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Levels of heavy metals in the «soil – medicinal plants» system in relation to the geographical location and ecological and genetic zone of the Irtysh river floodplain

The article provides the material on the levels of zinc, copper, and cadmium in the «soil-medicinal plants» system in relation to the territorial location and ecological and genetic zonality of the Irtysh river floodplain. The heavy metals (zinc, copper, cadmium) contents of medicinal plants growing in the Irtysh river floodplain (Semey, Ozerki village) were assessed in order to determine the safety of the medicinal plant therapeutic application. Standard procedures for collection, transportation, preparation and storage of soil and plant samples and also for chemical analysis were applied in the study. The contents of all studied chemical elements in the total aggregate of medicinal plants descend as follows: zinc 45.8 mg/kg; copper 6.2 mg/kg; cadmium 0.23 mg/kg. As is evident from the findings (*Glycyrrhiza glabra* (Zn = 17.3 ± 0.79 mg/kg); *Inula helenium* (Cu = 2.3 ± 0.17 mg/kg); *Taraxacum officinale* (Cd = 0.12 ± 0.01 mg/kg)), no average values were found to exceed the maximum permissible limits. This information is certainly essential for selecting sites for harvesting safe herbal raw materials; also, medicinal plants can be considered as indicators of environmental pollution. This determines the rationale for research study in this direction and puts forward a vital task: to strengthen quality control of herbal medicinal raw materials taking into account the content of heavy metals.

Keywords: zinc, copper, cadmium, metals, floodplain soils, medicinal plants, chemical analysis.

Introduction

The prospects for the use of medicinal plants are evaluated by their pharmacological properties and chemical composition. The use of many wild plants can be hampered by their capacity to accumulate toxic elements in their natural vegetation areas. Regional scope of the study of a problem of contamination of herbal raw materials is conditioned by varying geochemical and climatic conditions of territories where the raw materials are harvested [1].

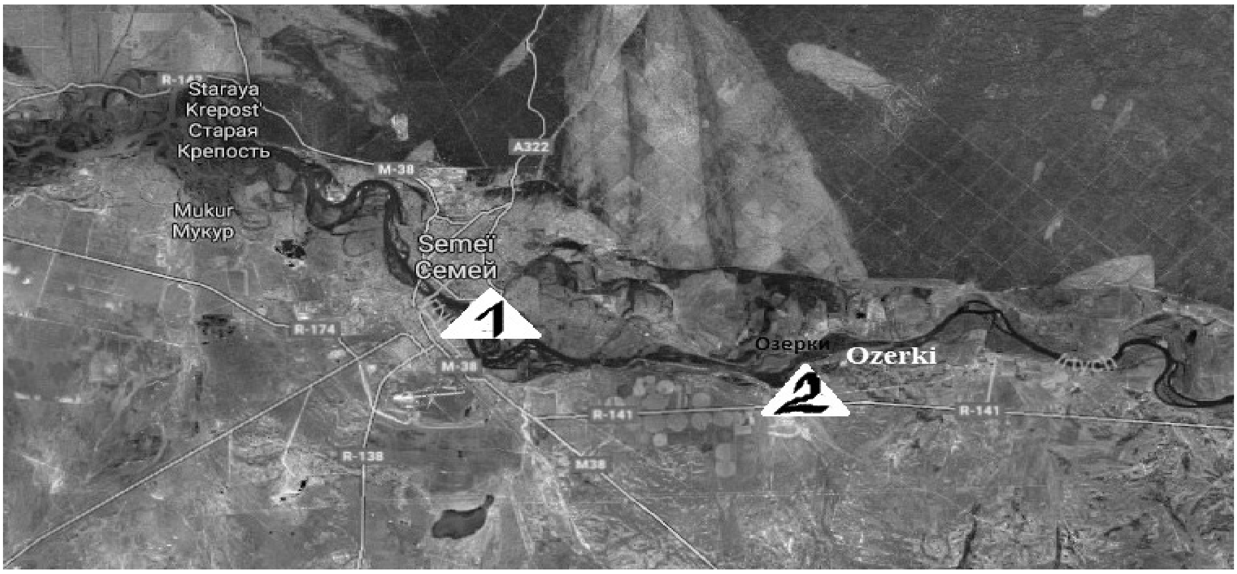
The study of the mineral composition of herbal raw materials has a two-part implication. In one respect, medicinal raw materials contain a rich complex of macro- and microelements and are a valuable source of substances essential for the human body. On the downside, the use of plants that accumulate elements, among which are toxic ones, is a potential threat to human health, as heavy metals are capable of being conveyed along the soil-plant-human continuum.

Both the increasing demand for herbal preparations and worsening environmental pollution require conducting regional research to study the impact of external conditions on the quality of herbal raw materials and to assess its environmental safety.

Scientists who dedicated their works to the study of heavy metal levels in various objects of the environment are: V.I. Vernadsky with his disciple A.P. Vinogradov [2] (20–40-ies of XX century), works of V.V. Kovalsky [3], A.L. Kovalevsky [4], V.B. Ilyin [5], V.V. Dobrovolsky [6]. Many scientists work on solving the problem of reducing the levels of heavy metals and radionuclides in the soil — plant link [7]. A number of scientists are also involved specifically with the problem of heavy metal content of herbal raw materials [8–15].

Experimental

The research was carried out in the period between 2013 and 2016 at the premises of the laboratory of Novosibirsk State Agricultural University. Field studies were conducted on the territory of the East Kazakhstan region in areas with various anthropogenic load; in particular, sampling sites were located in the Irtysh river floodplain — Semey city, the village of Ozerki (Fig. 1).



1 — Semey; 2 — Ozerki

Figure 1. Study areas

19 medicinal plant species belonging to 9 families were targets of research; plants were divided into morphological organs — flowers, leaves, roots, which made a total of over 342 samples; and soil samples were collected along with the plants (study design) (Table 1).

Table 1

Study design

Analytes	Plants/soils investigated	Plant parts investigated	Floodplain locations investigated	Ecological and genetic zones of floodplains	Sampling times	Number of plant and soil samples
Zn Cu Cd	Plants: Valeriana officinalis, Centaurea cyanus, Persicaria hydropiper, Inula helenium, Melilotus officinalis, Trifolium pratense, Urtica dioica, Sanguisorba officinalis, Potentílla erecta, Mentha piperita, Taraxacum officinale, Tanacetum vulgare, Plantago major, Artemisia absinthium, Matricaria chamomīlla, Glycyrrhiza glabra, Carum carvi, Cichorium intybus, Bídens tripartita Floodplain soils	inflorescences leaves roots	The Irtysh river floodplain: Semey city vil. Ozerki	channel-adjacent middle terrace-adjacent	during the vegetation period — August–September	342 plant samples (19 plant species × 3 eco-genetic zones × 2 investigated areas of each floodplain × 3 morphological organs = 171 ×2 floodplains) and 27 soil samples (from 3 eco-genetic zones ×2 floodplains)

Plant samples were collected by the average sample technique at the end of the vegetation season (August-September). Samples were washed with running and distilled water and conditioned to air-dry basis. Baitenov's illustrated field guide was used for the identification of plant species [16]. Latin names of medicinal plants are given according to Cherepanov [17].

Soils were collected by mixing 6–8 individual samples to obtain a composite sample. To determine the total heavy metals, the samples were digested by concentrated mineral acid mixture. Mobile forms of heavy metals in soil were also investigated: ion-exchangeable (acetate-ammonium buffer CH_3COONH_4, pH = 4.8), water-soluble (H_2O), acid-soluble (extraction agent 1 n. HC1).

The photocolorimetric dithizone assay by Rinkis [18] on the SF-2000 spectrophotometer was used to determine the contents of analytes in soil and plants. Analytical works were carried out at the premises of Novosibirsk State Agricultural University.

The observational material was processed by statistical methods given in Plokhinsky's guidances [19] with the use of Microsoft Excel software.

Results and discussions

The concentration of the element in soil is one of the main factors that determine the chemical element content of plants.

Table 2 provides total contents of heavy metals (Zn, Cu, Cd) in the floodplain soil profile investigated.

Table 2

Total content of heavy metals in soil profile of Irtysh river floodplains, mg/kg

Horzon	Depth, cm	Analytes					
		Zn		Cu		Cd	
Floodplain, chestnut, sod soils, Semey (channel-adjacent)							
A	0–10	67.1	64.7±2(2.8)	22.8	22.4±0.38(0.53)	1.45	1.33±0.12(0.17)
B	10–25	62.4		21.9		1.16	
B-C	25–45	64.7		22.5		1.39	
Floodplain meadow chestnut carbonate soils, Semey (central)							
A	0–20	86.9	77.1±8.9(12.4)	24.3	25.6±2.1(2.9)	1.46	1.55±0.25(0.35)
B_1	20–40	78.4		23.8		1.30	
B_2	40–60	66.0		28.7		1.89	
Floodplain meadow chestnut alkaline soils, Semey (terrace-adjacent)							
A	0–30	73.3	69.9±2.6(3.7)	27.8	25.0±2.4(3.4)	1.45	1.52±0.17(0.24)
B	30–50	69.5		25.2		1.35	
B-C	50–70	67.1		22.0		1.75	
Floodplain meadow light-brown stratified soils, Ozerki vill. (channel-adjacent)							
A	0–10	61.3	58.4±2.6(3.6)	16.4	15.3±0.76(1.07)	1.40	1.28±0.12(0.17)
B	10–25	55.2		14.6		1.11	
B-C	25–45	58.7		15.0		1.33	
Floodplain meadow light-brown middle loamy soils, Ozerki vill. (channel-adjacent)							
A	0–20	83.5	71.5±10.3(14.4)	20.3	19.6±2.1(2.9)	1.39	1.49±0.26(0.36)
B_1	20–40	71.8		16.9		1.23	
B_2	40–60	59.1		21.7		1.84	
Floodplain meadow light-brown saline, Ozerki vill. (terrace-adjacent)							
A	0–30	65.7	62.9±2.1(2.9)	21.6	19.1±2.3(3.2)	1.40	1.46±0.17(0.24)
B	30–50	62.3		19.5		1.29	
B-C	50–70	60.8		16.2		1.69	

Note. Arithmetic mean and its error (mg/kg); in brackets — standard deviations (mg/kg).

Elevated levels of zinc (77.1 mg/kg) and cadmium (1.55 mg/kg) were observed in the central zone of floodplain within Semey city; however, concentrations of copper in the central zone (25.6 mg/kg) and terrace-adjacent zone (25.0 g/kg) within Semey city were virtually equal.

Low levels of zinc (62.9 mg/kg) in the terrace-adjacent zone of vill. Ozerki, copper (15.3 mg/kg) and cadmium (1.28 mg/kg) in the channel-adjacent zone of vill. Ozerki were observed.

No regular patterns of distribution in soil profile of the investigated analytes (Zn, Cu, Cd) were found. There is accumulation in both upper and lower horizons. This distribution in the soil profile is probably due to different types of soils and different anthropogenic load on the soil cover of the investigated areas of the Irtysh floodplain.

In the soils of the channel-adjacent zone of the floodplain, the accumulation of the investigated analytes is significantly less prominent due to the light mechanical makeup, lower humus content and deep ground-water layer. Soils of the central and terrace-adjacent areas of the floodplain, that are characterized by more complex structure of the soil profile, heavy mechanical makeup, water regime of which is determined by not only surface but also ground waters, feature higher contents of the elements [20]. Table 3 provides the variation and statistical indicators of the total content of chemical elements in the aggregate in soils of the Irtysh river floodplain.

Table 3

Variation and statistical indicators of total heavy metal content in the aggregate in the soils of the Irtysh river floodplain, mg/kg

Analyte	n	Horizon			Average value in the profile depth	Clarke in the lithosphere [6]	Clarke in soil [6]
		A	B	C			
Zn	27	72.9±3.22(13.2) / 9.65; 61.3–86.9	66.6±2.55(11.5) / 7.66; 55.2–78.4	62.8±0.99(4.71) / 2.96; 58.7–67.1	67.4±2.25(9.80) / 6.76; 55.2–86.9	83	50
Cu	27	22.3±1.08(14.5) / 3.24; 16.4–27.8	20.4±1.18(17.4) / 3.54; 14.6–25.2	20.9±1.39(19.9) / 4.16; 15.0–28.7	21.2±1.22(17.3) / 3.65; 14.6–28.7	47	20
Cd	27	1.43±0.008(1.68) / 0.024; 1.39–1.46	1.24±0.03(7.26) / 0.09; 1.11–1.35	1.65±0.09(16.4) / 0.27; 1.33–1.89	1.44±0.04(8.45) / 0.13; 1.11–1.89	0.13	0.5

Note. In the numerator — arithmetic mean and its error (mg/kg); in brackets — coefficient of variation (%); in the denominator — standard deviations (mg/kg); and variation limits (mg/kg); clarke (%); *n* = 27.

As is evident from the data, the highest content of the element (mg/kg) in horizon A is typical for Zn (72.9), Cu (22.3); for Cd (1.65) — it is in horizon C. The lowest content (mg/kg) of Zn (62.8) falls on horizon C, Cu (20.4) and Cd (1.24) — on horizon B.

In terms of the total content in the humus horizon of floodplain soils, the following geochemical rank (mg/kg) is typical for the investigated elements: Zn (72.9) > Cu (22.3) > Cd (1.43).

According to GOST 25593–88, the term «mobility» is defined as the element capability to shift from the solid phase of the soil to the soil solution [21]. Table 4 provides data on the content of mobile forms of heavy metal compounds in the soils of the Irtysh river floodplain.

Table 4

Content of mobile forms of chemical elements compounds in soils of Irtysh river floodplain, mg/kg

Soils	Compound forms	Zn	Cu	Cd
1	2	3	4	5
Floodplain, chestnut, sod soils, Semey (channel-adjacent)	water-soluble	0.1± 0.03(0.05)	0.14±0.07(0.11)	0.04±0.01(0.02)
	exchangeable	0.26±0.03(0.05)	1.1±0.2(0.29)	0.08±0.03(0.05)
	acid-soluble	0.54±0.11(0.16)	2.9±1.3(1.83)	0.56±0.15(0.21)
Floodplain meadow chestnut carbonate soils, Semey (central)	water-soluble	0.06±0.03(0.05)	0.28±0.07(0.11)	0.08±0.01(0.02)
	exchangeable	0.35±0.03(0.05)	1.5±0.2(0.29)	0.16±0.03(0.05)
	acid-soluble	0.72±0.11(0.16)	6.0±1.3(1.83)	0.47±0.15(0.21)
Floodplain meadow chestnut alkaline soils, Semey (terrace-adjacent)	water-soluble	0.15±0.03(0.05)	0.33±0.07(0.11)	0.09±0.01(0.02)
	exchangeable	0.34±0.03(0.05)	1.6±0.2(0.29)	0.07±0.03(0.05)
	acid-soluble	0.44±0.11(0.16)	5.5±1.3(1.83)	0.84±0.15(0.21)
Floodplain meadow light-brown stratified soils, Ozerki vill. (channel-adjacent)	water-soluble	0.03±0.07(0.1)	0.28±0.07(0.11)	0.02±0.003(0.005)
	exchangeable	0.14±0.04(0.06)	1.6±0.33(0.47)	0.22±0.1(0.14)
	acid-soluble	0.3±0.05(0.08)	5.5±0.88(1.24)	0.48±0.12(0.17)
Floodplain meadow light-brown middle loamy soils, Ozerki vill. (channel-adjacent)	water-soluble	0.04±0.07(0.1)	0.1±0.07(0.11)	0.02±0.003(0.005)
	exchangeable	0.18±0.04(0.06)	1.3±0.33(0.47)	0.37±0.1(0.14)
	acid-soluble	0.21±0.05(0.08)	4.8±0.88(1.24)	0.41±0.12(0.17)

Continuation of Table 4

1	2	3	4	5
Floodplain meadow light-brown saline, Ozerki vill. (terrace-adjacent)	water-soluble	0.2±0.07(0.1)	0.09±0.07(0.11)	0.01±0.003(0.005)
	exchangeable	0.25±0.04(0.06)	0.8±0.33(0.47)	0.47±0.1(0.14)
	acid-soluble	0.35±0.05(0.08)	3.4±0.88(1.24)	0.19±0.12(0.17)

Note. Arithmetic mean and its error (mg/kg); in brackets — standard deviations (mg/kg).

A geochemical sequence by the content of water-soluble form of the elements is established: $Cu_{0.29}$>$Zn_{0.16}$>$Cd_{0.06}$.

By the exchangeable form content of elements, the investigated soils showed similar properties. The following geochemical sequence was established: $Cu_{1.4}$>$Zn_{0.33}$>$Cd_{0.16}$.

A geochemical sequence was derived by the content of heavy metals in the acid-soluble form for the investigated types of the floodplain soils: $Cu_{4.2}$>$Zn_{0.66}$>$Cd_{0.54}$.

In terms of the average concentration, heavy metals and their compound forms investigated are ranked in the following descending order: acid-soluble form>exchangeable form>water-soluble form.

The largest mobile portion of the elements is the acid-soluble fraction, followed by the exchangeable fraction, and then the water-soluble fraction.

The revealed wide range of variations for the investigated elements in all compound forms in the soil and narrow range of variations in the total content of the elements are explained by the fact that the total level of the elements is determined by the granulometric and mineralogical composition of parent rocks; the extent of mobile elements is affected, in addition to the content of organic matter in the soil, by the soil solution reaction, oxidation-reduction processes, and the physicochemical properties of the soil [20]. Table 5 provides data on the average contents of elements in the soil in comparison with their MPCs.

Table 5

Chemical element content in soils of Irtysh river floodplain versus MPC, mg/kg

Analyte	Content, mg/kg	MPC, mg/kg	MPC, mg/kg [22]
Zn	67.4±2.25	100	55.5
Cu	21.2±1.22	100	33.0
Cd	1.4±0.04	3	1.0

Also, the content of heavy metals in medicinal plants depends upon the conditions of their growth.

The peculiarities of heavy metal accumulation in different areas of the Irtysh river floodplains were investigated: Semey city; Ozerki village (Table 6).

Table 6

Heavy metal content of medicinal plants in different areas of the Irtysh river floodplain, mg/kg

Area of the Irtysh river floodplain	Analyte		
	Zn	Cu	Cd
Semey city	47.8±3.8 16.0 (18.6–77.7)	5.8±0.45 1.87 (2.6–9.5)	0.20±0.01 0.05 (0.14–0.31)
vil. Ozerki	43,1±3,8 15,8 (15,6–73,9)	5,3±0,45 1,87 (2–8,9)	0,16±0,01 0,05 (0,1–0,27)

Note: in the numerator — arithmetic mean and its error (mg/kg); in the denominator — standard deviations (mg/kg); and variation limits (mg/kg).

According to the findings, the highest concentrations of the investigated chemical elements are observed in Semey city, the lowest ones — in the village of Ozerki. This may be due to different levels of anthropogenic load in the investigated areas, namely, the activity of the industrial facilities and transport.

Depending on the proximity to the river channel, the territory of the river floodplain is divided into three ecological and genetic zones (parts) (by R. Williams): channel-adjacent, central and terrace-adjacent.

Peculiarities of heavy metal accumulation in medicinal plants growing within these ecological and genetic zones were studied. The regularities in the HM distribution in the same species of plants depending on their zone of growth are presented in Table 7.

Table 7

Distribution of heavy metals in plants by different ecological and genetic zones of the Irtysh floodplain, mg/kg

Ecological and genetic zones	Zn		Cu		Cd	
Semey city						
Channel-adjacent	45.3	47.7±3.8	5.6	5.8±0.45	0.18	0.20±0.01
Central	50.4		6.2		0.23	
Terrace-adjacent	47.5		5.8		0.20	
vil. Ozerki						
Channel-adjacent	41.3	43.1±3.8	5.0	5.3±0.45	0.14	0.16±0.01
Central	45.0		5.5		0.18	
Terrace-adjacent	43.1		5.3		0.16	

As can be seen from the Table 8, all floodplain areas investigated are characterized by the lowest accumulation of elements in the channel-adjacent zone. No pronounced pattern of the analyte distribution was found in the central and terrace-adjacent zones: Semey city: central > terrace-adjacent ≥ channel-adjacent; vill. Ozerki: central ≥ terrace-adjacent ≥ channel-adjacent.

Table 8

Average levels of heavy metals in vegetation, mg/kg

Analyte	Findings	Rest of the world	Summarized research data
Zn	45.3±3.8	31	33.1
Cu	5.6±0.43	5.9	8.6
Cd	0.18±0.01	0.21	–

According to A. Kloke (Kloke, 1980), MPC of Cd in plants = 1 mg/kg. Comparing the data on Cd content in floodplain plants with the data by A. Kloke, it can be concluded that the investigated plant species accumulate Cd to lower values than the MPC value.

The findings were multiple times read over at conferences and workshops of various levels and also were published in printed publications, including four publications of the State Commission for Academic Degrees and Titles of the Russian Federation [23].

Conclusions

None of the element contents in the soil exceed the MPC comparing with the data by A. Kloke [24]; comparing with the MPC (for Kazakhstan), the Cu content does not exceed the maximum permissible limit, and the Zn content in the soil exceeds the MPC by 1.2 times, Cd by 1.4 times.

Comparing the data obtained on the heavy metal content in plants of different areas of the Irtysh river floodplain with their levels in the vegetation of different regions and countries of the world, it can be concluded that a higher content of zinc (45.3 mg/kg) and a lower content of copper (5.6 mg/kg) and cadmium (0.18 mg/kg) is characteristic for medicinal plants of the Irtysh river floodplain.

There is a rather complex relationship between the content of heavy metals in plants and their concentration in soil, which exerts differently for each chemical element in different systematic groups of plants and their morphological organs. On that premise, it seems appropriate to conduct further research in this direction, thereby expanding the areal of research.

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Ертіс өзенінің аумақтық орналасуына және экологиялық-генетикалық аймағына байланысты «топырақ – дәрілік өсімдіктер» жүйесіндегі ауыр металдардың мөлшері

Мақалада Ертіс өзенінің алқабының аумақтық орналасуына және экологиялық-генетикалық аймағына байланысты «топырақ – дәрілік өсімдіктер» жүйесіндегі мырыш, мыс, кадмий деңгейлері туралы материал қарастырылған. Дәрілік өсімдіктерді емдік мақсаттарда пайдаланудың қауіпсіздігін анықтау үшін Ертіс су алқабында (Семей, Озерка ауылы) өсетін дәрілік өсімдіктердегі ауыр металдардың (мырыш, мыс, кадмий) деңгейі зерттелді. Топырақ пен өсімдік үлгілерін іріктеу, тасымалдау, дайындау және сақтау үшін, сондай-ақ химиялық талдау үшін стандартты әдістер қолданылды. Дәрілік өсімдіктердің жалпы санындағы барлық зерттелген химиялық элементтердің мазмұны мынадай тәртіппен төмендейді: мырыш үшін 45,8 мг/кг; мыс 6,2 мг/кг; кадмий 0,23 мг/кг. Алынған мәліметтерге сәйкес *(Glycyrrhiza glabra* (Zn = 17,3 ± 0,79 мг/кг); *Inula helenium* (Cu = 2,3 ± 0,17 мг/кг); *Taraxacum officinale* (Cd = 0,12 ± 0,01 мг/кг)) рұқсат етілген концентрацияның орташа мәндер бойынша асып кетуі анықталмады. Бұл ақпараттың қауіпсіз өсімдік шикізатын дайындауға арналған орындарды таңдау үшін маңызы зор, сондай-ақ дәрілік өсімдіктерді қоршаған табиғи ортаның ластану көрсеткіштері ретінде қарастыруға болады. Бұл осы бағыттағы зерттеулердің орындылығын айқындайды және ауыр металдардың мазмұнын есепке ала отырып, дәрілік өсімдік шикізатының сапасын бақылауды арттыру кажетігі туралы өзекті мәселені тудырады.

Кілт сөздер: мырыш, мыс, кадмий, металдар, тасты топырақ, дәрілік өсімдіктер, химиялық талдау.

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Содержание тяжелых металлов в системе «почва – лекарственные растения» в зависимости от территориальной расположенности и эколого-генетической зоны поймы реки Иртыш

В статье изложен материал по уровням содержания цинка, меди, кадмия в системе «почва – лекарственные растения» в зависимости от территориальной расположенности и эколого-генетической зональности поймы реки Иртыш. Для выявления безопасности использования лекарственных растений в лечебных целях исследованы уровни содержания тяжелых металлов (цинка, меди, кадмия) в лекарственных растениях, произрастающих в пойме реки Иртыш (г. Семей, с. Озёрки). При отборе, транспортировке, подготовке и хранении почвенных и растительных образцов для исследования, а также для проведения химического анализа использовались стандартные методики. Содержание всех изученных химических элементов в общей совокупности лекарственных растений убывает в следующем порядке: для цинка 45,8 мг/кг; меди 6,2 мг/кг; кадмия 0,23 мг/кг. По полученным данным *(Glycyrrhiza glabra* (Zn = 17,3 ± 0,79 мг/кг); *Inula helenium* (Cu = 2,3 ± 0,17 мг/кг); *Taraxacum officinale* (Cd = 0,12 ± 0,01 мг/кг)) превышения предельно допустимых концентраций по средним значениям не выявлено. Эти сведения, несомненно, имеют важное значение для выбора мест заготовки безопасного растительного сырья, также лекарственные растения можно рассматривать как индикаторы загрязнения окружающей природной среды. Это определяет целесообразность исследований в данном направлении и выдвигает актуальную задачу: увеличить контроль качества растительного лекарственного сырья с учётом содержания тяжёлых металлов.

Ключевые слова: цинк, медь, кадмий, металлы, пойменные почвы, лекарственные растения, химический анализ.

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