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TARAXACUM OFFICINALE AS A BIOMONITOR OF METALS AND TOXIC ELEMENTS (PLOVDIV, BULGARIA)

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Abstract

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The content of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in aboveground and underground phytomass samples of complex *Taraxacum officinale*, collected from seven selected sites with different anthropogenic activity in the town of Plovdiv (Bulgaria), was analyzed and assessed. This plant species is widely used for herbal remedy therefore the results were compared with Bulgarian hygiene norms for contaminants in foods. Significantly elevated concentrations of Cd and Cr in all samples, also of Pb and Ni in the most of samples, were registered, which may represent a risk for humans.

Key words: heavy metals, toxic elements, biomonitoring, *Taraxacum officinale*

Introduction

The air pollution is a topic of global concern. During the last decades, many studies have suggested the use of bioindicators in the monitoring of the air pollution (Martin and Coughtrey, 1982; Ali, 1991; Wittig, 1993; Aksoy et al., 1999; Keane et al., 2001). Plants can act as bioindicators of air pollution and habitat quality because of their wide distribution and high accessibility. The action of air pollutants to plants, mainly the bioaccumulation of heavy metals in different plant tissues, has long ago been the matter of several investigations (Aksoy et al., 2000; Keane et al., 2001; Malawska and Wilkomirski, 2001; Gjorgieva et al., 2011).

Recently, a presence of an elevated content of heavy metals and toxic elements in the air in many cities, including Plovdiv, is registered. The metals contamination has great significance due to their tendency to accumulate in different organs over a prolonged period. Thus, both the deficiency as well as an excess of essential micronutrients (e.g. Cu, Fe, Ni, Zn) may produce undesirable effects (Takacs and Tatar, 1978; Nath, 2000). The impact of toxic metals (e.g. As, Cd, Cr, Hg, Pb) on human health and their interactions with the essential trace elements may produce serious consequences (Nath, 2000; Takuchev, 2011).

Taraxacum officinale (dandelion) is a common herbaceous species that has been frequently selected as a possible biomonitor of heavy metal pollution because it is widespread distributed, easy to identify, easy and inexpensive to sample. The dandelion has been used in a number of regional scale studies as a biomonitor of environmental pollution in Bulgaria (Kuleff and Djingova, 1984; Djingova and Kuleff, 1999), Poland (Kabata-Pendias and Dudka, 1991), Hungary (Kovac et al., 1993), USA (Keane et al., 2001), Germany (Winter et al., 1999) and Canada (Marr et al., 1999).

The population generally uses the herbal medicine for a continuous period to achieve the desirable effects. A prolonged consumption of such plants, containing heavy metals at toxic concentrations, may cause a chronic health hazard. The simultaneous collection of

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aboveground and underground samples gives an additional possibility of distinguishing the possible source of trace metals for plant uptake, particularly of metallic pollutants (Kabata-Pendias and Tarlowski, 1981; Kabata-Pendias et al., 1989; Punz and Sieghardt, 1993).

As this species is commonly used as a natural drug in the traditional remedy, it is important to check whether the dandelion could accumulate heavy metals at higher concentrations than what are legally admitted in the recommended hygiene norms for contaminants in foods in Bulgaria, thus, the selection of the analyzed chemical elements was made according to the Regulation norm 31 (2004).

The aim of the present study was to quantify the content of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in aboveground and underground phytomass of dandelion plants, sampled from different areas of the town of Plovdiv, as well as assessed the pollution level at the studied urban area.

Material and Methods

Study area and sampling sites

This study was performed in the town of Plovdiv, one of the most densely populated cities in Bulgaria (over 340 000 inhabitants on 102 km^2).

Seven sampling sites with different type of anthropogenic activity were selected on the urban landscape (using GPS Garmin eTrex Vista HCx), as follows: Site 1 - near the north industrial zone, NE district; Site 2 – city park, East district; Site 3 – near the Rail station “Trakiya”, SE district; Site 4 (Ruski Bul.) and Site 5 (Nature monument Bunardzhik) – in the real center of Plovdiv; Site 6 – suburban zone, SW district; Site 7 – city park, West district (Figure 1).

Methodology of sampling

The sampling period was 10-12 April 2010. To minimize the effects of precipitation, no collections were made until at least 2 days of rain-free weather. In all sampling sites were taken at least five whole plants. The aboveground and underground phytomass were carefully separated and the representative samples were prepared for analyses. The plants were of a similar sun expose, height and growth form, growing at 5-10 m away from intense traffic. Exception was Site 4 – Ruski Bul., where plants were on the sidewalk, up to 1 m from the roadway. All the samples were stored in clean, labeled, polyethylene bags, closed tightly to avoid contamination during transportation. In the laboratory conditions, plant material was air dried for two weeks, ground to a powder and homogenized.

Chemical analysis

The chemical analyses were carried out in the Faculty of Chemistry, University of Plovdiv. About 1 g ground plant material was treated with 5 ml 65% nitric acid (Merck) for 24 h at room temperature. A Microwave Digestion System CEM MDS 81 D assisted the wet-ashed procedure. The elements Zn and Cu were determined by FAAS method using Atomic Absorption Spectrometer PERKIN-ELMER 4000 (flame air-acetylene). The content of As, Cr, Cd, Hg, Ni and Pb was determined by inductively coupled plasma mass spectrometry (ICP-MS) using instrument Agilent 7700 (2009), DF 1000. All samples, blanks and standards were spiked with internal standards - Ge 50 ppb and Rh 5 ppb final concentration in the solutions. The concentrations are presented in mg.kg^{-1} dry weight.

Statistical analysis

For evaluation of the determined concentrations, a descriptive statistical analysis was applied. Data were statistically processed using correlation analysis (Pearson correlation index). For all statistical analysis, the STATISTICA 7.0 statistical package was used (StatSoft Inc., 2004).

Results and Discussion

In the present study, the content of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn was determined in aboveground and underground phytomass of dandelion plants, sampled from selected sites in the town of Plovdiv (Figure 1). The data for the concentrations of investigated heavy metals and toxic elements in plant tissues were present in Figure 2.

No recommended levels of contaminants (including heavy metals) in the medicinal plants are accepted in Bulgaria, thus the hygiene norms for the permissible content in dry vegetables of the elements As, Cd, Cr, Cu, Hg, Ni, Pb and Zn, were used (Regulation norm 31, 2004).

***Arsenic*: Arsenic uptake by plants has been shown to be associated with phosphate, where presumably arsenate is taken up as a phosphate analog (Robinson, 2003). Several reports on the linear relationship between As content of vegetation and concentrations in soil suggest that plant take up As passively with the water flow. Concentrations of As in plants grown on uncontaminated soils vary from 0.009 to 1.5 mg.kg^{-1} (Kabata-Pendias and Pendias, 1992). In our study, the arsenic concentration in aboveground phytomass of all sampling sites was under the detection limit (<0.5 mg.kg^{-1}). We found an average concentration of As in underground phytomass of 1.1±0.5 mg.kg^{-1}. As the hygiene norm for As content in dry vegetables is 5.0 mg.kg^{-1}, so the observed values from the town of Plovdiv were quite low. These values are similar to the data from Sofia reported by Yurukova (2004) for the same species.

***Cadmium*: Cadmium is a very toxic metal to all living organisms. Plants take it up primarily from the soil through the roots and from the air through the leaves. Generally, it is accepted that the normal Cd concentrations in plants are 0.2-0.8 mg.kg^{-1} and toxic levels are defined as 5-30 mg.kg^{-1} (Kloke et al., 1984; Kabata-Pendias and Pendias, 1992). According these criterions, the area of Plovdiv is not highly polluted by Cd since its content in all samples was not exceeding the upper limit – 0.516±0.01 mg.kg^{-1} in aboveground and 0.399±0.03 mg.kg^{-1} in the underground phytomass. The levels of this element were beyond Bulgarian hygiene norms. It can also be noted that the Cd values obtained for different samples were very similar – the correlation coefficient between aboveground and underground phytomass was

Fig. 1. Location of the selected sampling sites (Plovdiv, Bulgaria).
Site 1 - near the north industrial zone, NE district; Site 2 – city park, East district; Site 3 – near the Rail station "Trakiya", SE district; Site 4 (Ruski Bul.) and Site 5 (Nature monument Bunardzhik) – in the real center of Plovdiv; Site 6 – suburban zone, SW district; Site 7 – city park, West district

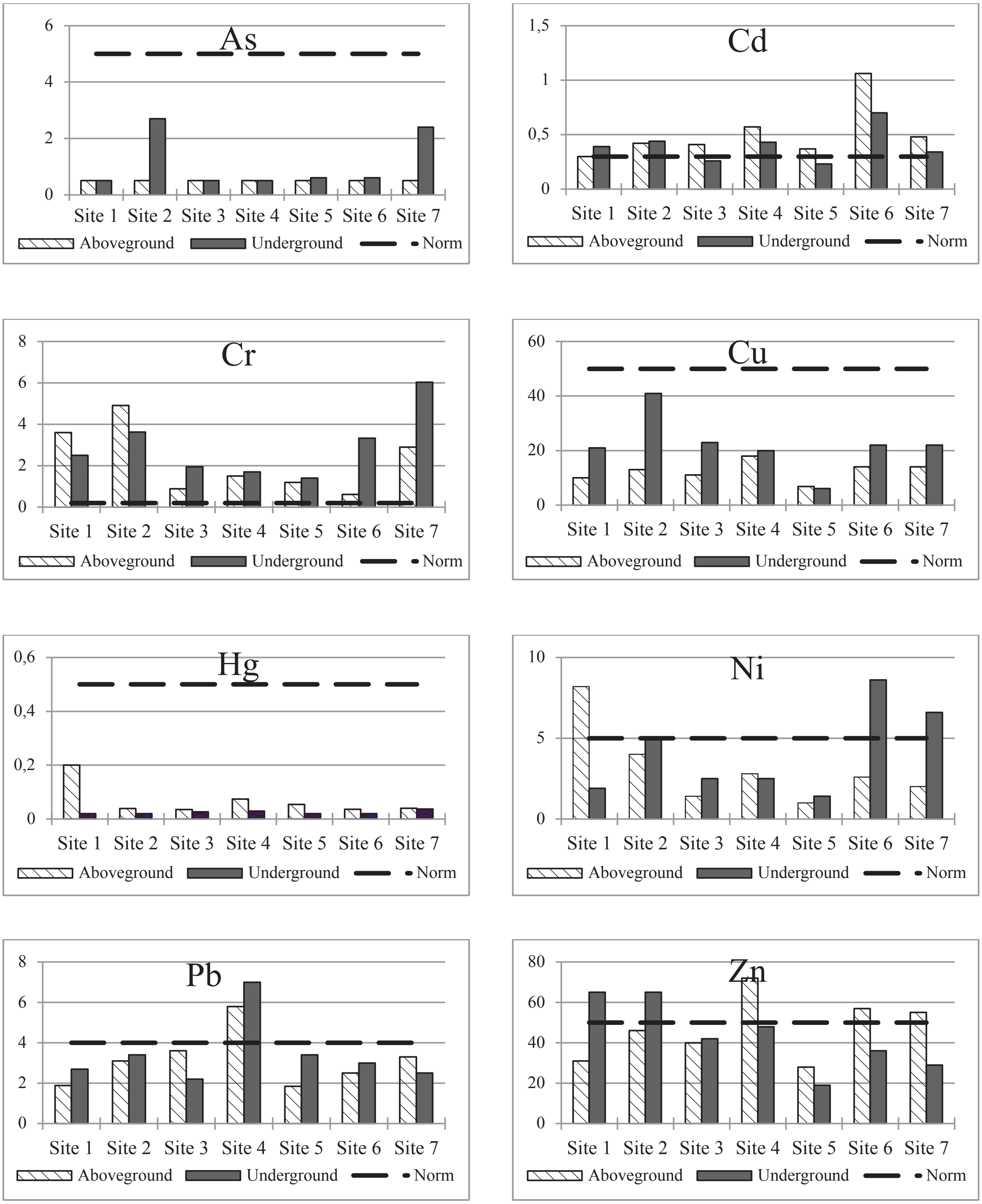

Fig. 2. Concentrations of analyzed elements (mg.kg^{-1} dry weight) in aboveground and underground phytomass and recommended hygiene norms in Bulgaria for As, Cd, Cr, Cu, Hg, Ni, Pb and Zn content in dry vegetables (dotted line)

0.86 ($p<0.05$). This may support the known fact that Cd root-to-shoot transport is most likely driven by a transpiration stream (Salt et al., 1995). Cadmium content, measured in the collected aboveground phytomass from Plovdiv, was significantly higher in comparison with data from other authors: 0.06-0.08±0.02 $mg.kg^{-1}$ in Switzerland (Rosselli et al., 2006), <0.2 $mg.kg^{-1}$ in Peshawar, Pakistan (Hussain and Khan, 2010), 0.39±0.09 $mg.kg^{-1}$ in Sofia (Yurukova, 2004).

Chromium**:** Chromium is also well known as a very toxic element. The Cr content of plants has received much attention since the relatively recent discovery that Cr participates in glucose and cholesterol metabolism, and therefore is essential to man and animals. Its content in plants is controlled mainly by the soluble Cr content of the soils. Usually, a higher level is observed in roots that in leaves, and the lowest concentration is in grain (Kabata-Pendias and Pendias, 1992). The detected content of Cr (2.23±0.02 $mg.kg^{-1}$ in avoveground phytomass, 2.93±0.4 $mg.kg^{-1}$ in underground phytomass) exceeds the hygiene norm in all cases and was maximal in samples from Site 2 and Site 7. The excess of chromium was observed in underground organs, except Site 1 and Site 2. Probably, this metal is translocated from air dust through precipitation into the soil. These values exceed the data for Sofia reported by Kuleff and Djingova (1984) and Yurukova (2004).

Copper**:** The appropriate content of Cu in plants is essential both for the health of the plant and for the nutrient supply to man and animals. Although copper is an essential enzymatic element for normal plant growth and development, it can be toxic at concentrations above 25 $mg.kg^{-1}$ (Allen, 1989). The mean values for Cu concentrations in dandelion aboveground and underground phytomass from examined sites in Plovdiv reached 12.4±2.7 $mg.kg^{-1}$ and 22.16±2.7 $mg.kg^{-1}$, respectively. Copper was the metal which content varied most between the analyzed samples, but it stayed rather below the recommended hygiene norm. The movement of Cu among various parts of plants plays a predominant role in the plant's utilization of Cu. The strong capability of root tissues to hold Cu against the transport to shoots under conditions of both Cu deficiency and Cu excess has been reported by many authors (Loneragan, 1981; Kabata-Pendias and Pendias, 1992)

Lead**:** Lead is regarded as very hazardous for the biota. Normal concentrations in plants are 0.1-10 $mg.kg^{-1}$ according to Kabata-Pendias and Pendias (1992). Bioaccumulation levels and average content of Pb in both aboveground (3.15±0.7 $mg.kg^{-1}$) and underground samples (3.46±0.14 $mg.kg^{-1}$) from Plovdiv were below the hygiene norms, except the values in phytomass from Site 4, which is characterized with an intense traffic. Obviously, the high Pb concentrations in aerial parts of dandelion is due to the lead coming from the emission of vehicles as well as its presence in the rhizomes through soils polluted with wastes from different operations and wet deposition.

Zinc**:** Zinc is an essential element in all organisms and plays an important role in the biosynthesis of enzymes, auxins and proteins. This metal is not considered to be highly phytotoxic and its toxicity limit varied between 300 and 400 $mg.kg^{-1}$ (Kabata-Pendias and Pendias, 1992). Many authors (Allen, 1989) have quoted a plant foliar concentration of 100 mg.kg-1 as a critical indicator of whether the environment is polluted with Zn. In our study, the mean values for Zn concentration were 47±3.8 $mg.kg^{-1}$ and 43.43±2.7 $mg.kg^{-1}$ in aboveground and underground phytomass, respectively. According to Allen's criterion (1989), it can be concluded that Plovdiv was not contaminated and the dominant zinc content in the aboveground, rather than the underground plant samples is evidence for its aerial origin.

Nickel**:** Nickel is an abundant element; it is required in minute quantity for body as it is mostly present in the pancreas and hence plays an important role in the production of insulin. Its deficiency results in a disorder of the liver (Nath, 1996). Exceeding the optimal values, it shows a toxic effect. With respect to the fact that Ni uptake depends on plant species, and that some of them act as hyper accumulators, Ni concentrations in normal plants range from 0.5 to 5 $mg.kg^{-1}$ dw (Allen, 1989). The obtained mean values in this study for Ni in the aboveground phytomass were 3.143±0.2 $mg.kg^{-1}$ and 4.057±0.2 $mg.kg^{-1}$ in underground organs. Maximal content (8.2 $mg.kg^{-1}$) was observed in aboveground sample from Site 1, also in the underground samples from Site 6 (8.6 $mg.kg^{-1}$) and Site 7 (6.6 $mg.kg^{-1}$).

Mercury**:** The major source of Hg in plant species are both the existence of ore deposits with Hg near the sampling place or its release into the atmosphere, soil and water mainly because of combustion of large quantities of coal (Huckabee, 1973). Since in the area of Plovdiv there are no Hg deposits, the increase in the Hg concentration in collected dandelion samples could be explained as a direct result from the anthropogenic and industrial pollution of the urban environment. The Hg concentrations, found by us, were of an average of 0.043±0.03 $mg.kg^{-1}$ and 0.025±0.01 $mg.kg^{-1}$ in aboveground and underground phytomass, respectively. The ratio between these two concentrations was calculated to be 1.723, and this value supports the presumption that Hg uptake is mainly from the atmospheric deposition.

The statistical analysis showed a strong positive correlation between concentrations of Cu and Zn (0.97, $p<0.05$), Cu and Pb (0.82, $p<0.05$), and for the elements Pb and Zn (0.81, $p<0.05$) in the aboveground phytomass samples. The Pearson analysis showed positive correlation between metal content in both aboveground and underground phytomass samples only for Cr (0.86, $p<0.05$) and Pb (0.76, $p<0.05$).

This study confirmed that the aboveground and underground phytomass of the dandelion were relatively useful environmental indicators for some heavy metals and toxic elements. The descending order of analyzed elements was found to be Zn>Cu>Pb>Ni>Cr>Cd>Hg>As for the aboveground parts of dandelion and Zn>Cu>Ni>Pb>Cr>Cd>As>Hg for the underground organs. We registered markedly higher concentrations of Pb, Zn, Cu and Cd in the aboveground phytomass from Site 4 (Ruski Bul.), situated into the real center of the town. These results confirm that the increased heavy metal content in urban roadside plant samples is mostly due to the density of traffic, which is considered one of the major sources of heavy metal contamination in Plovdiv.

Conclusions

Our results suggest that the distribution of the heavy metals and toxic elements in the plant organs of *Taraxacum officinale* is not homogenous as it depends of the physicochemical characteristics and bioavailability of the element, specific uptake processes and transfer in the tissues. Most of the analyzed elements showed a tendency to accumulate into the underground organs, except Cd, Hg and Zn.

In summary, the dandelion plants from the studied area showed an increased content of Cd and Cr in all sampling sites in comparison with the permitted hygiene norms for contaminants in dry vegetables in Bulgaria. The concentrations of the elements As, Hg and Cu were quite low and did not exceed the mentioned norms in all sampling sites. For the elements Pb and Zn critical levels were registered only in Site 4 (high traffic activity), while the maximal value for nickel was measured in Site 1 (near an industrial zone). Based on the obtained results, the use of plants, collected from the city area, is not recommended for phytotherapeutic or cosmetic purposes.

The conducted research approves *Taraxacum officinale* as a good biomonitor of urban contamination, which can be successfully used for the biomonitoring of the environmental quality.

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