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The peculiarities of heavy metals accumulation by wild medicinal and fruit plants

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Abstract: *The peculiarities of heavy metals accumulation by wild medicinal and fruit plants.* The article shows the results of studies of heavy metals accumulation by wild medicinal and fruit plants. Special attention is given to the investigation of roadside phytocenoses. Reliable differences in chemical composition of plants from background and transformed habitats are revealed. The influence of morphological and phenological characteristics of the species on the peculiarities of heavy metals accumulation is also determined.

Key words: heavy metals, medicinal plants, fruit plants.

INTRODUCTION

Nowadays the problem of ecological safety of use of wild medicinal plants and fruits is particularly important. One of the most dangerous pollutants of plant products are heavy metals. The patterns of accumulation of different macro- and microelements are based mainly on ecological conditions. Thus it is essential to study distribution and accumulation of contaminants in various species of wild medicinal and fruit pants in natural and transformed ecosystems like urban areas, surroundings and territories of industrial enterprises, slime deposits, roadside areas.

High concentrations of heavy metals (HM) accumulated in fruits can have toxic and carcinogenic effects what is not safe when using them for food. Existing norms of maximum permitted concentrations (MPC) (SanPiN 2.3.4.560-96; SanPiN 2.3.2. 1078-01) and recommended concentrations of HM for vegetables, fruits and mushrooms [Gabovich and Priputina 1987] are used to estimate toxicity of fruit plants raw material for people. MPC of HM for medicinal raw material are not developed so to estimate toxicity we have to use above-named norms of MPC and recommended concentrations of HM for vegetables, fruits and tea [Gabovich and Priputina 1987; Ecological aspects of inventions examination, 1989].

MATERIALS AND METHODS

To investigate the peculiarities of HM accumulation by wild medicinal and fruit plants in conditions of technogeneous load we collected samples of plants and fruits within Kirov region in ecosystems with different pollution level. We concentrated especially on the peculiarities of HM accumulation by plants of roadside areas, because they are among main pollutants this kind of areas together with fuels, lubricants and freely soluble salts [Air pollution…, 1988].

For our studies we selected the following species of medicinal plants: lingonberry (*Vaccinium vitis-idaea* L.), common valerian (*Valeriana officinalis* L.), may lily (*Convallaria majalis* L.), *Hypericum maculatum* Crantz., *Tussilago farfara* L., *Tanacetum vulgare* L., *Plantago major* L., bearberry (*Arctostaphylos uva – ursi* (L.) Spreng), *Achillea millefolium* L.; and wild fruit plants that are common for the region.

RESULTS AND DISCUSSION

We have studies concentrations of the following elements: Fe, Cu, Ni, Cd, Pb, Zn, Cr (Table).

Iron is a main bioelement. Daily need of iron for man is 10–20 mg [Vigorov 1976]. Significant accumulation of the element is marked for wood strawberry (*Fragaria vesca*) – 75.7 ±6.6 mg·kg^{-1}, raspberry (*Rubus idaeus*) – 77.39 ±4.68 mg·kg^{-1}, bilberry (*Vaccinium myrtillus*) – 80.77 ±11.6 mg·kg^{-1}, cranberry (*Oxycoccus palustris*) – 92.92 ±18.23 mg·kg^{-1}, ashberry (*Sorbus aucuparia*) – 95.95 ±6.84 mg·kg^{-1}. There is species-specific differences of iron concentration in fruits from polluted areas. High content of iron is typical for lingonberry, wood strawberry, bilberry and dog-rose (*Rosa majalis*).

Iron content of 50.0–240.0 mg·kg^{-1} dry matter is considered normal for phytomass of shrubs and herbs [Cottenie et al. 1976]. The concentration of the element in all studied samples of medicinal plants was significantly lower than regional clarke for forest herbs. Maximum concentration of iron was marked for *C. majalis*, growing 1 m from roadway (84.61 ±11.84 mg·kg^{-1} dry matter).

Zinc is among HM which content in vegetable food products is limited by operating standard acts. Permitted level of zinc in fruits of wild food plants must not exceed 10 mg·kg^{-1}. For majority of fruit plants there is no reliable difference between zinc concentration in fruits from polluted areas and in ones from the background. Zinc concentration does not reach MPC level in most of fruit samples (94%).

Normal content of zinc in plants phytomass is 25.0–150.0 mg·kg^{-1} dry matter [Cottenie et al. 1976; Kabata-Pendias and Pendias 1989; Ilyin 1991]. Concentration of 300.0 mg·kg^{-1} is considered critical [Tarabrin 1980]. Studied samples of plants from background phytocenoses are characterized by high zinc concentration (from 40.2 to 58.2 mg·kg^{-1} dry matter) in phytomass which is more than 2 times higher than regional clarke for forest herbs. Zinc concentration in *C. majalis* shoots from roadside phytocenoses was lower than in samples from background habitats but higher than regional clarke. This is probably explained by increased content of lead and cadmium which are the antagonists of zinc, in phytomass of roadside plants.

Copper – vitally important biomicroelement. Daily need of the element for people reaches 2 mg [Vigorov 1976]. Concentration of the element in fruits of studied plants from natural phytocenoses does not exceed 10 mg·kg^{-1}. No clear species-specific peculiarities of copper

TABLE. The content of HM in plants from background and roadside habitats (mg·kg^{-1})

Species of plant, raw material	Habitat	Cu	Ni	Cd	Pb	Zn	Fe	Cr
Vaccinium vitis-idaea, shoots	background	4.06	1.24	0.56	1.39	17.65	75.55	2.88
	1 m	5.37	1.88	0.28	0.80	20.48	47.43	1.98
	5 m	6.47	2.12	0.75	2.04	21.09	63.19	2.06
	10 m	6.20	1.55	0.43	1.55	18.97	62.56	1.85
Arctostaphylosuva-ursi. shoots	background	2.78	1.17	0.41	1.75	16.04	28.00	1.94
	5 m	2.61	2.17	0.65	3.03	16.62	30.20	3.87
	10 m	3.51	1.20	0.19	1.03	15.65	28.15	2.29
	20 m	2.69	1.21	0.37	1.10	15.12	23.26	1.98
Tanacetum vulgare, herb	background	7.82	1.59	0.81	1.39	22.61	54.04	1.52
	federal roads	8.85	1.36	0.91	2.16	20.71	37.93	3.54
Achillea millefolium, herb	background	7.21	1.30	0.61	2.24	25.63	87.83	1.72
	federal roads	6.81	1.06	0.94	2.30	20.42	48.77	2.26
Tussilago farfara, leaves	background	9.48	1.58	0.46	1.46	19.40	54.03	1.87
	1–10 m	8.40	2.71	1.21	4.36	20.38	60.93	3.39
	50–400 m	8.42	1.38	1.39	3.78	21.82	49.93	3.20
Plantago major, leaves	background	8.16	1.68	1.02	2.30	22.16	86.43	1.58
	1–20 m	7.97	1.85	1.18	2.79	34.47	57.66	3.53
	50–400 m	8.06	1.69	1.37	2.50	22.43	54.46	2.66
Valeriana officinalis, roots	background	7.50	1.72	0.42	1.69	26.43	70.23	3.70
	1–15 m	6.38	1.39	1.20	3.01	29.15	51.48	5.26
	100– 400 m	6.78	2.11	0.81	1.80	27.65	55.90	10.12
Convallaria majalis, shoots	background	7.06	1.36	0.44	1.70	47.4	52.85	2.82
	1 m	10.72	3.01	0.38	2.81	39.17	84.61	4.43
	200 m	8.57	1.44	1.28	2.37	41.57	45.19	2.22

accumulation were revealed. Copper content in all fruits from polluted areas was increased, but the level differs significantly between the species. Copper concentration increases 12.5% in lingonberry fruits and 3 times in dog-rose.

Copper MPC for vegetable products is 5.0 mg·kg^{-1} of raw mass. And the range of 5.0 to 30 mg·kg^{-1} is considered normal for plants [Cottenie et al. 1976; Kabata--Pendias and Pendias 1989]. Tarabrin [1980] marks that 150.0 mg·kg^{-1} is critical copper concentration for plants. It is determined that majority of vascular plants in background phytocenoses of the region contains insignificant quantities of copper – from 0.88 mg·kg^{-1} to 18.05 mg·kg^{-1} dry mass [Shikhova and Egoshina 2004]. Maximum copper concentration was revealed in shoots of plants 1 m from the roadway (10.72 ±1.11 mg·kg^{-1}). At larger distances from the roadway copper content decreases and reaches almost background values at 300 m.

Chromium in adequate quantities is an important vital element for animals and people. Compounds containing chromium are often found as technogeneous pollutants of anthropogenic nature. Fruits collected on technogeneous areas usually have larger content of chromium compared to plants from background natural phytocenoses. This is typical for lingonberry (2.65 ±0.57 $mg \cdot kg^{-1}$ and 1.39 ±0.25 $mg \cdot kg^{-1}$ correspondingly), wood strawberry (5.11 ±1.58 and 1.50 ±0.54 $mg \cdot kg^{-1}$), ashberry (3.47 ±0.18 and 2.32 ±0.28 $mg \cdot kg^{-1}$), birdcherry (2.24 ±0.25 and 1.67 ±0.34 $mg \cdot kg^{-1}$), dog-rose (2.42 ±0.37 and 1.81 ±0.25 $mg \cdot kg^{-1}$). These values exceed recommended norms.

Maximum concentration of chromium was revealed in bilberry (50.15 $mg \cdot kg^{-1}$) and ashberry fruits (13.1 $mg \cdot kg^{-1}$) from urban and suburban habitats.

Nickel is probably necessary for human organism in small quantities. Recommended norm of nickel content in vegetable products is 0.5 $mg \cdot kg^{-1}$. Nickel content in fruits of studied plant species is rather stable. Increase of anthropogenic pollution is not always accompanied by adequate increase of nickel concentration in plant tissues. There is no reliable difference in nickel concentration between species.

Offered nickel MPC for plants is in the range of 20.0 to 30.0 $mg \cdot kg^{-1}$ dry matter [Sauerbeck 1982]. Nickel content in shoots of *C. majalis* from background habitats reaches 1.36 ±0.24 $mg \cdot kg^{-1}$. Maximum values are marked for plants 1 m away from the roadway (3.01 ±0.52 $mg \cdot kg^{-1}$).

Lead – the most toxic and widely spread technogeneous contaminant. Natural levels of lead content in plants from unpolluted and barren regions are apparently constant and lie in the range of 0.1–10.0 $mg \cdot kg^{-1}$ dry mass (average – 2 $mg \cdot kg^{-1}$) [Kabata-Pendias and Pendias 1989; Cannon 1976]. MPC levels of lead for plants are in a wide range from 0.5–1.2 $mg \cdot kg^{-1}$ [Prokhorova et al. 1998] to 10.0–20.0 $mg \cdot kg^{-1}$ [Sauerbeck 1982]. MPC norms for fruits reach 0.4 $mg \cdot kg^{-1}$ raw mass. Lead concentration in fruits of plants from relatively clean habitats and polluted territories reliably differ.

It is significant that average lead concentration in fruits and vegetative mass of plants that have edible fruits does not differ much within background areas. But the difference is significant on technogeneous territories. At that dog-rose and ashberry accumulate more lead in fruits, and raspberry and wood strawberry – in leaves. Maximum number of samples that had higher lead concentration than MPC was marked for ashberry fruits.

Results of our research showed reliable differences between lead content in phytomass of plants from background and technogeneous areas. And lead concentrations of plants from the same phytocenosis vary. The volume of lead accumulation is probably determined by species-specificity of a plant. Most of studied species accumulate lead in phytomass in polluted habitats. But samples from the immediate vicinity of the road sometimes contain less lead than distant areas samples. This is probably explained by low availability of the element for plants in soils of roadside areas which have high pH level, and also by the profile of roadway, filling and edging.

Maximum concentration of the element is found in phytomass collected in the immediate vicinity of roads 1–20 m distant from the roadway. The content of the element in 50–200 m distant areas gradually gets lower. Lead concentration in phytomass of plants from 200–300 m zone sometimes exceeds MPC but mostly is only higher than background values. At a distance of 300–400 m metal content gets constant and close to average concentration for background areas.

Cadmium as well as lead is one of the most toxic heavy metals. Cadmium MPC for fruits is 0.03 mg·kg^{-1} raw mass. Fruits of the most wild plants in Kirov region have heightened level of cadmium content. It can exceed MPC several times even on relatively safe territories. For example, average cadmium concentration in fruits of dog-rose, raspberry, lingonberry, bilberry, wood strawberry, bird cherry, ashberry reaches 0.16–0.46 mg·kg^{-1}. This is probably explained by geochemical peculiarities of Kirov region [Shikhova and Egoshina 2004] and species-specific features of cadmium accumulation [Lovkova et al. 1990]. We registered even higher concentrations of cadmium in fruits of wood strawberry, ashberry and dog-rose on polluted territories.

CONCLUSIONS

Our data showed that in spite of significant level of pollution of roadside territories, productional and morphometric indices of plants were often even higher than on distant areas. Apparently roads as sources of pollution at the same time have barriers which decrease contaminants activity for plants (alkaline, humic barriers). Abundance of mineral elements improves nutrition conditions. Competitive relations of plants are often weakened near the roads; moreover the problem of competition for light is solved for forest species.

But chemical composition of plants from roadside habitats differs significantly from the one of background plants and is characterized by higher content of heavy metals. Shoots of forest plants (lingonberry, bearberry) growing 1–10 m away from the road accumulate significant quantities of copper (up to 8.40 mg·kg^{-1}). The content of nickel is increased almost twice compared to the background (up to 2.71 mg·kg^{-1}), cadmium – 2–3 times (up to 1.56 mg·kg^{-1}). Lead concentration is close to the background in lingonberry shoots but twice that much in bearberry and exceeds MPC significantly. Zinc content in shoots of forest plants is quite constant and slightly changes as the distance from the road increases. But zinc concentration in *C. majalis* shoots from any habitat is 2 times higher than the one in lingonberry and bearberry shoots.

Iron content in shoots of lingonberry and bearberry from roadside areas is slightly lower than background values.

Chromium content in lingonberry shoots from polluted areas is lower (and in bearberry is higher) than background. Maximum concentration of chromium in lingonberry shoots was marked in the area 5 m away from the roadway and it reached 2.06 mg·kg^{-1}, in lingonberry shoots from background areas it was 2.88 mg·kg^{-1}, bearberry – 3.87 mg·kg^{-1} and 1.94 mg·kg^{-1} correspondingly.

Phytomass of *T. vulgare* and *A. millefolium* from roadside areas accumulate cadmium, lead and chromium. But the content of nickel, zinc and iron in these plants is lower than in the background habitats.

Leaves of *T. farfara* and *P. major* growing 1–20 m away from the roadway have heightened content of nickel, cadmium, lead and chromium.

Higher concentrations of cadmium, lead, zinc and chromium are revealed for valerian roots compared to the background.

Studied plants of roadside phytocenoses have higher concentration of the most dangerous contaminants – cadmium and lead.

Maximum concentration of the metals which exceed MPC is revealed in plant vegetal medicinal raw material collected in the immediate vicinity of the roads at a distance of 1–20 m from the roadway. At a distance of 5–200 m from the roadway the content of metals in the raw material of different species gets close to the background values and gradually decreases. The content of the most dangerous HM in phytomass of medicinal plants in 200–300 m zone along the roads sometimes exceeds MPC but we mostly marked only the excess of background values. At a distance of 300–400 m from the roadway we marked the excess of background values only for valerian roots (cadmium – 0.81 $mg \cdot kg^{-1}$, chromium – 10.12 $mg \cdot kg^{-1}$) and for *C. majalis* shoots (cadmium – 0.49 $mg \cdot kg^{-1}$). The rest of the species had metal concentrations which were close to the background. The highest level of metals content is typical for the raw material that consists of the leaves with large, downy laminas (*T. farfara*, *P. major*). Raw material that includes small, coriaceous leaves covered by thick cuticle, is less polluted.

Raw material of medicinal and fruit plants from technogeneous and roadside habitats is significantly polluted by HM. The level of accumulation depends on morphologic and phenological peculiarities of the species.

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Streszczenie: *Szczególne cechy akumulacji metali ciężkich w dziko rosnących roślinach leczniczych i owocowych.* Przedstawiono wyniki badań akumulacji metali ciężkich w dziko rosnących roślinach leczniczych i owocowych, ze szczególnym uwzględnieniem roślin przydrożnych. Stwierdzono znaczące różnice w składzie chemicznym roślin podłoża i przekształconych siedlisk. Określono wpływ charakterystyki morfologicznej i fenologicznej gatunków na szczególne cechy akumulacji metali ciężkich.

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