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ENVIROMENTAL PHYSICS

ASSESSMENT OF HEAVY METALS LEVEL IN SOME PERENNIAL MEDICINAL PLANTS BY FLAME ATOMIC ABSORPTION SPECTROMETRY

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Abstract. Heavy metals in four perennial medicinal plants such as *Matricaria recutita*, *Taraxacum officinale, Achillea millefolium*, and *Hypericum perforatum*, collected from Navodari region, have been quantitatively analyzed by using Flame Atomic Absorption Spectrometry (FAAS). Seven heavy metals (Cd, Cr, Co, Cu, Pb, Ni, and Zn) in plant samples and nine heavy metals (Cd, Cr, Co, Cu, Pb, Fe, Mn, Sn, and Zn) in soil were selected on the basis of their effects upon health. Absorption of heavy metal in medicinal plant is governed by soil characteristics such as pH, salinity, conductivity and organic matter content. In this respect zinc concentration ranged between 12.180 mg/kg in *Taraxacum officinale* collected from Ovidiu zone and 48.976 mg/kg in *Achillea millefolium* collected from Rompetrol Refinery location. The physiological activities of the medicinal plant influence Zn absorption and the interactions with many elements such as Fe and Cu. *Taraxacum officinale* was able to accumulate more Cd (*e.g.* 0.783 mg/kg d.w. in Channel of Rompetrol Refinery location) than *Achillea millefolium, Matricaria recutita* and *Hypericum perforatum*. These plants can absorb Pb from soil and from $PbEt_2$ traffic-induced contaminated atmosphere, because the collected points are near roads. The analysis of Cr in medicinal plants indicated that Cr concentration ranged between 0.127 mg/kg to 0.970 mg/kg on Channel of Rompetrol Refinery and 0.059 mg/kg to 0.704 mg/kg on Rompetrol Refinery, respectively.

Key words: medicinal plant, heavy metal, FAAS, accumulation.

1. INTRODUCTION

Thanks its geographical position, a varied landscape and favorable climate for development of rich vegetation, in Romania grow over 2000 species of superior plants, from which over 200 have become medicinal plants. Most of these plants, even today, are collected and used by population from Romanian villages. But it is true that the continued commercial exploitation and particulary the anthropogenic pollution led to the disappeareance of many species from their natural habitat. It is well known that heavy metals aerosols pollute soil and herbal plants as well. Sometimes in polluted sites the higher herbal plants, with well therapeutical properties, mostly used by peoples but are often ruderal plants, accumulate aerial heavy metals from the soil as well as intercept the pollutants from atmospheric deposition. Small particulates deposition from air, which can contain some toxic heavy metals, on the leaf surfaces of medicinal plants, may be affected by a variety of factors, including particle size and mass, wind velocity, leaf orientation, moisture level and characteristic reactions which occur at the surface of plant leaves as well. These deposited particles may be washed by rain into the soil, resuspended or retained on plant foliage. The retention degree of metals is influenced by weather conditions, pollutant nature, plant surface characteristics and particle size as well. Several studies [1–4] demonstrated experimentally the significance of foliar accumulation and translocation of air derived metal pollutants. Therefore, the foliar way was found to be of similar importance to the soil-root pathway [1]. In other studies [5–7], the ruderal plants such as *Achillea millefolium* or *Matricaria recutita* are considered as bioaccumulative indicators due to their ability to accumulate metals in high quantities without visible injury. But the mechanism of the toxic metal absorption processes are still unclear. Some heavy metals at low levels are essential micronutrients for plants, but in higher concentrations they may cause metabolic disorders and growth inhibition [8] as well, for some of the medicinal plant species. For example, the response of medicinal plants to copper is a result of exposure to the metal either in the soil or as an aerosol. Copper absorbed by plants, apparently accumulates in roots, even in cases where roots have been damaged by copper toxicity. Copper deficiency can lead to yield loss and disease problems if is reduced chlorophyll content [9]. The excess of copper inhibits a large number of enzymes as well and interferes with several aspects of plant biochemistry, including photosynthesis or pigment synthesis.

Products based on natural medicinal plants enjoy an increasing economic importance in different domains, such as food, pharmaceutical and cosmetic industry. Several of medicinal plants produce specific secondary metabolites, which can detoxify some of toxic heavy metals [9]. Thus, medicinal plants can have nontraditional use (*e.g.* phytoremediation technologies [10, 11]).

In the last decade the practical use of alternative medicine in healing processes showed a continuous increasing tendency. Several species of medicinal plants can be used as supplementary nutrition [12] due to their ability to accumulate some essential elements (*e.g.* Se [13], Zn, and Fe [14]) in the edible parts of these plants (*e.g. Taraxacum officinale*). In the same time some mixtures of medicinal plants are prescribed by the traditional methods for diseases ranging from common colds to malaria, arthritis, ulcers, etc. Therefore it should be stressed that the use of medicinal plants has to respect the potential hazard connected with environmental contamination [15], mainly with toxic metals.

The aim of this study was to determine the metal contents of several plants used for several purposes in eastern Romania (Navodari area; Table 1 and Fig. 1) and the soils in which they grew in the period May, 2011 to September, 2011.

The main activities of the Navodari village, but also the main sources of pollution in this region are "Rompetrol" and former “Marway Fertilchim” Chemical Fertilizer Factory. Treatment plant of oil refinery discharged wastewaters into the Black Sea, in the northern of Năvodari. Chemical fertilizer factory was closed, but around the sole remained sections was huge amounts of toxic waste (some radioactive), serious sources of environmental pollution. Moreover, it was discovered that the pipe that leave from the former settling basins of the plant and stops in the see, still flows water with phosphogypsum. In 2008, the National Commission for Control of Nuclear Activities (CNCAN) concluded that the phosphogypsum deposits which are located inside of the factory, have a radioactive content which exceeding the normal range. In addition to the phosphogypsum waste (2.5 million tones in settling basins), on the plant land still is 5 tonnes of sulfuric acid sludge deposited on the bottom collector basins, almost 100 tons of pyrite ash, and over 120 tons of vanadium catalysts, which still existed in contact stoves. These sources are toxic for peoples and potentially polluted sources for environment. However, these anthropogenic activities, auto traffic and its effects on environment can be showed by medicinal plants which can respond at the pollution degree of the region in the changing climatic conditions. Invariably this pollution, directly affects the population from this region. These plants could potentially be either dangerous or useful for humans who are consuming medicinal plants or to animals feeding on these economically important plants.

2. MATERIALS AND METHODS

2.1. MATERIALS

All selected plants for this study are perennials and grow in different areas without special growth conditions, being used in herbal treatment of several diseases by the Romanian peoples. It was chosen the Navodari area because here was observed an increasing of the peoples, due to the development of oil platform, chemical industry and not lastly this zone has become a searched tourist destination at the Black Sea.

Trace elements in several perennial plants such as *Matricaria recutita* (Chamomilla), *Taraxacum officinale* (Dandelion), *Achillea millefolium*, and *Hypericum perforatum* were analyzed in this study by using Flame Atomic

Absorption Spectrometry (FAAS). The reason to choose these species was those are common plants, and can be found anywhere, in uncultivated areas, on fields, on road edges and so on. Aerial heavy metal deposit are taken up from the soil by plants via their root system and translocated to other regions of the plant (leaves and flowers). In this respect, all samples were collected as mixture leaves and flowers ($n = 5$), in the period May–September, 2011.

The chamomile (family *Asteraceae*) stem, reaching growing up to 60 cm, is striated and ramified at its base, and each branch has small leaves and flowers. Chamomile flowers contain: essential oils (etheric oil: 0.38 - 0.81%), vitamins B1 and C, mineral substances (phosphorus, potassium, silicon, iron, manganese, calcium, copper, lead, zinc, zirconium), glucides, lipids (in small quantities) and acids [8]. The plant has calming, analgesic, disinfecting and antiseptic, antispasmotic and tonic actions. Externally, chamomile has cicatrizing, emollient and anti-inflammatory effects.

Taraxacum officinale (family *Asteraceae*) grows from generally unbranched roots and produces one to more than ten stems that were between 40 to 70 cm tall according with the collected period. The leaf margins are typically shallowly lobed to deeply lobed and often lacerate or toothed with sharp or dull teeth. The florets number 40 to over 100 per head, having corollas that are yellow or orange-yellow in color [8]. The leaves of *Taraxacum officinale* (called dandelion greens) can be eaten cooked or raw in various forms, such as in soup or salad. The leaves are high in vitamin A, vitamin C and iron, carrying more iron and calcium than spinach [8]. Dandelion flowers can be used to make dandelion wine.

It is well known that, in traditional medicine, the *Achillea millefolium* (family Asteraceae) has a diaphoretic, astringent, tonic, stimulant and mild aromatic effect. It contains isovaleric acid, salicylic acid, asparagin, sterols, flavonoids, bitters, tannins, and coumarins [8]. The flowers of *Achillea millefolium* are used to treat various allergic mucus problems (due to the anti-allergenic compounds can be extracted from the flowers by steam distillation), including hay fever. Also, the dark blue essential oil, extracted by steam distillation of the flowers, is generally used as an anti-inflammatory. The collected leaves of *Achillea millefolium* have varying degrees of hairiness. The leaves had 5–20 cm long, bipinnate or tripinnate, almost feathery, and were arranged spirally on the stems.

The leaves of *Hypericum perforatum* (family *Hypericaceae*) are yellow-green in color, with transparent dots throughout the tissue and occasionally with a few black dots on the lower surface. Their flowers measures up to 2.5 cm across, have five petals, and are colored bright yellow with conspicuous black dots.

The unwashed leaves and flowers mixture of plant samples were dried at 600°C in 24 hours. Soil samples have been dried at 700°C in 24 hours as well. After drying the solid samples have been grinded until to fine powder and weighed in order to digestion.

The chemicals included nitric acid (65% Aldrich), hydrochloric acid (37% Fluka), hydrogen peroxide (30% Fluka), and potassium chloride (Aldrich) are used for digestion. Distilled deionised water with a rezistivity better than 17.5 MΩcm was used for sample dilution. The solutions used for calibration of FAAS were prepared from standard solution (Merck) of the studied elements.

2.2. METHODS

2.2.1. Sample Preparation

Dried plant samples were digested in an acid solution using a Berghoff MWS-2 microwave digestion system. Dried samples (200 mg) were introduced into the digestion vessels; then 8 mL nitric acid and 10 mL hydrogen peroxide were added. After digestion time (30 min) the vessels were cooled at room temperature and then each solution volume was made up to 50 mL for each sample using deionised water. Certified Standard Reference Material SRM 1515 (Apple Leaves) from the National Institute of Standards and Technologies was used to verify the obtained values.

Dried soil samples (500 mg) were introduced into the digestion vessels and then 3 mL nitric acid and 9 mL hydrochloric acid (aqua regia) were added. After digestion time (60 min) the vessels were cooled at room temperature and then each solution volume was made up to 50 mL for each sample using deionised water. Certified Standard Reference Material SRM 2710 and 2711 (Montana Soil) for soil was used, too.

2.2.2. Flame Atomic Absorption Spectrometry

The elemental content of samples was determined by Flame Atomic Absorption Spectrometry (FAAS). The Cu, Cd, Cr, Co, Ni, Zn and Pb elements from samples were determined by using an AVANTA GBC flame atomic absorption spectrometer with hollow cathode lamps, which provide a good sensitivity and requires less sample volume [16-23]. Due to the specificity of this spectrometer, the obtained results are accurate and seldom require confirmation.

Determination of elemental concentrations in medicinal plants samples and their substrate were performed using the method of calibration curve according to the absorber concentration. Several 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.

In this study to estimate the analytical precession and accuracy and to assure the proper quality of analytical results, some necessary requirements were performed. Analysis of duplicate samples was performed. Also, replication improves the quality of the results and provides a measure of their reliability. Blank and standard solutions have been used to calibrate the devices. A typical set of standard calibration curves with good linear regression and better relative standard deviations that were employed to measure the concentration of heavy metals in mushrooms and their substrate samples. Also, periodic testing of standard solutions to verify of reliability of the measuring apparatus was achieved. Accuracy has been checked using quality control test for medicinal plant and their substrate to show the degree of agreement between the standard values and measured values, the difference was less than 5%.

2.2.3. pH and conductivity of soil

The pH of solid substrate was determined according to ISO 10390:2005 method. The solid samples (weight 10 g) were treated with 50 ml KCl 0.1N, under stirring for 30 min. After, 1 hour, the pH for the each sample was measured with a pH meter Consort P501 at room temperature. Electrical conductivity was measured in saturated extract of soil using HACH CO150 apparatus.

3. RESULTS AND DISCUSSION

Seven metals including Pb, Cr, Cd, Ni, Cu, Zn and Co were analysed in *Matricaria recutita* (Chamomilla), *Taraxacum officinale* (Dandelion), *Achillea millefolium*, and *Hypericum perforatum* perennial medicinal plants. The same metals, and in addition Mn and Sn, in soil samples from selected zones of Navodari, Romania (Table 1 and Fig. 1) were determined by FAAS.

The characteristics of soil including pH and conductivity were measured. The pH of examined soil samples was moderately basic. The result showed that the mean pH were between 7.44 and 7.82. The smaller values of pH were observed in samples collected from Rompetrol Refinery area (S 5, S 15, S 25, S 35) thus resulting a weak basic character for these soils. For electrical conductivity, the measured conductivities of the water-extracted soils indicate the relative water-soluble salt content of the soil. The mean conductivity values of the water-extracted soil were between 12.67 and 12.91 mS (Table 2).

Table 1

Sampling area (Navodari)

Code	Coordinates		Sampling area
	Longitude	Latitude	
Pm 1	44º21’03.89”	28º39’14.04”	Channel of Rompetrol Refinery
Pm 2	44º20’24.69”	28º38’19.26”	Rompetrol Refinery zone
Pm 3	44º21’14.61”	28º40’10.67”	Lake Corbu to Refinery
Pm 4	44º20’00.65”	28º37’34.00”	Lake Taşaul to Refinery
Pm 5	44º18’40.29”	28º35’32.56”	The former Chemical Plant
Pm 6	44º15’53.63”	28º33’50.17”	Ovidiu zone
Pm 7	44º12’55.77”	28º38’0.11”	Mamaia - Lake Tăbăcăriei
Pm 8	44º16’50.88”	28º35’36.69”	Lake Siutghiol to the Chemical Plant

Table 2

Sampling area (Navodari)

Soil sample	pH	Conductivity [mS]	Salinity [‰]
S5 (Pm 1)	7.72	12.67	7.3
S10 (Pm 2)	7.44	12.72	7.3
S15 (Pm 3)	7.63	12.91	7.3
S20 (Pm 4)	7.49	12.85	7.3
S25 (Pm 5)	7.82	12.74	7.3
S30 (Pm 6)	7.74	12.71	7.3
S35 (Pm 7)	7.82	12.73	7.4
S40 (Pm 8)	7.53	12.69	7.3

Fig. 1 – The arrangement of sampling point.

Several studies [24-26] have demonstrated that pH, conductivity and salinity of the soil influence the absorption and migration of toxic metals (*e.g.* chromium, lead, copper, cadmium, zinc, etc.) from soil in medicinal plants. These metals in small quantities ensure a good functioning of plant metabolism but are toxic in high concentration. It is well known [9] that acidic soils increase the absorption of metals in plants.

In this study, the analyses of soil samples collected from Navodari region (Pm1 – Pm8) shown that the pH is weakly basic (Pm1 – Pm4) or moderate basic (Pm5 – Pm8), and it can concluded that in monitored area is expected a lower concentration of heavy metals in plant samples.

In Table 3 are presented the mean concentrations and relative standard deviation (RSD) of several metals in perennial medicinal plant (*Matricaria recutita* – Ct1, Ct6, Ct11, Ct16, Ct21, Ct26, Ct31, Ct36), *Taraxacum officinale* – Ct2, Ct7, Ct12, Ct17, Ct22, Ct27, Ct32, Ct37, *Achillea millefolium* – Ct3, Ct8, Ct13, Ct18, Ct23, Ct28, Ct33, Ct38, and *Hypericum perforatum* – Ct4, Ct9, Ct14, Ct19, Ct24, Ct29, Ct34, Ct39) collected from Navodari polluted zone (Pm1 – Pm8) from May to September, 2011.

It is very important to estimate the effects of heavy metals on plants since they are influenced by other elements. These interactions would include antagonism and synergism.

Absorption of heavy metal in medicinal plant is governed by soil characteristics such as pH, salinity, conductivity and organic matter content. In this respect, high levels of heavy metals in the soil (Table 4) do not indicate similar high concentrations in plants (Table 3). The extent of accumulation and toxic level will depend on the perennial plant and analyzed heavy metal. The high concentration obtained for Pb, Cd and Cu (Table 3) by *Achillea millefolium* and *Matricaria recutita* in analyzed region, concluded that Cu and Pb concentrations of these plants must be correlated with deposition of toxic particulate matter from polluted air but not with soil concentrations. In contrast, Ni and Co content in selected medicinal plants was correlated with deposition and soil content. The environmental factors including atmosphere and pollution, season of collection sample (end of spring, summer and beginning of autumn), age of plant (depending of season) and soil conditions (arid summer in 2011 and late summer in September 2011) in which plant grows influence the concentration of elements in plants. In Fig. 2 are presented the concentration of several metals in selected species.

Table 3

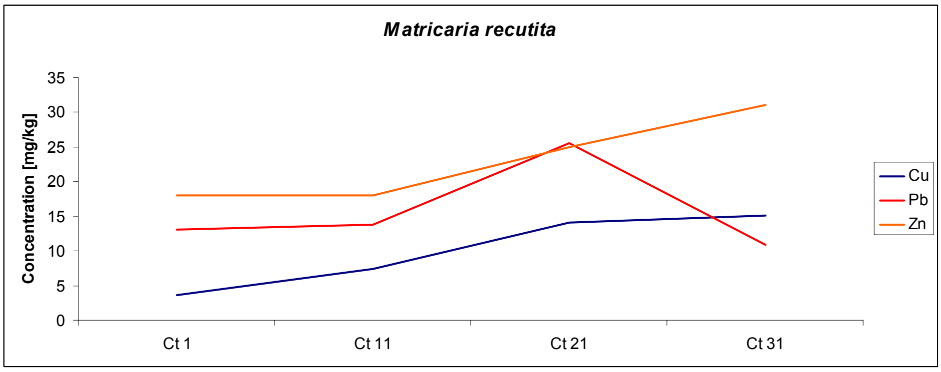
The mean concentration values (5 month) of several elements [mg/kg] in some medicinal plants (Navodari)

Sample (n=5)	Code	Metal concentration [mg/kg d.w]						
		Cu	**Ni**	**Pb**	**Zn**	**Co**	**Cr**	**Cd**
Ct 1	**Pm1**	3.589	0.371	13.050	17.993	nd	0.970	0.525
Ct 2		1.441	0.223	11.921	15.592	nd	0.432	0.783
Ct 3		8.219	0.514	14.467	44.861	nd	0.720	0.672
Ct 4		4.029	0.462	13.696	42.697	nd	0.127	0.637
Ct 6	**Pm2**	3.831	1.105	18.805	38.365	nd	0.704	0.447
Ct 7		2.270	0.194	11.016	29.890	nd	0.419	0.765
Ct 8		5.731	0.996	12.011	48.976	nd	0.059	0.391
Ct 9		0.976	0.755	11.884	26.095	nd	0.282	0.247

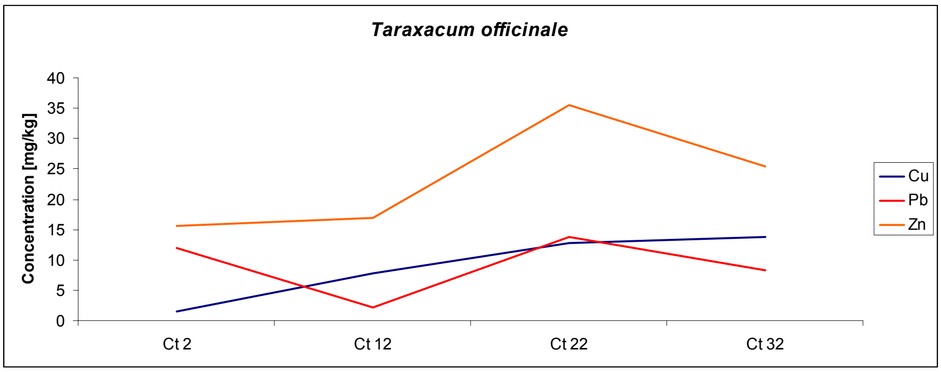
Table 3 (continued)

Ct 11	**Pm3**	7.386	0.189	13.787	17.992	0.019	0.019	0.279
Ct 12		7.752	0.211	2.180	16.914	0.024	0.003	0.311
Ct 13		7.012	0.271	9.228	18.127	0.001	0.002	0.208
Ct 14		11.887	0.315	12.550	24.600	0.047	0.005	0.211
Ct 16	**Pm4**	8.056	0.496	2.274	20.450	0.025	nd	0.011
Ct 17		5.179	0.211	2.198	12.660	0.008	nd	0.101
Ct 18		3.634	0.173	5.833	23.847	0.036	nd	0.021
Ct 19		20.547	0.196	3.027	24.510	0.047	0.002	0.036
Ct 21	**Pm5**	14.130	0.322	25.632	25.037	0.025	nd	0.021
Ct 22		12.723	0.313	13.728	35.491	0.022	0.002	0.008
Ct 23		9.822	0.235	12.989	30.363	0.018	0.003	0.011
Ct 24		12.110	0.246	20.966	33.946	0.017	0.002	0.009
Ct 26	**Pm6**	13.447	0.214	23.445	25.062	0.018	0.002	0.017
Ct 27		11.860	0.297	8.349	12.180	0.004	0.001	0.005
Ct 28		7.391	0.222	16.208	24.389	0.029	nd	0.021
Ct 29		16.028	0.267	18.661	25.606	0.025	nd	0.081
Ct 31	**Pm7**	15.096	0.288	10.951	31.007	0.019	nd	0.091
Ct 32		13.838	0.261	8.283	25.430	0.080	nd	0.072
Ct 33		9.133	0.233	14.877	22.265	0.093	0.001	0.043
Ct 34		12.500	0.301	14.167	33.634	0.013	nd	0.061
Ct 36	**Pm8**	15.206	0.257	13.471	27.200	0.002	0.001	0.025
Ct 37		13.674	0.189	9.593	24.614	0.013	0.001	0.035
Ct 38		9.611	0.234	19.080	27.193	0.046	0.001	0.033
Ct 39		16.360	0.217	25.492	27.663	0.010	0.001	0.014
RSD [%]		0.1-1.48	0.1-0.52	0.1-1.27	0.1-0.77	0.001-0.03	0.00-0.01	0.01-0.07

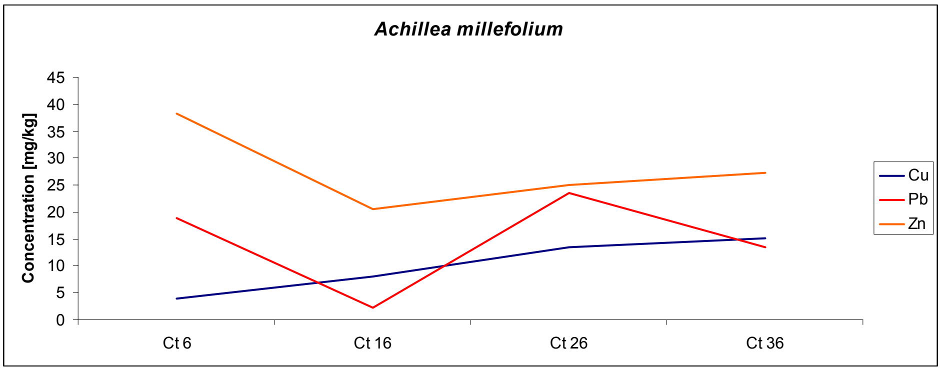
A higher concentration of Zn was observed in all analyzed plants, especially in summer months, depending by the climatic condition (August was a raining period and was possible that increase the accumulation of zinc in soil). Plants have absorbed Zn as Zn^{2+}, Zn being widely distributed in soils. Zinc concentration ranged between 12.180 mg/kg in *Taraxacum officinale* collected from Ovidiu zone (Pm6) and 48.976 mg/kg in *Achillea millefolium* collected from Rompetrol Refinery location (Pm2) (Table 3). The physiological activities of the medicinal plant influence Zn absorption and the interactions with many elements such as Fe and Cu. These elements play a vital role in the formation of secondary metabolites [27] which are responsible for pharmacological actions of medicinal plants.


Matricaria recutita
Concentration [mg/kg]
0
5
10
15
20
25
30
35
Ct 1
Ct 11
Ct 21
Ct 31
Cu
Pb
Zn

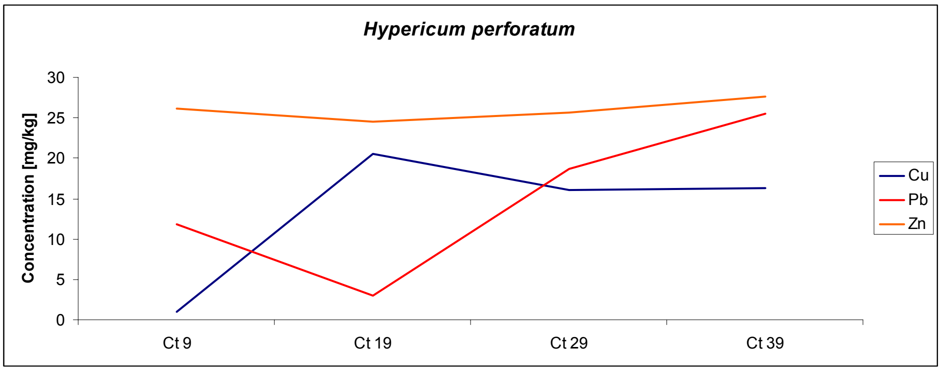
a


Taraxacum officinale
Concentration [mg/kg]
0
5
10
15
20
25
30
35
40
Ct 2
Ct 12
Ct 22
Ct 32
Cu
Pb
Zn

b


Achillea millefolium
Concentration [mg/kg]
0
5
10
15
20
25
30
35
40
45
Ct 6
Ct 16
Ct 26
Ct 36
Cu
Pb
Zn

c



d

Fig. 2 – Cu, Pb and Zn concentration in collected medicinal plants: a) *Matricaria recutita*; b) *Taraxacum officinale*; c) *Achillea millefolium*; d) *Hypericum perforatum*.

Availability and uptake of Cu (Table 3) in medicinal plant (leaves and flowers) are affected by interaction with other trace metals as well as by the concentration and type of major nutrients, such as Fe, Ca, Mg, K, P and Zn. Demands for copper is changed during the growth of a plant, with resultant changes in uptake and potential changes in tissue concentrations. Copper deficiency can lead to yield loss and disease problems in had reduced chlorophyll content of medicinal plants. Chloroplast structure of leaves can be affected by a low concentration in copper (e.g. Pm2 location, *Matricaria recutita* has 0.831 mg/kg Cu concentration and *Hypericum perforatum* has 0.976 mg/kg Cu content as mean of five month). In other locations such as Pm4 – Pm8 the copper concentration ranged between 16.360 mg/kg (Pm8) to 20.547 mg/kg (Pm4) in *Hypericum perforatum* and it was observed an inhibition process of pollen germination. The concentration of Cd and Pb may depend on the sampling location. As can be seen from the data in Table 3, spatial variability is particularly high in elements which show different degrees of bioavailability depending on sampling parameters. Heavy metals may also show high spatial variability depending on the pattern of emission sources and processes of transportation prevailing in the atmosphere and in deposition. Among the heavy metals, Pb and Cd concentrations are higher in samples collected from traffic areas (Pm1 –Pm3 and Pm5 – Pm8). The concentration of Cd in medicinal plants is related to its level in the soil and its bioavailability. All collected plants which grow in contaminated soil, such as Rompetrol Refinery zone (Pm1, Pm2 and Pm3), present higher concentrations of Cd than those with lower concentration in Cd (Pm4 – Pm8). *Taraxacum officinale* is able to accumulate more Cd (e.g. 0.783 mg/kg d.w. in Pm1 location) than *Achillea millefolium*, *Matricaria recutita* and *Hypericum perforatum* (Table 3). Selected medicinal plants can absorb Pb (Table 3) from soil and from

PbEt2 traffic-induced contaminated atmosphere, because the collected points are near roads (except the point Pm4). It can say that this source was responsible for more than 90% of total Pb emissions into the atmosphere, in studied points, especially in Pm5 – Pm8. The analysis of Cr in the sampled medicinal plants indicated (Table 3) that Cr concentration ranged between 0.127 mg/kg to 0.970 mg/kg in Pm1 zone (Channel of Rompetrol Refinery) and 0.059 mg/kg to 0.704 mg/kg in Pm2 location (Rompetrol Refinery), respectively. The concentration of Cr in the other locations (Pm3 – Pm8) is mostly undetectable (nd) by FAAS, being in the order of ppb. Also, the concentration of Ni and Co (which certainly interfere) are very lower or undetectable (especially at Co), as can see in Table 3.

Soil pH is important in controlling bioavailability and uptake, tissue metal levels generally decreasing with increasing pH. From Table 4 it can see that elevated levels of soil copper can be associated with reduced iron uptake, apparently a result of metal-metal competition. It should be noted that in sampling point of Rompetrol Refinery area, the concentrations of Fe, Cu and Pb are constant, during the monitored period, and in the Chemical Plant Factory area these concentrations vary between sampling periods. From Table 4 and Figs. 3, 4 and 5, it can observe that is some easy exceeding of several heavy metal concentrations (Pb, Cd, Zn and Cu depending by sampling points) according with normal levels of Romanian Order no 756/1997, but without reaching the maximum level.

Tabel 4

The mean concentration values (5 month) of several metals [mg/kg] in soil samples collected from Navodari region

Location	**Soil sample**	**pH**	**Metals concentration [mg/kg d.w.]**								
			Fe	**Zn**	**Cd**	**Cr**	**Cu**	**Mn**	**Pb**	**Co**	**Sn**
Pm1	S 5	7.720	601.121	328.965	1.886	0.281	37.705	144.500	15.020	0.013	0.001
Pm2	S 10	7.440	619.547	169.941	0.959	0.231	24.444	204.150	18.260	0.022	0.004
Pm3	S 15	7.630	593.633	254.038	1.152	0.234	41.859	196.620	21.230	0.016	0.003
Pm4	S 20	7.490	271.232	194.550	0.409	0.105	24.221	195.230	47.876	0.011	0.002
Pm5	S 25	7.820	582.739	244.156	0.893	0.181	51.396	189.030	18.509	0.026	0.001
Pm6	S 30	7.740	473.008	139.002	0.531	0.399	29.003	169.050	37.893	0.092	0.002
Pm7	S 35	7.820	623.098	196.709	0.800	0.326	46.007	173.520	16.009	0.079	0.005
Pm8	S 40	7.530	389.529	136.899	0.578	0.451	24.409	164.980	30.672	0.089	0.001
Romanian Order no 756/1997											
Normal level			3000	100	1	30	20	900	20	15	20
Maximum level			4500	700	5	300	250	2000	250	100	100
Intervention level			7000	1500	10	600	500	4000	1000	250	300

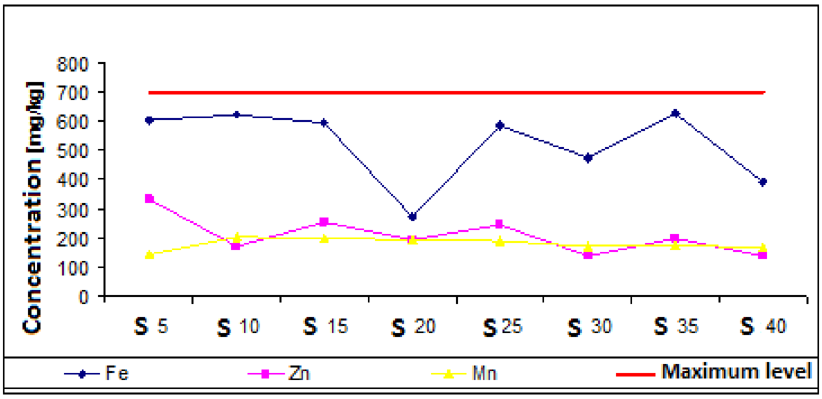


Fig. 3 – Fe, Zn and Mn concentrations in soil samples collected from Navodari.

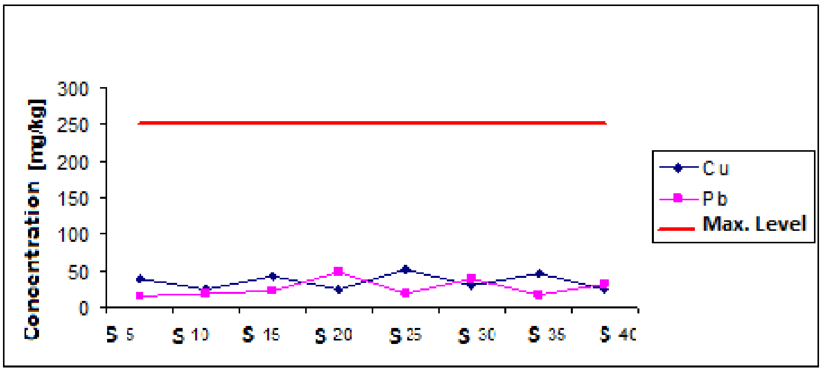


Fig. 4 – Cu and Pb concentrations in soil samples collected from Navodari.

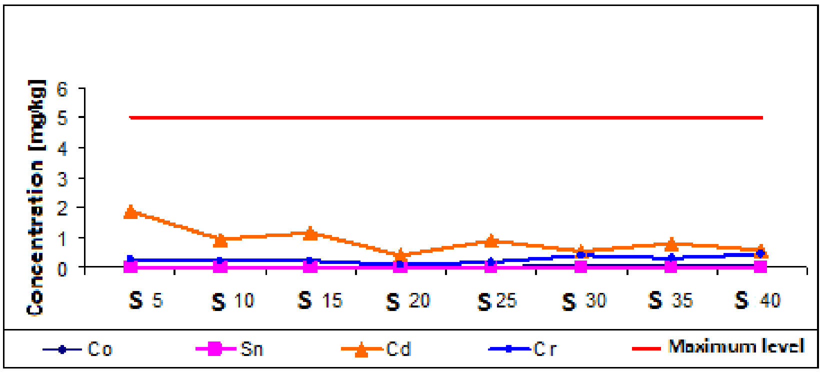


Fig. 5 – Co, Sn, Cd and Cr concentrations in soil samples collected from Navodari.

4. CONCLUSIONS

This study gives a new perspective about the presence of some trace elements in several indigenous medicinal plants, such as *Matricaria recutita*, *Taraxacum officinale*, *Achillea millefolium,* and *Hypericum perforatum,* and the soils in they grow. The metal composition of these perennial medicinal plants is mainly dependent on the composition of the soil and pH. The rain, temperature and humidity conditions of the air layer right above the ground entail extreme fluctuations of element concentration as well as the pollution sources which are not easy to assess. The obtained data indicates that these plants can accumulate certain metals, and this property can be exploited by the use of these plants for medicinal purposes in addition to their bioactive secondary metabolites constituents. Often, these medicinal plants demonstrate good morphological and physiological responses to heavy metal pollution and from this reason these species can be utilised as bioindicators.

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