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The Regularities of Heavy Metals and Arsenic Accumulation in the Vegetation of Riverside Depending on the Level of Technogenic Load

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Abstract

The regularities of heavy metals (Fe, Cu, Zn, Cd, Pb) and arsenic accumulation in various types of aquatic vegetation have been studied, depending on the season and the levels of pollution of the Srepok River (Vietnam). It has been found that the concentrations of Fe, Cu, Zn, As, Cd and Pb in all studied areas of the river in the roots of water hyacinth and common reed were higher than those in the stems. It has been shown that the content of toxicants in plants varied widely, depending on the level of pollution in the adjacent area. The maximum concentrations of Cu, Zn and Pb were noted in the organs of the water hyacinth and reeds in the lands within the industrial areas, and the highest levels of As and Cd were noted up the stream, before the river entrance into the industrial area. The content of Fe in all areas remained stable. The difference in heavy metals' concentrations in plants close to the banks in the provinces and in the middle of the river in most cases was not statistically significant.

Keywords: industrial areas, pollution, heavy metals, the levels of content, common reed, water hyacinth.

INTRODUCTION

Significant reduction in the quality of river water in the areas with high technogenic load is caused by the presence of toxic substances in the wastes, including heavy metals and metalloids. The role of heavy metals in vital functions of plants is complex. Some heavy metals, such as copper and zinc, play an important role for the plants, but they are required only in low concentration, while other heavy metals are not essential for plants, and if the permissible levels of their concentration are exceeded, they are harmful and considered toxic. For example, cadmium inhibits photosynthesis and absorption of mineral substances; due to the action of cadmium, leaves get yellow and die off, which is a symptom of toxicity; mercury retards growth and development of roots and prevents photosynthesis [1].

Several studies have shown the ability of stems and roots of water hyacinth and reeds to accumulate heavy metals, which was the basis for creating wastewater treatment systems in many countries for removing heavy metals with the use of these plants [2-7]. In Vietnam, many water plants, including water hyacinth and reeds, are usually used as food for many species of herbivores, which results in promotion of these heavy metals further along the food chain, causing their biological accumulation [8].

According to numerous studies [9-12], the levels of heavy metals in plants greatly vary, depending on the season.

To date, the content of heavy metals and arsenic in water plants in the territory of industrially developed areas of Vietnam has not been studied enough.

The study is aimed at assessing the regularities of accumulation of some heavy metals (Fe, Cu, Zn, Cd, Pb) and arsenic (As) in organs of water hyacinth and reeds by seasons (in the rainy season and the dry season) in the sections of the Srepok River subject to various anthropogenic loads.

MATERIALS AND METHODS

The objects of the study were common or southern reeds (*Phragmites australis*) and water hyacinth (*Eichhornia crassipes*) growing in the Srepok River.

The location of the study was the section of the Srepok River flowing through industrial zones Hoa Phu and Tam Thang before the water basin of the Srepok 3 HPP.

Depending on the topography and distribution of waste sources, the sampling points in the river have been divided into 4 sections (zones):

- zone 1 is the area before the river enters the territory of industrial regions Hoa Phu and Tam Thang, which is to some extent influenced by the wastewater from the city;
- zone 2 is the area of the river within the industrial areas of Hoa Phu and Tam Thang influenced by wastewater from these industrial regions and the wastewater from the city through small streams and rainwater drains;
- zone 3 is the area after the river exits the industrial areas of Hoa Phu and Tam Thang before the HPP at the Dray Hling reservoir (the distance from the industrial areas to the HPP at the Dray Hling reservoir is 7.5 km) partly influenced by sewage from the city and industrial areas; and
- zone 4 is the area located 17.4 km from industrial zones Hoa Phu and Tam Thang down the river before the HPP at reservoir Srepok 3. The site is located far away from industrial areas and the city, thus, the impact of wastewater discharged from these sources is negligible.

The samples were taken during the rainy season and during the dry season (2 seasons per year). The study was performed in 4 stages:

– stage 1 - 10/2015 (the rainy season);
– stage 2 - 3/2016 (the dry season);
– stage 3 - 10/2016 (the rainy season); and
– stage 4 - 3/2017 (the dry season).

Field sampling was performed at the site of the research. Plants were extracted with roots, cleaned and placed into plastic bags to be stored in the cold, and sent to the laboratory for analysis.

Preliminary preparation of the samples was performed immediately after their collection:

– the part of the plants needed for analysis (stem, root) was separated, placed into separate porcelain cups numbered for accounting;

- the sample was dried in a drying cabinet at 105^{o}C for 24 hours;

– 3 g of the dried sample (with its exact weight recorded) was placed into a porcelain cup, into which 1 ml of concentrated H_4SO_4 acid was added, after which the sample was placed in an oven heated to 500^{o}C for ashing for 12 hours until the process completion;

– 5 ml of HCl acid was added in the ratio of 1:2, the sample was heated to 80^{o}C for about 2 hours, and left to cool in the fume hood, filtered with filtering paper and a funnel, after which the resulting solution was diluted with deionized water in a flask until the volume reached 50 ml; and

– each indicator was analyzed separately by an appropriate method.

Each sample was studied 3 times. The obtained results were shown as the mean arithmetic and the standard deviation ($M \pm m$).

The data were processed using the Microsoft Excel 2010, SPSS and Statistica applications.

To compare the differences among groups of metals by zones, seasons and sampling locations, the one-way ANOVA test was used, combined with the Tukey test in case of equal variance, and the Tamhane's test in case of unequal variance.

Research methods

During the research, the following methods were used for determining the content of heavy metals in organs of plants:

- – for As: Vietnamese standard 7601:2007;
- – for Pb: SMEWW 8126:2009;
- – for Cd: SMEWW 8126:2009;
- – for Cu: Vietnamese standard 8126:2009;
- – for Zn: Vietnamese standard 8126:2009; and
- – for Fe: SMEWW 8126:2009.

RESULTS AND DISCUSSION

Regularities of heavy metals and arsenic accumulation in riverside aquatic vegetation

The content of heavy metals was determined in the stems and roots of two plant species: common or southern reed (*Phragmites australis*) and water hyacinth (*Eichhornia crassipes*), depending on the degree of river contamination and the season (Tables 1-4).

The content of heavy metals and arsenic in the reeds varied depending on the level of the river pollution. However, according to the studies (see Tables 1, 2), the general tendency of increasing accumulation of the studied elements was observed in the roots of reeds, compared to the stems, which was consistent with the data obtained by other researchers [9; 11; 13-15].

In water hyacinth, same as in the reeds, the content of the studied elements in the roots was much higher than in the stems (Tables 3, 4), which did not contradict the data of other studies of elements' distribution in organs of this type of plants [8; 16].

Table 1. The levels of elements' content in the stems and the roots of reeds by the zones of the Srepok River (p< 0.05)

Element	*Organ*	*Content, mg/kg*			
		Zone 1	*Zone 2*	*Zone 3*	*Zone 4*
Fe	Stems	184.3 ± 58.2	170.9 ± 63.7	184.5 ± 34.2	183.7 ± 57.5
	Roots	311.3 ± 101.0	351.5 ± 113.4	337.4 ± 85.7	360.5 ± 85.2
Cu	Stems	3.97 ± 0.90	12.43 ± 5.14	7.84 ± 2.12	6.43 ± 1.81
	Roots	6.72 ± 1.15	37.35 ± 20.56	21.01 ± 10.03	12.72 ± 5.12
Zn	Stems	16.07 ± 3.92	44.20 ± 14.17	25.07 ± 2.92	21.98 ± 2.56
	Roots	27.01 ± 6.63	97.73 ± 50.05	53.86 ± 22.51	34.78 ± 3.27
As	Stems	6.48 ± 1.66	5.46 ± 1.57	5.36 ± 1.40	4.40 ± 2.02
	Roots	11.00 ± 3.39	8.80 ± 1.98	9.79 ± 2.41	6.70 ± 2.70
Cd	Stems	0.214 ± 0.072	0.113 ± 0.110	0.116 ± 0.076	0.128 ± 0.067
	Roots	0.626 ± 0.188	0.407 ± 0.196	0.289 ± 0.149	0.302 ± 0.119
Pb	Stems	4.39 ± 1.56	13.05 ± 4.36	7.48 ± 2.64	7.04 ± 2.68
	Roots	7.62 ± 2.43	31.95 ± 15.02	19.68 ± 9.34	16.39 ± 5.70

Table 2. The levels of elements' content in reeds by seasons (p< 0.05)

Element	*Organ*	*Content, mg/kg*	
		The rainy season	*The dry season*
Fe	Stems	157.6 ± 48.6	206.5 ± 50.0
	Roots	304.2 ± 106.6	381.0 ± 69.5
Cu	Stems	7.92 ± 5.52	8.17 ± 3.40
	Roots	20.21 ± 17.07	21.85 ± 18.95
Zn	Stems	27.12 ± 13.57	29.75 ± 15.37
	Roots	54.40 ± 39.40	61.06 ± 46.40
As	Stems	6.06 ± 1.55	4.89 ± 1.79
	Roots	9.09 ± 2.89	9.41 ± 3.11
Cd	Stems	0.157 ± 0.099	0.127 ± 0.088
	Roots	0.448 ± 0.231	0.391 ± 0.194
Pb	Stems	8.22 ± 4.74	8.59 ± 4.58
	Roots	19.27 ± 14.15	20.46 ± 13.45

Table 3. The levels of elements' content in the stems and in the roots of water hyacinth by zones of the Srepok River ($p< 0.05$)

Element	*Organ*	*Content, mg/kg*			
		Zone 1	*Zone 2*	*Zone 3*	*Zone 4*
Fe	Stems	285.1 ± 75.6	292.4 ± 61.9	304.0 ± 49.9	256.3 ± 91.1
	Roots	296.3 ± 67.7	340.9 ± 42.47	343.9 ± 50.0	299.2 ± 92.8
Cu	Stems	11.47 ± 5.51	21.48 ± 17.8	11.50 ± 2.75	11.90 ± 4.28
	Roots	19.53 ± 10.64	48.38 ± 19.32	33.42 ± 8.93	18.88 ± 6.86
Zn	Stems	19.55 ± 7.50	63.81 ± 50.34	46.36 ± 21.06	30.03 ± 13.94
	Roots	33.24 ± 7.30	107.9 ± 45.5	72.29 ± 21.21	44.29 ± 8.41
As	Stems	6.68 ± 1.47	5.11 ± 1.22	5.28 ± 2.10	4.28 ± 1.49
	Roots	12.58 ± 2.92	8.99 ± 2.37	10.37 ± 4.20	7.01 ± 2.11
Cd	Stems	0.296 ± 0.240	0.144 ± 0.100	0.088 ± 0.080	0.093 ± 0.059
	Roots	0.956 ± 0.371	0.411 ± 0.269	0.439 ± 0.267	0.314 ± 0.294
Pb	Stems	5.90 ± 1.67	12.30 ± 4.60	8.89 ± 2.20	7.05 ± 2.64
	Roots	10.23 ± 3.76	28.99 ± 13.06	15.39 ± 5.31	11.31 ± 4.26

Table 4. The content of heavy metals and arsenic in the stems and the roots of water hyacinth by seasons ($p< 0.05$)

Element	*Organ*	*Content, mg/kg*	
		The rainy season	*The dry season*
Fe	Stems	305.6 ± 42.8	261.3 ± 89.1
	Roots	322.4 ± 73.3	319.9 ± 66.5
Cu	Stems	15.36 ± 13.60	12.67 ± 4.88
	Roots	32.13 ± 18.32	28.12 ± 15.19
Zn	Stems	35.53 ± 28.30	46.03 ± 35.08
	Roots	62.11 ± 32.54	68.53 ± 42.29
As	Stems	5.80 ± 1.66	4.61 ± 1.74
	Roots	10.36 ± 3.74	8.58 ± 3.19
Cd	Stems	0.168 ± 0.182	0.116 ± 0.093
	Roots	0.476 ± 0.380	0.513 ± 0.367
Pb	Stems	8.17 ± 3.75	9.05 ± 3.77
	Roots	16.16 ± 10.43	16.84 ± 10.53

Table 5. The levels of elements' content in the stems and in the roots of reeds from various habitats ($p< 0.05$)

Element	*Organ*	*Content, mg/kg*		
		On the bank of the Dak Lak province	*In the middle of the river*	*On the bank of the Dak Nong province*
Fe	Stems	198.1 ± 27.0	123.3 ± 38.0	184.3 ± 65.2
	Roots	395.5 ± 76.6	234.6 ± 63.8	326.6 ± 93.0
Cu	Stems	7.16 ± 2.89	9.27 ± 6.65	8.36 ± 5.10
	Roots	23.47 ± 21.90	15.76 ± 12.30	20.59 ± 15.38
Zn	Stems	28.38 ± 15.16	23.07 ± 8.02	30.22 ± 15.36
	Roots	73.55 ± 53.45	37.41 ± 17.89	50.15 ± 32.39
As	Stems	5.09 ± 1.57	6.15 ± 1.21	5.69 ± 2.02
	Roots	9.36 ± 2.33	8.05 ± 2.38	9.56 ± 3.62
Cd	Stems	0.109 ± 0.084	0.123 ± 0.120	0.183 ± 0.081
	Roots	0.392 ± 0.263	0.441 ± 0.214	0.442 ± 0.167
Pb	Stems	9.50 ± 5.61	6.01 ± 4.15	8.24 ± 3.48
	Roots	23.73 ± 16.98	14.99 ± 9.42	18.03 ± 10.99

Table 6. The levels of elements' content in the stems and in the roots of water hyacinth from various habitats ($p< 0.05$)

Element	*Organ*	*Content, mg/kg*		
		On the bank of the Dak Lak province	*In the middle of the river*	*On the bank of the Dak Nong province*
Fe	Stems	275.8 ± 74.1	274.3 ± 93.7	298.5 ± 51.0
	Roots	326.6 ± 68.0	316.0 ± 65.1	319.4 ± 76.1
Cu	Stems	18.45 ± 15.01	12.17 ± 4.62	10.85 ± 3.95
	Roots	36.26 ± 19.77	25.54 ± 16.30	27.38 ± 12.20
Zn	Stems	60.86 ± 42.96	26.64 ± 12.48	30.76 ± 15.31
	Roots	85.76 ± 50.65	50.81 ± 23.05	55.28 ± 17.06
As	Stems	4.59 ± 1.91	5.70 ± 1.74	5.49 ± 1.58
	Roots	8.67 ± 3.54	9.78 ± 4.14	10.07 ± 3.12
Cd	Stems	0.146 ± 0.140	0.138 ± 0.130	0.143 ± 0.168
	Roots	0.617 ± 0.396	0.412 ± 0.356	0.430 ± 0.335
Pb	Stems	9.81 ± 4.47	7.58 ± 2.36	8.14 ± 3.59
	Roots	19.87 ± 14.15	15.35 ± 6.00	13.95 ± 7.54

As evidenced by the comparative analysis of the data obtained in the studies, and results of studying the content of metals in the rivers of some regions of the world, the content of Cu, Zn, Cd in the stems and roots of water hyacinth in the Srepok River is lower than that in the stems and the roots of water hyacinth in the Nhue and To Lich Rivers [8]. The content of most metals in the stems and the roots of water hyacinth in the Hindon River (India) is lower, while the content of Cd is higher [16] than that in the Srepok River. Compared to the study by Olivares-Rieumont et al. [17], the obtained values of the Zn, Pb, Cd content in the roots of water hyacinth are lower than these metals' content in the roots of water hyacinth in the Almendares River (Cuba). It is obvious that the content of the studied elements in the roots of water hyacinth may vary largely, depending on the geographical area of the study. This conclusion is also confirmed by the data in Tables 5 and 6, which illustrate the variability of the elements' content in plants depending on the area where they grow.

The changes in the content of heavy metals and arsenic in the reeds, depending on the level of contamination of the Srepok River, are shown in Table 1. As shown by the data in the table, the Fe content in the stems and the roots of reeds in the four areas of the study was not significantly different. The content of Cu and Zn in the stems and the roots of reeds in zone 2 was higher than in zones 3 and 4, while the lowest value was observed in zone 1. The content of As in the stems of reeds in all four zones was relatively the same, and the content in the roots was the highest in zone 1 and slightly lower in zones 2 and 3, while the lowest value was observed in zone 4. The content of Cd in the stems and the roots of reeds was the highest in zone 1; while no significant difference in the concentration of Cd was observed in other zones. The content of Pb in the stems and the roots of reeds was the highest in zone 2, and the lowest – in zones 1 and 4.

The changes in the content of studied elements in the stems and the roots of water hyacinth in the studied areas are shown in Table 3. The content of Fe in the stems and the roots of water hyacinth, same as in reeds, was not significantly different in all four zones. The content of Cu in the stems and the roots in all areas was relatively the same. The highest concentration of Cu was observed in zone 2, then zone 3, and the lowest - in zones 1 and 4. The content of Zn in the stems of water hyacinth was the lowest in zone 1; while no significant difference was observed in other zones. The highest value of Zn content in the roots of water hyacinth was observed in zone 2, and the lowest – in zone 1.

The content of heavy metals and arsenic in various organs of reeds, depending on the habitat, is shown in Table 5. The levels of Fe in the stems of reeds at the riversides of Dak Lak and Dak Nong provinces were similar; however, they were higher than those in the middle of the river. In the roots of reeds, the content of iron is distributed as follows: at the riverside of the Dak Lak province > at the riverside of the Dak Nong province > in the middle of the river. The difference in the content of Cu, As, Pb in the stems and the roots of plants at the riversides of the Dak Lak and Dak Nong provinces and in the middle of the river was not statistically significant. The difference in the content of Zn in the stems and Cd in the roots in the same locations was also unreliable.

The changes in the content of heavy metals in the stems and the roots of water hyacinth, depending on the habitat, are shown in Table 6. No veracious difference was detected in the content of Fe, As, Cd, Pb in the stems and the roots of water hyacinth at the riverside of Dak Lak and Dak Nong provinces, and in the middle of the river. The difference in the Cu content in the roots of water hyacinth in the same locations was also statistically insignificant. The highest content of Zn in the stems and the roots of water hyacinth was observed at the riverside of Dak Lak province, a bit lower – at the riverside of Dak Nong province, and the lowest – in the middle of the river.

It should be noted that the content of the studied elements in the stems and the roots of reeds varied depending on the season – during the dry season and the rainy season. For most metals and arsenic, these changes were insignificant. However, the content of Fe in the stems and the roots of reeds during the dry season was higher than during the rainy season (Table 2).

The content of Fe in the stems of water hyacinth, unlike in reeds, during the rainy season was higher than during the dry season; no significant changes were observed in the roots (Table 4). The difference in the content of other elements in the stems and the roots of water hyacinth, like in the stems and the roots of reeds, was not statistically significant by seasons.

Comparison of the obtained regularities with the results of similar studies by other authors is of interest. Thus, Duman et al. [11] showed that the content of Cu, Zn, Pb in the reeds reached the highest values in the winter, and the concentration of Cd – in the autumn. According to Nikolaidis et al. [18], the content of heavy metals in reeds was the highest in early autumn. In the paper of Mulkeen et al. [19] the highest content of metals in the roots of reeds was observed as well during the autumn and winter.

Reeds and water hyacinth are typically used in Vietnam as fodder for livestock and poultry (buffaloes, cows, pigs and chicken). However, the research has established the levels of As and Pb in the plants, which exceed the permissible Vietnamese standards of the animal feeds quality. Therefore, it is not recommended to use reeds and water hyacinth from the Srepok River for feeding livestock and poultry.

CONCLUSION

As a result of the research, the following regularities have been obtained:

– the content of Fe, Cu, Zn, As, Cd and Pb in the roots of water hyacinth and common reeds is higher than that in the stems throughout the entire course of the Srepok River, regardless of the pollution levels and the season;

– the content of heavy metals and arsenic in the organs of aquatic plants varies considerably, depending on the zone of the river. The maximum content of Cu, Zn, Pb was observed in the roots and the stems of water hyacinth and reeds in the zone of industrial areas subjected to the wastewater from the city (coming in through small streams and with rainwater). The difference in the concentration of elements in other zones was not statistically significant. The highest content of As and Cd in plants was observed in the part of the river before entering the industrial areas, to some extent influenced by waste water from the city. With that, the concentrations of Fe in all four zones were not significantly different.

– the content of Fe in the stems and the roots of reeds during the dry season is higher than during the rainy season. For other elements, the difference in their content in the stems and the roots of reeds by season was not reliable; and

– the content of Fe in the stems of water hyacinth during the rainy season is higher than during the dry season. The difference in the content of other studied heavy metals and arsenic in the stems and the roots of water hyacinth by season was not statistically significant.

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