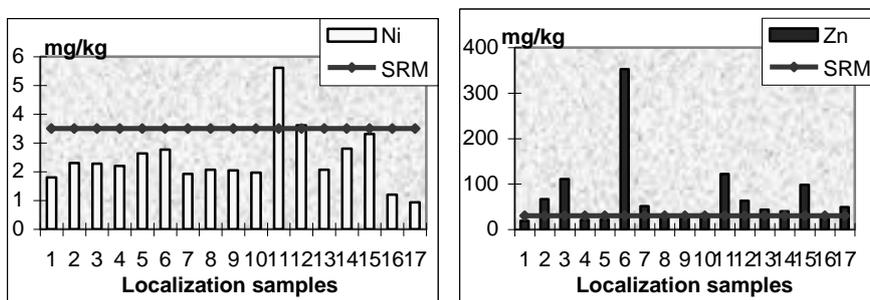


Fig. 7. The comparison between the Ni and Zn concentrations from moss determinate by NAA and their concentration from standard reference material

In the last part of our experiment we applied the NAA, AAS and ICP-AES methods in determination of the Fe concentration from the same type of samples: moss *Sphagnum girgensohnii*. The comparisons of results are given in table 3 and figure 8.

Table 3. The mean values of Fe concentration (mg/kg) determined in moss by NAA, AAS and ICP-AES methods

Samples code	Fe		
	NAA	AAS	ICP-AES
1	430.10±27.38	436.14 ± 55.82	469.33±70.39
2	579.23±46.15	571.41 ± 51.42	617.67± 92.65
3	601.47±32.88	589.43 ± 42.52	645.00±96.75
4	549.27±43.94	545.68 ± 49.11	609.00±121.35
5	582.77±44.48	555.79 ± 40.03	577.67±101.65
6	503.65±42.56	504.72 ± 50.66	519.00± 83.86
7	550.43±49.54	565.37 ± 45.23	521.33±100.98
8	528.87±126.40	561.23 ± 39.28	496.67± 95.60
9	595.93±33.77	558.14 ± 50.23	562.33± 91.48
10	577.97±97.10	585.76 ± 35.14	611.67± 87.80
11	2056.3±128.9	1939.0±155.1	2038.3±93.45
12	1397.4±91.30	1286.7 ± 102.9	1332.3±65.91
13	513.10±60.89	502.36 ± 40.19	532.00± 87.85
14	963.60±47.22	946.12 ± 75.69	986.00± 84.38
15	951.63±120.22	962.86 ± 77.03	983.67±111.28
16	487.10±68.36	483.93 ± 43.55	475.00± 91.06
17	377.20±64.31	307.95 ± 23.40	345.00± 86.57
SRM-336, [10]	430±10.75		

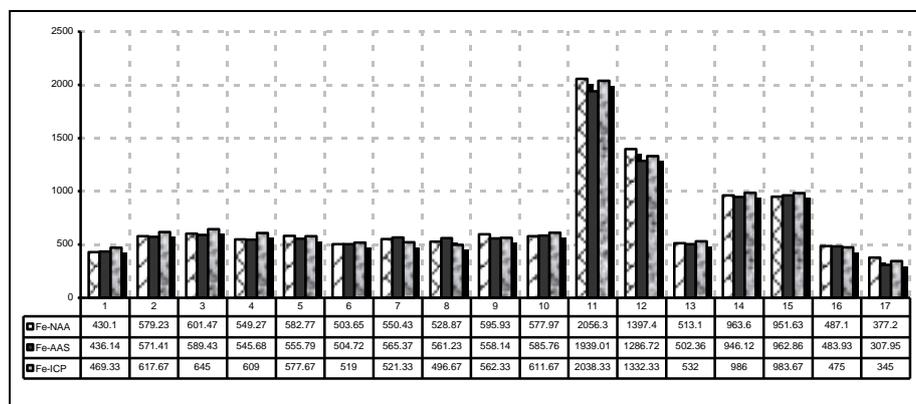


Fig. 8. Comparing values of Fe concentrations determinate by NAA, AAS and ICP-AES, respectively

We can concluded that it is a very good agreement, in statistical limits between the concentrations values of Fe determined with NAA, AAS and ICP-AES analytical techniques applied on the same type of mosses samples.

A high concentration of Cr (26 mg/kg) was found in the samples transplanted in Targoviste zones, which can be explained by the presence of a steel processing plant. Also, from the same reason we can explain the high content of Fe (2056 mg/kg) Ni (5.62 mg/kg) and Zn (126.4 mg/kg) in moss samples transplanted also in Targoviste zones.

This study is the first attempt to apply the moss-bag technique to a region scale in Romania. Our results demonstrate the capability of these analytical methods to be applied on a large spectrum of environmental samples.

3.3. Comparative studies of air pollution with heavy metals, by atomic spectrometry techniques using as bioindicators: moss and lichens [39, 40, 41, 42].

The study was done in the year 2009, and was dedicated to the analysis of air pollution level with heavy metals in Dambovita County; maps of the concentration distributions for air pollutants were drawn. The concentrations of heavy metals in lichens and moss depend especially on the industrial activity and then on the traffic values from every place. The main polluting economic units in this area are Steelmaking and Stainless Steelmaking from Târgoviște and the Thermal Power Plant from Doicesti.

The analytical methods used in this research were *Atomic Absorption Spectroscopy* (AAS) and *Energy Dispersive X-ray Fluorescence* (EDXRF); instruments used were *GBC Avanta AAS* spectrometer and *Elvatech Elvax EDXRF* spectrometer; both instruments are part of specialized laboratories from the *Multidisciplinary Institute for Scientific and Technological Researches of Valahia*.

University from Targoviste. The lichen species sampled were *Xanthoria Parietina* (in most of the cases), *Parmelia Furfuracea* and *Peltigera Canina* and the moss ones were *Hylocomium Splendens*. All the samples were collected between Aprilie and June 2009. For each sample the information regarding the characteristics of location, weather and time of sampling was noted. Through EDXRF method was analyzed 31 mosses samples and 27 lichen samples; also, through AAS method, 18 moss and 18 lichen samples were analyzed. For EDXRF analyses, the samples were prepared by drying followed by shredding and placing them into plastic cylinders covered with Mylar foils. For AAS analyses the samples were prepared by digestion with nitric acid followed by a specific heat treatment program in a microwave oven.

Concentrations of Cr, Cu, Fe, Ni, Pb and Zn were determined. The content of these heavy metals is reflected by moss and lichens samples taking into consideration the following aspects: the number of samples is limited by the number of trees in the given area, especially in the areas with high values of element concentrations, which require an significant covering with biomonitors; the economical activities or road traffic, as random pollution factors, may influence the experimental results in a way that cannot be anticipated.

The distribution maps obtained for Cr, Cu, Fe, Ni, Pb and Zn concentrations enables the identification of the pollution sources, the limits of areas with very high levels of pollution, the comparison of the concentration gradients in some areas and the influence of woodlands on the spread of pollutants through the air. Dambovita County is located in the south of Romania and its main sources of metal pollution are the steel and cement works, agricultural activities, roads and railways traffic and pit ballasts.

Their contribution to environment pollution is significant, having maximums that exceed from 11.9 up to 33.43 times for Cr, Cu, Fe, Ni, Pb and Zn. The minimal values that were obtained at distances about 15 km, deep in forest. Of course, the Pb concentrations are strongly influenced by the intense road traffic. A statistical analysis includes calculation of the background concentrations and the contamination factors. The highest values of the contamination factor CF is 63.1 ± 6.63 for mosses samples and 33.12 ± 3.96 for lichens and it indicates extreme contaminations in the surroundings of steel works and an electric plant.

The detection limits for each element and for both methods are shown in Table 1.

Table 4. Detection limits for AAS and EDXRF methods

Element/ Method	Cr	Cu	Fe	Ni	Pb	Zn
AAS detection limit (mg/kg)	5	1.6	8.3	15	16.6	0.83
EDXRF detection limit (mg/kg)	3.78	0.81	89.5	0.61	3.78	10.2

In table 5 there are shown the heavy metals concentrations in moss, respectively lichens, obtained by AAS method, which is necessary to determine the contamination factor CF (Fernandez, 2001) by formula: $CF = c_m/c_b$, where c_m is the maximum value of element concentration measured in that area and c_b is the background concentration. From the statistical analysis on the concentrations of Cr, Cu, Fe, Ni, Pb, Zn obtained by AAS method for moss and lichens have resulted the following contamination factor CF:

Table 5.

Element	CF, for mosses	CF, for lichens
Cr	53.37	11.11
Cu	9.02	12.34
Fe	9.63	14.33
Ni	18.36	13.78
Pb	63.10	13.51
Zn	25.28	33.12
Relative standard deviation RSD	5% - 11%	5% - 11%

The CF values are interpreted as follows (Fernández, 2001): for $1 \leq CF < 2$ – no contamination, for $2 \leq CF < 3.5$ - low contamination, for $3.5 \leq CF < 8$ – moderate contamination, for $8 \leq CF < 27$ - severe contamination; for $CF > 27$ – extreme contamination. Our values show that on the industrial area of *Târgoviște* and near the power plant of *Doicești* there are severe or extreme levels of pollution, with maximum CF of 63.1 ± 6.63 for mosses and 33.12 ± 3.96 for lichens. The values of CF in one place from *Târgoviște* (table 4) and the comparisons between the CF values from another place in from *Târgoviște* and village *Văcărești* (Table 5.) allows the evaluation of the altitude of airborne particles. While *National College "Ienăchiță Văcărescu"* from *Târgoviște* is located at about 3 km from the industrial area within the town, village *Văcărești* is located at about 10 km in the open land. It can see that for Cu, Fe, Ni and Pb contamination factor values are close, which indicates that the altitude of the dust particles is low, because the first location and the mains sources of pollution are separated by many buildings, some with 10 floors. This conclusion is supported also by the significant attenuation effect of the forests situated in West and South-West of each map on the spread of airborne particles containing metals (the trees have heights up to 10m).

The following figures represents the distribution curves of isoconcentrations for the heavy metals (Cr, Cu, Fe, Ni, Pb, Zn) corresponding to the data obtained by the EDXRF and AAS methods in the samples of moss and lichens. The graphs were drawn with Surfer 9 software. Colours were associated to the numeric values and their significance is shown in the legend from the right of each map; they allow an easy identification of the pollution sources.

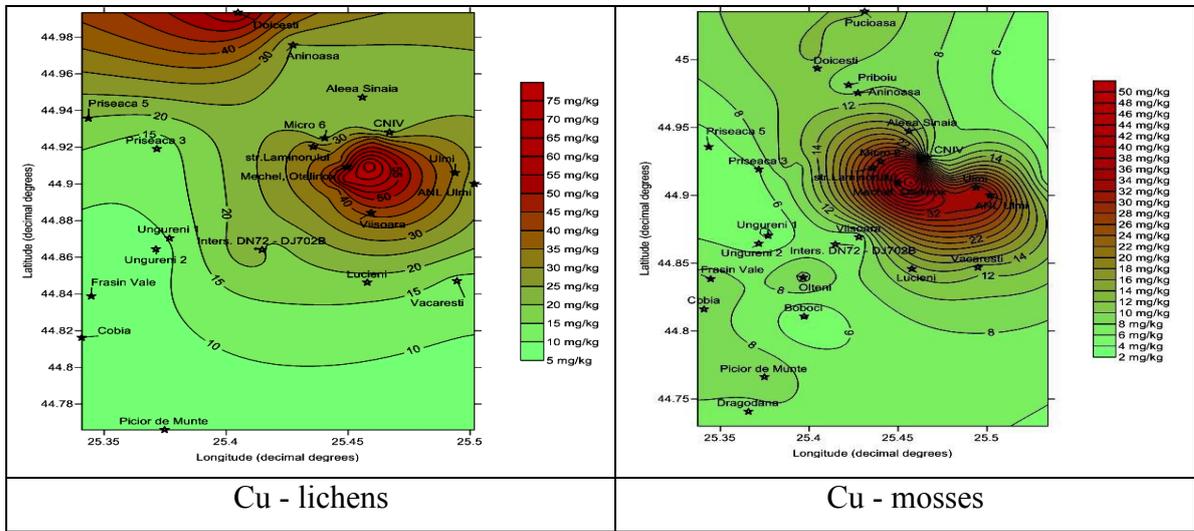


Fig. 9. Distribution curves of isoconcentrations for Cu in lichens and moss samples.

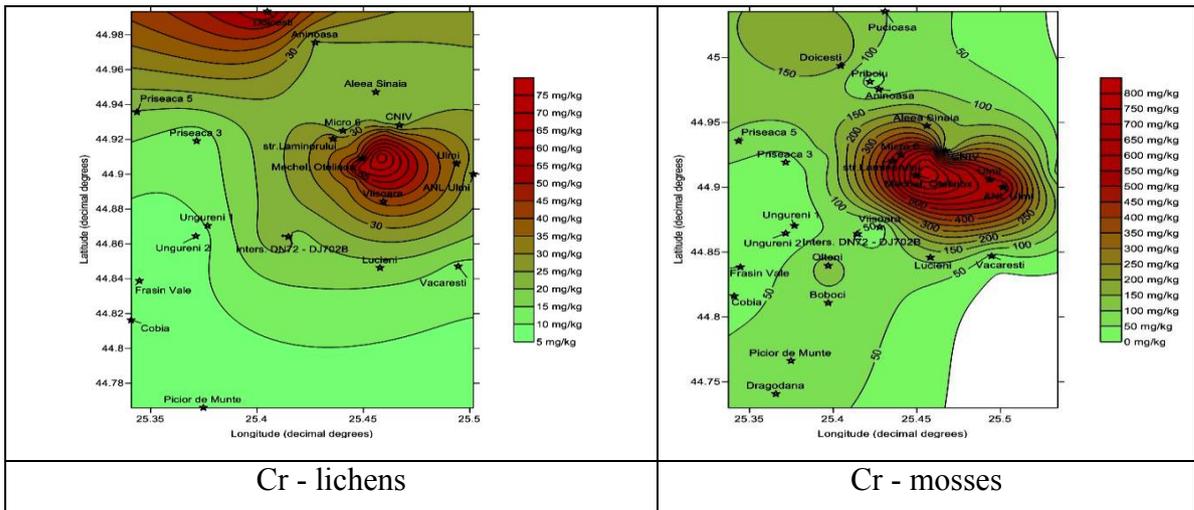


Fig. 10. Distribution curves of isoconcentrations for Cr in lichens and moss samples.

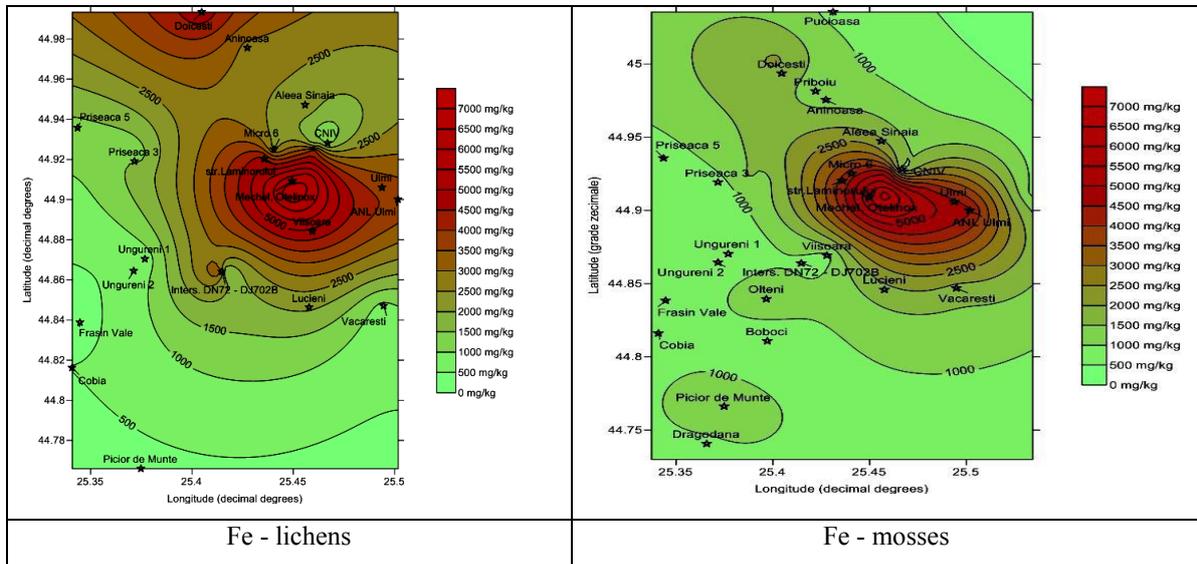


Fig. 11. Distribution curves of isoconcentrations for Fe in lichens and moss samples.

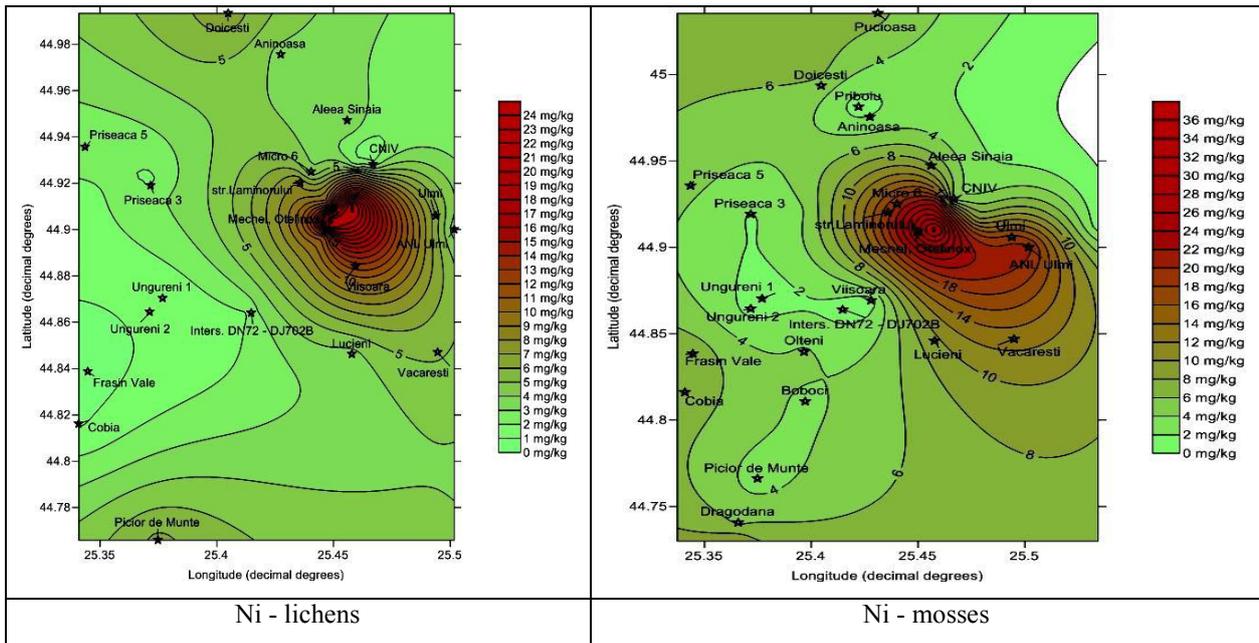


Fig. 12. Distribution curves of isoconcentrations for Ni in lichens and moss samples.

The maps are different for the two biomonitors and they reveal that lichens samples are useful to monitoring the open areas because they grow particularly in areas with low humidity, on roadsides or in open lands; moss grow especially inside forests, in places with high humidity or on the bark of old trees and these features recommend them for background pollution monitoring. It can distinguish two main sources of pollution: factories producing and processing steel in the centre of the map and a power plant which is located in the north. Also, it highlights the low level of pollution in forests from West and South-West of each map (*Ungureni, Frasin Vale, Cobia, Picior de Munte*). This comparative study showed that the simultaneous use of moss and lichens as bioindicators can provide important information on air pollution with metals on a given area, even if they are spread unevenly. Element concentrations were compared with the values obtained from other studies for the same type of biomonitor and the same species (Dzubaj et al. 2008; Anicić et al. 2009; Coskun et al. 2009). We have found that the concentrations obtained in this study are within the range of values from mentioned.

3.4. Studies on accumulation of heavy metals from substrate to edible wild mushrooms[43,44,45, 46]

The aim of this study was to determine the heavy metal content of the fruiting bodies of *Lycoperdon perlatum* and *Pleurotus ostreatus* and their substrate collected at various distances from a metal smelter in Dambovita County, Romania. The concentrations of Mn, Fe, Cu, and Zn in the samples were determined by Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry and the concentrations of Cr, Ni, Se, Cd and Pb were determined by Atomic Absorption (AA) spectrometry. The coefficient of accumulation of heavy metals was calculated and a highest accumulation of Fe, Cu and Zn from substrate was observed for all the analyzed mushrooms samples. Furthermore, a high accumulation of Pb was observed in mushrooms growing in the vicinity of the metal smelter. The determination of heavy metal concentration in the fruiting bodies of mushrooms is essential in dietary intake studies. Different heavy metals are toxic, such as As, Cd, Ni, and Hg; on the other hand many elements are essential for the human metabolism, such as Fe, Zn, Mn, Cu, Cr, and Se These elements to be determined by X-ray fluorescence spectrometry and atomic absorbtion spectroscopy Young mushrooms species *Lycoperdon perlatum* and *Pleurotus ostreatus* were collected from different areas easy woodland of Dambovita County, Romania, at various distances (0.5 km, 4.5 km and 10.5 km respectively) from a metal smelter, in the same direction of wind. From the same collecting point were taken n=5 samples from the young fruiting bodies of mushrooms and their substrate. The substrate from *Pleurotus ostreatus* was poplar bark with a pH ranged from 7.35-7.50 and from *Lycoperdon perlatum* was soil with a pH ranged from 6.35-7.60.

Sample preparation: Two grams of each sample (n=5 for each species collected at various distances from a metal smelter in Dambovita County, Romania) were pressed manually, without any chemical treatment, in a plastic vial with Mylar in the bottom and then analysed.

Experimental condition: The concentrations of Mn, Fe, Cu and Zn in the samples were determined by Energy Dispersive X-Ray Fluorescence (EDXRF) technique, using the ElvaX spectrometer having a X-ray tube with Rh anode, operated at 50 kV and 100 μ A. Samples were excited for 300 s and the characteristic X-rays were detected by a multichannel spectrometer based on a solid state Si-pin-diode X-ray detector with a 140 μ m Be window and a energy resolution of 200eV at 5.9 KeV. ElvaX software was used to interpret the EDXRF spectra. The accuracy of the results as evaluated by measuring a certified reference sample (NIST-1515: apple leaves). Good agreements were achieved between certified values and data obtained, with recoveries ranging from 98 to 104%.

Atomic absorption spectrometry: The dried samples were digested in an acid solution using a Berghof MWS-2 microwave digestion system. Dried fungus samples (500 mg) were introduced into the digestion vessels together with 3 mL nitric acid and 5 mL hydrogen peroxide. After the digestion time (40 min) the vessels have cooled to room temperature (about 30 min.). The clear solution volume was made up to 50 mL for each sample using deionised water. Dried solid substrates (500 mg) were introduced into the digestion vessels together with 3 mL nitric acid and 9 mL hydrochloric acid (aqua regia). After digestion time (30 min) the vessels have cooled to room temperature and the clear solution volume is made up to 50 mL for each sample using deionised water. The concentrations of Cr, Ni, Se, Cd and Pb in the samples were determined by Atomic Absorption spectrometry using the AVANTA GBC spectrometer with flame and hollow cathode lamps (HCL). Determination of elemental concentrations in

samples of mushrooms and their substrate were performed using the method of calibration curve according to the absorber concentration. Several standard solutions of different known concentrations have been prepared and the elemental concentration in unknown sample was determined by extrapolation from the calibration curve. All samples concentrations were reported as mg/kg dry weight of material.

3.4.2. Results and discussions

The concentrations of Mn, Fe, Cu and Zn were greater than 10 mg/kg and were determined by EDXRF technique. To determine the concentrations of Cr, Ni, Se, Cd and Pb, which were below 10 mg/kg and greater than 0.1 mg/kg, was used the AAS spectrometry.

The content of heavy metals of the fruiting bodies of *Pleurotus ostreatus* ranged from 1.08-1.81, 11.8-12.4, 284-387, 1.29-1.85, 10.2-12.5, 37.9-41.3, 2.57-2.79 and 0.87-0.95 mg/kg dw. for Cr, Mn, Fe, Ni, Cu, Zn, Se and Cd, respectively. The Pb in the *Pleurotus ostreatus* fruiting body was detected only in the sample collected in the vicinity of the metal smelter.

The content of heavy metals of the fruiting bodies of *Lycoperdon perlatum* ranged from 1.87-1.94, 12.6-13.9, 623-782, 1.83-1.96, 10.2-11.8, 127-134, 14.2-15.4, 1.58-1.73 and 0.71-3.47 mg/kg d.w. for Cr, Mn, Fe, Ni, Cu, Zn, Se, Cd and Pb, respectively.

The relative standard deviation (RSD) values, less than 10%, excepting the results for Fe, indicate a precise quantitative measurements in this work. The relative standard deviation less than 13% for Fe can be done by the interference of Mn and Fe X-ray lines.

A great attention was done to the Cd and Pb content in the analyzed mushrooms, because these elements are toxic elements included in the hygiene norms concerning the foods security. The highest Cd content determined was 1.73 mg/kg in *Lycoperdon perlatum* collected in the vicinity of the metal smelter. The highest Pb content was 3.47 mg/kg also in *Lycoperdon perlatum* collected all in the vicinity of the metal smelter. In comparison with other studies, the Cd levels determined in *Pleurotus ostreatus* and *Lycoperdon perlatum* are in the agreement with literature values. The Pb concentrations in previous studies were between 0.1 and 40 mg/kg [43]. A heavy metal accumulation takes place in the analysed mushrooms species. The coefficient of accumulation of heavy metals was calculated using relation:

$$K_a = \frac{C_m}{C_s},$$

where C_m is the concentration of heavy metal in mushroom and C_s is the concentration of heavy metal in mushroom substrate.

In the table 6 and table 7 are given the coefficients of accumulation of Cr, Mn, Fe, Ni, Cu, Zn, Se, Cd and Pb, respectively in the fruiting body of the analysed mushrooms.

Table 6. K_a - accumulation coefficient of heavy metals in *Pleurotus ostreatus* fruiting body

Distance from metal smelter (km)	Cr	Mn	Fe	Ni	Cu	Zn	Se	Cd	Pb
0.5	0.53	0.42	0.95	0.52	0.82	1.01	0.62	0.42	0.12
4.5	0.53	0.41	0.91	0.47	0.89	1.03	0.50	0.41	0.00
10.5	0.39	0.42	0.93	0.48	0.81	1.07	0.58	0.41	0.00

Table 7. Ka - accumulation coefficient of heavy metals in *Lycoperdon perlatum* fruiting body

Distance from metal smelter (km)	Cr	Mn	Fe	Ni	Cu	Zn	Se	Cd	Pb
0.5	0.10	0.08	0.12	0.20	0.44	1.78	0.74	0.31	0.28
4.5	0.16	0.09	0.12	0.22	0.49	2.01	0.68	0.35	0.15
10.5	0.16	0.09	0.14	0.22	0.55	1.74	0.75	0.37	0.14

The dependencies of coefficients of accumulation of Fe and Pb on distance from metal smelter are given in figure 15.

The coefficients of accumulation of Fe, and Pb are higher inside both species in the vicinity of the metal smelter.

The coefficients of accumulation of Zn and Pb are higher from *Lycoperdon perlatum* comparative with *Pleurotus ostreatus* species and ranged from 1.01-1.07 and 0.14-0.28. We conclude that *Lycoperdon perlatum* species is a Zn and Pb accumulator.

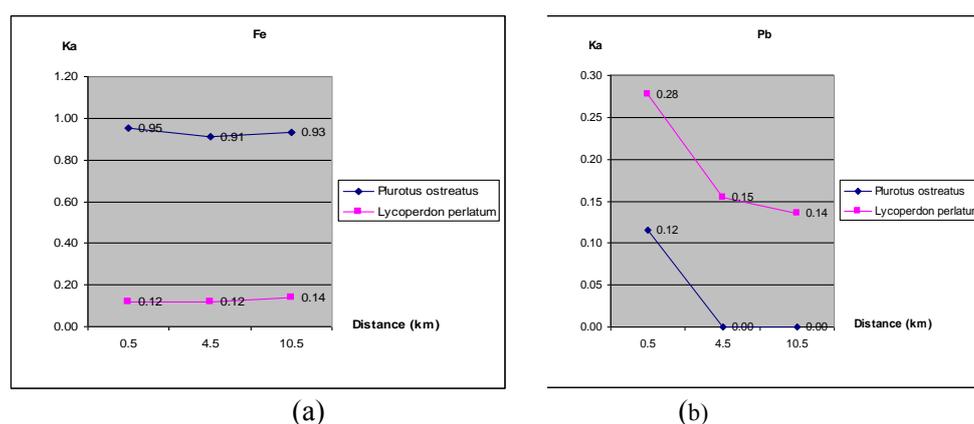


Figure 15. Dependency of accumulation coefficients of the analyzed heavy metals on distance from metal smelter: (a) – Fe storage; (b) Pb storage;

The heavy metals concentrations obtained in this study in the fruiting body of the mushrooms were compared with the admitted maximum level of certain contaminants in foodstuffs, established by the Commission of the European Communities (Commission Regulation [EC] No 466/2001).

The admitted maximum level for Cd and Pb is set about 2 and 3 mg/kg d.w., in cultivated mushrooms. Our results reveal that only the samples of *Lycoperdon perlatum* collected in the vicinity of the metal smelter had Pb concentration higher than European limits for cultivated mushrooms.

The combination of two different techniques, EDXRF and AAS, was well suited to this analysis. EDXRF technique enable simultaneous determination of all the elements present in the sample ($Z > 13$), don't require a chemical sample preparation but, is limited by the detection limit. For this reason the elements which are a concentration less then 10 mg/kg had to be studied by the AAS technique.

The studied mushrooms: *Lycoperdon perlatum* and *Pleurotus ostreatus* contain minerals required in the human diet, such as Fe, Zn, Mn, Cu, Cr and Se and also toxic elements, such as Cd, Ni and Pb. The level of toxic elements was lower than that of minerals.

We must emphasize that the results obtained in this work are the first ones reported in the literature for the wild-grown edible mushrooms collected from the Dambovita County, Romania. This information can be extremely important considering that the analysed mushrooms are common mushrooms, collected in many sites from people for consumption.

3.5. Analysis of surface waters

3.5.1. Characterization of Olt river water quality using analytical methods.[47,48, 50,51,52]

In this study are presented experimental results obtained by investigation of water samples collected from different zones of Olt River (Superior Hydrographic Basin – Fagaras Depression, Romania) in order to characterize the quality of water.

Total Dissolved Solids (TDS), electrical conductivity, salinity, and other physicochemical indicators of samples including NO_3^- , pH, turbidity, and total hardness were investigated in the order to establish the real pollution degree of Olt River. The heavy metals concentrations including Pb, Cd, Zn, Ni, Cr, Mn, and Fe were determined by Flame Atomic Absorption Spectrometry (FAAS). The results demonstrated that heavy metals are originated from various pollutant sources; however, the main anthropogenic sources were industrial waters (e.g. effluents of Chemical Factories from studied area), municipal wastewaters and run-off waters from agricultural fields.

It is well known that certain changes in water quality occur naturally along the length of a river, and most of changes may be significantly influenced by anthropogenic activities. The water quality can be affected mostly by industries, agriculture and urban settlements which can produce sewage effluent, fertilizers, and other poisonous substances. The toxic action of a water pollutant, its intensity and velocity with which that pollutants affect the aquatic organisms depends on many factors: internal (species of organisms that are present in water, the development and the physiological stage of organism, etc.) and external

(temperature, turbidity, pH, dissolved oxygen, etc.). Some heavy metals (*e.g.* Mn, Ni, Cr, Zn and Fe) occur naturally in the environment and in small concentrations are essential for all life forms including humans and others are toxic (*i.e.* Pb and Cd). The main problem is represented by the heavy metals accumulation and related diseases, as well as, the impossibility of human body to remove these toxic elements through natural processes.

In this current study was to determine the heavy metal concentrations (*e.g.* Pb, Cd, Zn, Ni, Cr, Mn, and Fe) of some water samples collected from Olt River (Superior Hydrographic Basin - Fagaras Depression, Romania) by using Flame Atomic Absorption Spectrometry [8-13].

These results were interpreted in relation with the physicochemical indicators including total dissolved solids, electrical conductivity, salinity, turbidity, NO₃ - pH, and total hardness in order to establish the water quality of Olt River and their classification in a specified category according with the Romanian Regulation (*i.e.* Order 161/2006).

In Olt hydrographic basin have been identified 622 rivers (with surfaces higher than 10 km²) and 33 accumulation lakes (with surfaces higher than 50 ha), and Olt River is one of the important affluent of Danube. Determination of the pollution degree of Olt River in Fagaras Depression, between Fagaras City and Victoria City where was developed important chemical industrial activities, water the subject of this study (Fig. 1). All samples have been collected in April 2012, on a distance of about 30 km (Table 1 and Fig. 2).

The water samples were collected, preserved, handled and transported, according with ISO 5667-3:2012 "Water quality - Sampling - Part 3: Preservation and handling of water samples". The water samples was collected from 12 points identified by geographic coordinates.

The samples was marked with S₁ up to S₁₂, respectively, collected from the following locations: Mandra Hidro power plant (barrage), Berivoi Creek, Beclean Creek, Voila Hidro power plant (barrage), Voila Creek, Sambata Creek, Oltet Creek, Vistea Hidro power plant (barrage), Corbul Ucii Creek, Ucea Creek, Ghirlotel-Arpas Creek and Arpas Hidro power plant (barrage).

For AAS analysis all samples were mineralized with aqua regia (*i.e.* using 2.5 mL HNO₃ 67% and 7.5 mL HCl 37%) by using Bergof MWS-2 Digester. The heavy metal concentrations obtained by Atomic Absorption Spectrometry are presented in Table 9.

The values of quality indicators of samples collected from Olt River (pH, conductivity, salinity, turbidity, and TDS) are shown in Table 8.

Table 8. Physicochemical indicators of surface water samples collected from Olt River

No	Quality indicators						
	NO ₃ [mg/L]	pH	Conductivity [mS/cm]	Salinity [‰]	Turbidity [NTU]	TDS [mg/mL]	GH [°G]
S1	17.93	7.38	304	0.1	15.1	144	19.1
S2	15	6.83	128.9	0.1	0.07	61	13.2
S3	21.62	6.04	96.3	0	0.4	46	12.1
S4	36.28	7.5	309	0.1	5.7	147	19.7
S5	31.6	6.24	118.1	0.1	0	56	12.3
S6	21.86	6.33	108.1	0.1	5.39	51	11.8
S7	30.5	7.23	101.5	0	0.28	48	11.4
S8	35.2	7.52	329	0.2	14.42	157	19.7
S9	46.7	7.68	348.2	0.2	11.24	170	18.7
S9	21.3	6.78	78.8	0	0	37	12.1
QC-I	5	6.5-8.5	-	-	-	-	-
QC-II	15						
QC-III	25						
QC-IV	50						

It was observed high nitrate concentrations between 15.00 mg/L (S2 Berivoi Creek) and 46.70 mg/L (S9 Corbul Ucii Creek). The highest value recorded in S9 can be explained by the presence of Chemical Factory from Victoria City and agricultural activities as well. In Fig.16 is represented the nitrates content related to pH values.

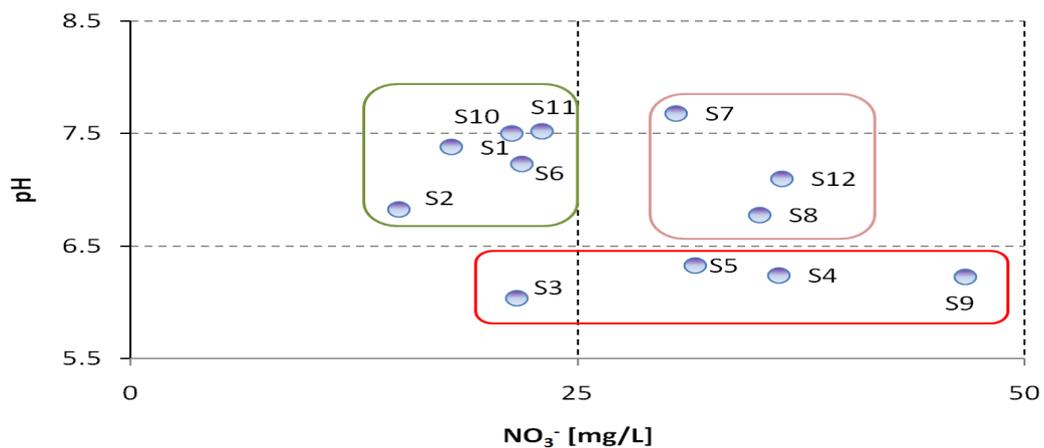


Fig.16. – Nitrates content related to pH.

Therefore, it can be observed a high nitrates concentration and a weak acid pH – under the minimum admitted limit, 6.5 (the red rectangle) in S3, S4, S5, and S9 samples. The pink rectangle including S7, S8, and S12 samples show a high nitrates concentration and a pH value according with Order 161/2006 (Romanian legislation). The green rectangle including S1, S2, S6, S10, S11 samples show a low nitrates concentration and a pH value in conformity with Romanian Regulation. A linear correlation between TDS and electrical conductivity (Fig12, $R^2 = 0.999$) and total hardness and conductivity (Fig.13, $R^2 = 0.970$) was observed.

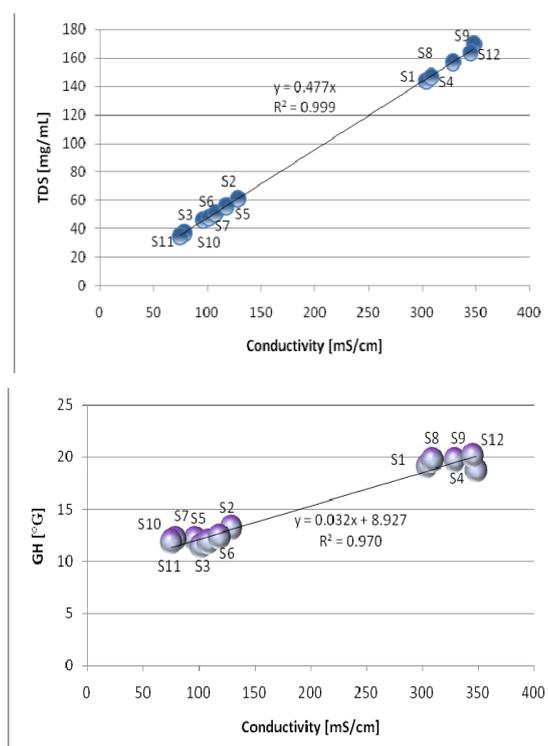


Fig. 17. – Linear correlation between TDS and conductivity

Fig. 18. – Linear correlation between total hardness and conductivity..

As can be shown in Figs. 17 and 18, the water samples collected from Olt River are grouped in two categories: * Low conductivity and low TDS and total hardness (S2, S3, S5, S6, S7, S10, and S11); * High conductivity and high TDS and total hardness (S1, S4, S8, S12, and S9). In first category are included all creeks (Berivoi, Beclean, Voila, Sambata, Oltet, Ucea, Ghirlotel-Arpaș), and in second category are included all waters barrages (Mandra, Voila, Vistea, Arpaș) and Corbul Ucii Creek– which passes the land of Victoria Industrial Factory.

The results obtained by Flame Atomic Absorption Spectrometry (FAAS), regarding the heavy metal concentrations, are presented in Table 9.

Table 9. Heavy metals concentration of surface water samples collected from Olt River

No	Heavy metals [mg/l]						
	Pb	Cd	Zn	Ni	Cr	Mn	Fe
S1	10.153±0.5	0.954±0.2	257.077±7.2	12.154±1.2	4.973±0.2	37.830±3.3	351.63±5.2
S2	8.216±0.1	0.025±0.01	230.441±6.8	5.525±1.1	4.783±0.2	22.285±3.5	471.71±7.2
S3	6.211±3.5	0.901±1.2	234.567±6.7	11.901±1.0	1.857±0.6	34.032±3.4	440.31±4.6
S4	9.540±3.6	0.082±0.01	232.781±6.7	4.982±1.1	5.758±0.1	33.027±3.2	460.11±4.5
S5	3.112±1.9	0.112±1.0	220.803±6.9	10.112±1.0	1.723±0.5	29.394±3.1	311.22±4.5
S6	6.353±0.01	0.092±0.02	238.365±7.0	3.892±0.9	1.745±0.3	13.815±2.7	241.19±4.3
S7	7.889±1.2	0.873±0.1	229.890±6.5	9.873±1.0	3.601±0.2	22.228±2.8	349.12±4.5
S8	10.487±0.2	0.032±0.01	226.095±6.5	8.932±0.9	4.452±0.1	31.777±2.5	399.59±4.3
S9	9.366±0.9	0.761±0.1	242.697±6.3	7.761±0.8	3.092±0.1	21.098±2.5	381.34±8.0
S10	6.208±0.2	0.052±0.02	231.190±6.3	1.652±0.8	0.532±0.2	10.821±2.5	372.55±5.0
S11	5.159±0.9	0.542±0.3	226.921±6.2	7.542±0.7	3.201±0.7	30.126±2.4	321.20±3.7
S12	9.399±0.08	0.091±0.01	223.632±5.5	0.691±0.8	4.306±0.8	30.892±2.4	351.37±3.8

Table 10. Quality classes (QC) of surface waters – Order 161/2006 [mg/l] [8]

QC	Heavy metals [mg/l]						
	Pb	Cd	Zn	Ni	Cr	Mn	Fe
I	5	0.5	100	10	25	50	300
II	10	1	200	25	50	100	500
III	20	2	500	50	100	300	1000
IV	50	5	1000	100	250	1000	2000
V	>50	>5	>1000	>100	>250	>1000	>2000

A comparison between Pb, Cd, Zn, Ni, and Fe concentrations and QC values of surface waters – Order 161/2006 (Table 4) was achieved (Figs. 19–23).

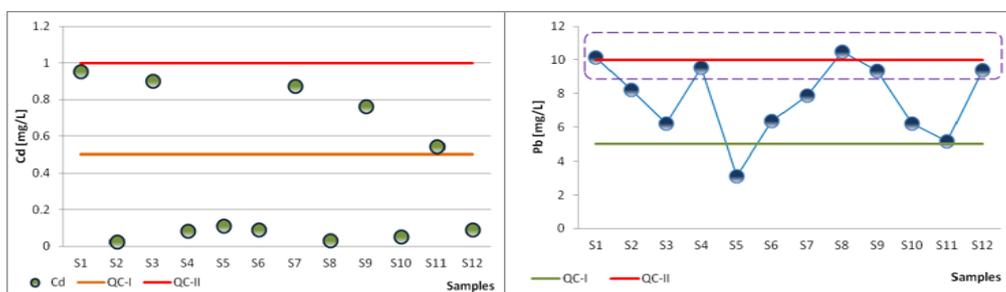


Fig. 19– Lead concentration in surface water Fig.20 – Cadmium concentration in surface water samples collected from Olt River samples collected from Olt River.

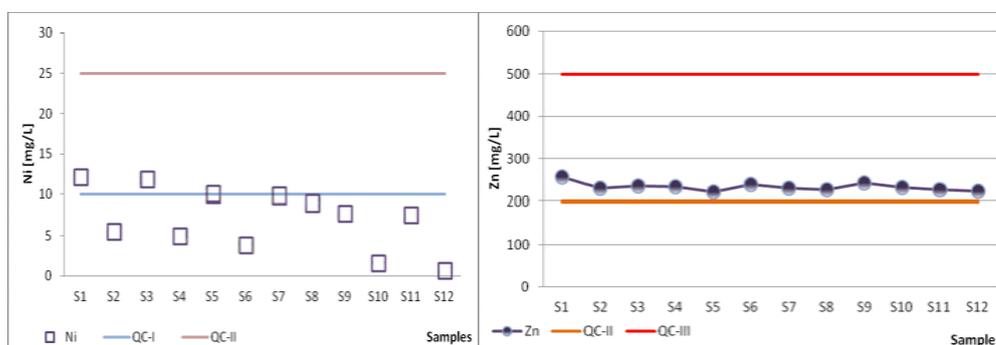


Fig. 21– Zinc concentration in surface water samples collected from Olt River.

Fig.22 – Nickel concentration in surface water samples collected from Olt River

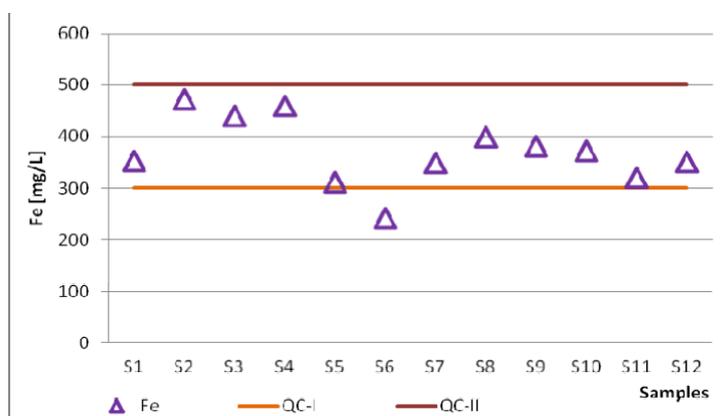


Fig. 23 – Iron concentration in surface water samples collected from Olt River.

Lead concentrations for S1 and S8 samples exceeded the QC-II values, and for the samples S2, S3, S4, S5, S6, S7, S9, S10, S11 and S12 were between the QC-I and QC-II values. Only S4 samples was included in QC-I. Cadmium concentrations for S1, S3, S7, S9, and S11 samples were between the QC-I and QC-II values and all the other samples were included in QC-I.

Zinc concentrations for all the samples were slightly higher that QC-II values. Nickel concentrations for S1 and S3 samples were slightly higher that QC-I values and all the other samples were included in QC-I. Iron concentrations for all samples were between the QC-I and QC-II values except the S6 sample which was included in QC-I.

In accordance with the Framework Directive 96/61/EC (IPPC Directive), the requirements of Directive 2006/11/EC which replaced Directive 76/464/EEC on pollution caused by dangerous substances discharged into the aquatic environment of the Community and the Implementation Plan of Directive 91/271/EEC concerning urban wastewater, the present study aimed to determine the pollution degree of the Olt River, on Fagaras – Victoria sector.

Concerning the nitrates concentrations can conclude that the water of Olt River (Superior Hydrographic Basin – Fagaras Depression, Romania) may be included in QC-II and QC-III, except water from Voila Hidro power plant (S4), Vistea Hidro power plant (S8), Corbul Ucii Creek (S9) and Arpas Hidro power plant (S12) which is included in QC-IV. Concerning the heavy metal concentrations can conclude that the water of Olt River (Superior Hydrographic Basin – Fagaras Depression, Romania) may be included in QC-I and QC-II.

3.5.2. Characterization of Potop river water quality using analytical methods [49 – 51].

In this study are presented some experimental results obtained by investigation of water samples collected from different zones of Potop River for characterization of river water quality. The experimental results, Total Dissolved Solids (TDS), evolution of electrical conductivity σ (μS), salinity, and the concentrations measurements by atomic absorption spectrometry technique (AAS) of Fe, Zn and Cd from water samples collected of different geographical points of the Potop River in the April 2008 and April 2010 are presented. All samples of water were collected in successive three weeks. The quality parameters of Potop River, which arose from the Piedmont Căndești, Dambovită County, were interpreted. During on the monitoring period the recorded values of chemical and physical parameters indicates a tendency to maintain constant the water quality parameters in the same collection points of the Potop River. The analyzes of surface waters from the Argeș - Vedea river basin are presented, zone which is affected by the activities of oil extraction. Representative water samples have been collected in order to be able to take into account the presence of suspended particles, both at point of collection, and beyond, in the sample preparation in laboratory. The sampling procedure was performed 3 days, 3 consecutive weeks in April 2008. The collecting points of water samples from Potop river were established by geographical informations with following 8 codes: samples code from 1 up to 8, respectively, Potop 1, Potop 2, Potop Hulubesti, Valea Hotarului, Valea Gaterului, Valea Banului, Potocelu and Prodila. The sampling and storage of samples was made in sterile high-density polyethylene bottles, and analysis was carried out immediately after sampling. Most contaminants in water are inorganic salts which are in dissolved state. Thus, TDS parameter has relevant. Usually, TDS is correlated well with total hardness (expressed as total $[\text{Ca}^{2+}] + [\text{Mg}^{2+}]$), which is a useful parameter for evaluating the softening need as well as the corrosiveness of water. The method used for the analysis of TDS in water is the measurement of specific conductivity with a conductivity probe that detects the presence of ions in water. Conductivity measurements are converted to TDS values by a factor that varies with the type of water. Determination of TDS of water samples was performed at the sampling places with the portable conductometer HACH CO150, which has a conductometric cell having platinum electrodes.

The experimental results have been correlated with the concentrations of Fe, Zn and Cd determined using the atomic absorption spectrometry method [2]. The AAS measurements were performed at ICSTM-UVT, using an atomic absorption spectrometer with flame AVANTA GBC. The results that have been obtained by TDS measurements of the surface water samples are presented in figure 24.

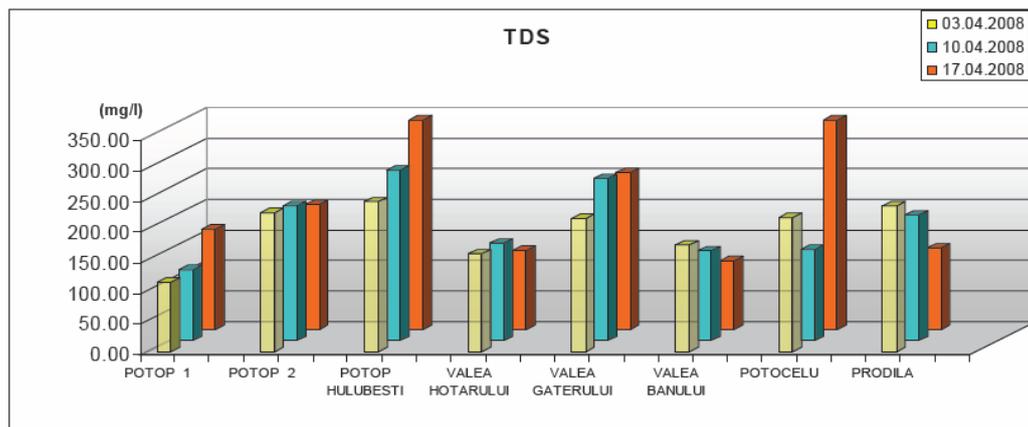


Figure 24. TDS variation along the Potop River.

From the obtained dates it can be seen that in the Potop Hulubesti collecting point have been obtained the biggest values of TDS. We can see from figure 19 that the values of TDS not exceeded the maximum admissible value (1000 mg/L).

Admitted values of heavy metals (Fe, Zn, Cd) in surface water for class 1, 2 and 3, according with Romanian laws, are presented in the Table 11 which means: class1 - very clean fresh surface water, ecosystem consumption where basic organisms can breed naturally, resources used for consumption which requires ordinary water treatment processes before use; aquatic organism of conservation, fisheries an recreation; class 2 - medium clean fresh surface water sources used for: consumption, but passing through and ordinary treatment process before use and agriculture; fairly clean fresh surface water resources used for consumption which requires special water; treatment process before use and industry.

Table 11. Admitted values of surface water for Class1, 2 and 3

Element	Class 1 (mg/L)	Class 2 (mg/L)	Class 3 (mg/L)
Fe	0.300	1.000	1.000
Zn	0.030	0.030	0.030
Cd	0.003	0.003	0.003

The concentrations of Fe, Zn and Cd in surface water of potop River, obtained by the atomic absorption spectrometry, are shown in tables 12. Standard error was less than 5%.

Table 12. The concentration (mg/L) of Fe, Zn and Cd in surface water measured by AAS method.

Collecting points	Fe			Zn			Cd		
	week 1	week 2	week 3	week 1	week 2	week 3	week 1	week 2	week 3
Potop 1	0.033	0.000	0.222	1.364	0.798	0.028	0.078	0.019	0.001
Potop 2	0.097	0.000	0.352	1.367	0.782	0.051	0.078	0.025	0.007
Potop Hulubesti	0.038	0.000	0.212	1.364	0.779	0.038	0.077	0.030	0.029
Valea Hotarului	0.020	0.000	0.223	1.363	0.777	0.002	0.077	0.030	0.036
Valea Gaterului	0.068	0.056	0.113	1.357	0.801	0.022	0.079	0.006	0.005
Valea Banului	0.131	0.099	0.470	1.363	0.789	0.027	0.079	0.006	0.002
Potocelu	0.056	0.000	0.043	1.366	0.118	0.266	0.078	0.009	0.005
Prodila	0.312	0.199	0.227	1.365	0.660	0.061	0.077	0.030	0.025

In figures 25, 26 and 27 are shown the concentrations variation of Fe, Zn and Cd in surface water samples for a period of 3 weeks compared with the admissible value for water samples from the first class category.

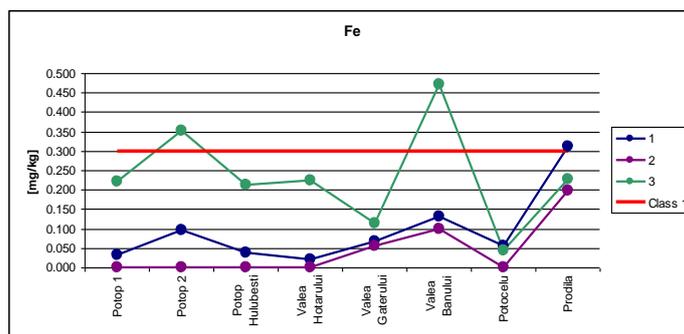


Figure 25. The variation of Fe concentration in surface water of Potop River.

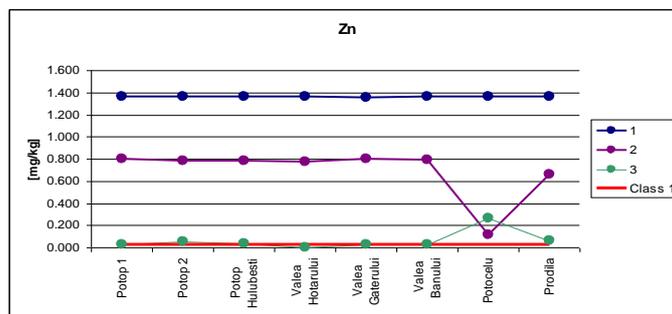


Figure 26. The variation of Zn concentration in surface water of potop River.

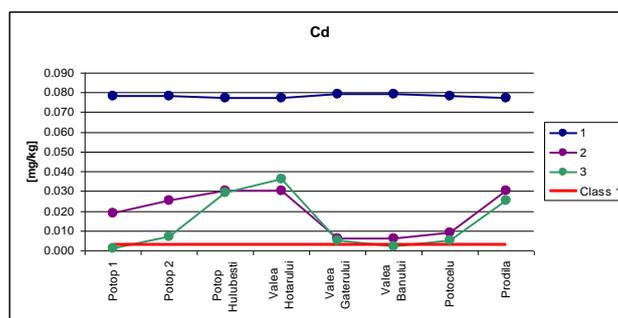


Figure 27. The variation of Cd concentration in surface water of Potop River.

Analyzing the results it can be concluded that during on the monitoring period the recorded values of chemical and physical indicators indicates a tendency to maintain constant the water quality parameters in the same collection points. This is explained first of all by the fact that not exist the industrial centers, near of collected points, which may cause environmental pollution, with one exception, Potop Hulubesti, where maximum values were recorded significantly above the average value. Physical and chemical indicators of Potop River classified the water in Category II and III of quality, so it is not potable, but not exceed the permissible limits for surface waters in accordance with Romanian legislation.

Conclusions

Increasing the level of environmental pollution due to anthropogenic activities requires a careful analysis of the pollutants of air, water, soil and vegetation, which is the support of life. The study of heavy metals emissions worldwide has shown that the impact of anthropogenic action becomes decisive in the global cycle of many chemical elements. The main source of atmospheric pollution with heavy metals is the industrial processes (steel, chemistry and petrochemistry, material processing, mining, etc.), thermal power stations and motor vehicles (road traffic). The extraction of ores leads inevitably to the pollution of soils and, implicitly, water. All these types of pollution sources are frequently found in Romania and the concentration of several industrial objectives in certain geographic regions in the country leads to the accumulation of pollutants that can produce a real ecological stress. Due to environmental pollution with effects on ecosystems and population health, it is necessary to carry out, continuously, researchers for the identification and quantitative determination of chemical pollutants by developing and implementing modern, high-precision and sensitive analytical techniques.

In this syntesis were presented Atomic and Nuclear Analytical Methods (ANM): Atomic Absorbption Spectrometry (AAS); Atomic Emission Spectrometry in the variants Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS); X-Ray Fluorescence Spectrometry(XRF) in three variants: Energy Dispersive X-Ray Fluorescence (EDXRF), Wave Dispersive X-Ray Fluorescence(WDXRF)) and Particle Induced X-Ray Emission Spectrometry (PIXE) and Neutron Activation Analysis Spectrometry (NAA), in correlation with biomonitoring technique using bioindicators. As bioindicators we used the following samples: moss, lichens, vegetables and fruits, soils, surface water , methods that apply in the study of environment pollution with heavy metals and with other chemical pollutants using bioindicators as part of biomonitoring technique.

The comparative analysis of the methods approached has shown that these techniques, used individually, are not fully satisfactory for the wide variety of issues involved in analyzing chemical elements at trace elements level. In order to cover the entire range of elements to be analyzed in a sample, it has proved necessary to use these methods in a complementary manner, obtaining for a series of correlated results.

Up to now in Multidisciplinary Research Institute of Science and Technology of Valahia University of Targoviste (ICSTM-UVT), as responding to many requests from different fields have been implemented the analytical methods, with high sensitivity and applicability in different domains. At the same time UVT have partnership agreements for using experimental facilities with National Institute for Physics and Nuclear Engineering Horia Hulubei (IFIN-HH) from Bucharest and Joint Institute for Nuclear Research from Dubna-Rusia(JINR-Dubna).

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