

The impact of plant protection on the ecological state of the urban ecosystem in Kaliningrad

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Abstract

Iron is an essential heavy metal for plants. In hemoproteins (all cytochromes, catalase, peroxidase) and non-heme proteins (iron-sulphur clusters), iron is crucial to the functioning of redox systems of photosynthesis and respiration. This article studies the accumulation of iron in the soil/plant system of urban phytocoenoses in the city of Kaliningrad. The authors analysed iron content in the accumulation horizon of urban soils (in agricultural/residential, residential, and industrial landscapes) and in tree, shrub, and herb species most common in urban landscapes (22 species). The maximum iron content in soils was observed in industrial and residential landscapes and high-rise residential areas with heavy traffic (2.1-2.8%). Iron content in the leaves of urban plants was proven to depend on both iron concentration in the soil ($r=0.92-1.0$; $p<0.05$) and the stage of vegetation. Background iron levels in plants were studied. Plant species actively accumulating iron were identified, namely, the silver birch (*Betula pendula*), the small-leaved lime (*Tilia cordata*) (545,1-647,5 mg/kg), the sweet mock-orange (*Philadelphus coronarius*) (542.1 mg/kg), the white clover (*Trifolium repens*) (740.6 mg/kg), the cock's foot (*Dactylis glomerata*) (379.4 mg/kg), and the common dandelion (*Taraxacum officinale*) (290.8 mg/kg). These species can be used in the phytoremediation of iron-contaminated urban areas. Most plants tested showed a low rate of Fe accumulation from the soil (a biological accumulation coefficient of 0.1-0.4). The BAC significantly decreased in most species as iron content in the soil increased. Plant species capable of limiting the uptake of iron from the environment were identified. The Mn/Fe, Ni/Fe, and Co/Fe ratios in soils from different functional areas were proven comparable. A low Fe/Mn ratio in the leaves of the Norway maple (*Acer platanoides*) was found indicative of irregular iron uptake. Plants showing Fe/Mn ratios below control levels (*Philadelphus coronarius*, *Achillea millefolium*, *Trifolium repens*) may be affected by iron toxicity.

1. Introduction

The most dangerous toxic heavy metals are the chemicals of hazard group 1 (Hg, Pb, Cd, Zn, As, Se, Be). As impurities, they cause deleterious health effects and death in living organisms. An important factor is the content of biogenic elements necessary for the normal functioning of living organisms, in particular, plants. However, in high concentrations, essential metals become dangerous [1-4].

This holds true for iron and manganese (hazard group 3) [5-7]. Iron is an essential heavy metal for plants. The average iron level in plants ranges from 0.02 to 0.08% (20-80 mg/kg, dry mass) [8-10]. Fe^{3+} found in the soil solution is reduced to Fe^{2+} by the redox system of plasmalemma of rhizodermis cells. In this form, iron reaches the root.

In hemoproteins (all cytochromes, catalase, peroxidase) and non-heme proteins (iron-sulphur clusters), iron is crucial to the functioning of redox systems of photosynthesis and respiration [11-13]. Through forming nitrogenases and nitrate reductases with molybdenum, iron is involved in the reduction of nitrates and fixation of molecular nitrogen with rhizobia. Iron-containing organic compounds are essential for biochemical processes

accompanying respiration and photosynthesis, which is explained by the catalytic properties of such substances [14, 15]. Inorganic iron compounds are also capable of catalysing reactions. However, the catalytic properties of iron are particularly pronounced in organic compounds. The catalytic effect is explained by the ability of the metal to change its oxidation state. An atom of iron easily oxidises and reduces, which makes it possible for iron compounds to transfer electrons in biochemical processes. Reactions associated with plant respiration are based on the electron transfer process. This process is carried out by enzymes – iron-containing dehydrogenases and cytochromes [6; 9; 16; 17].

Iron serves as a catalyser at the initial stages of chlorophyll synthesis (formation of δ -aminolevulinic acid and protoporphyrins) [14, 15]. Inadequate iron supply leads to unwanted conditions in plants, in particular, chlorosis. Photosynthesis and respiration disorders resulting from the irregular formation of constituting organic substances and the lack of organic reserves distort metabolism. Therefore, a substantial iron deficiency inevitably leads to the death of plants. Top leaves of trees and shrubs lose their green colouring becoming almost white and withering. Lack of iron is observed in alkali and lime soils, where high pH levels hamper the absorption of the metal. In soils rich in soluble forms of iron, excessive Fe absorption can have a toxic effect on plants. The symptoms of iron toxicity are not specific and their manifestations differ depending on the plant species and development stage [6; 9; 16; 17].

Soil chemical elements collectively affect a plant and they can strengthen or weaken each other. The Fe/Mn ratio is of crucial importance in assessing plant resistance to iron toxicity [17]. Manganese is another element involved in chlorophyll biosynthesis and it intensifies photosynthesis. It has a positive effect on the formation and accumulation of the terpenoids, including essential oils, steroidal and triterpenoid saponins, and cardiac glycoside and glycoalkaloids [18]. Mn plays an important role in regulating the genetic function in plants and is crucial to biosynthesis and maintaining the DNA structure in the nucleus [17]. A broader interpretation classifies nickel as an essential microelement alongside ‘classic’ biogenic materials [19]. Biologically, nickel is involved in the structural organisation and functioning of DNA, RNA, and proteins. It is also essential for hormonal regulation. Excessive nickel content in plants suppresses photosynthesis and transpiration processes and leads to leaf chlorosis [17].

This work sets out to study the properties of iron accumulation in the soil-plant system of urban phytocoenoses in the city of Kaliningrad.

2. Experimental

The accumulation of iron, manganese, and nickel was studied in the accumulation horizon of urban soils and tree, shrub, and herb species most common in urban landscapes. The study area included 12 permanent test sites in different functional zones in the city of Kaliningrad – recreational zones (RecZ, control), agricultural/residential zones (ARZ), residential zones (RZ), and industrial/transport zones (ITZ). Recreation landscapes situated 40-50 km from large industrial sources of pollution and least affected by human impact and pollutants (Svetlogorsk) were used as the control.

Biogeochemical tests were performed on tree species – the silver birch (*Betula pendula* Roth), the small-leaved lime (*Tilia cordata* Mill.), the Norway maple (*Acer platanoides* L.), the black poplar (*Populus nigra* L.) - and herb species - the cock's foot (*Dactylis glomerata* L.), the common tansy (*Tanacetum vulgare* L.), the broadleaf plantain (*Plantago major* L.), the common dandelion (*Taraxacum officinale* Wigg.s.l.), the common yarrow (*Achillea millefolium* L.), the red clover (*Trifolium pratense* L.), the white clover (*Trifolium repens* L.), the perforate St John's wort (*Hypericum perforatum* L.), the rosebay willowherb (*Chamerion angustifolium* (L.) Holub), and the European goldenrod (*Solidago virgaurea* L.). Shrub species tested included the wild privet (*Ligustrum vulgare* L.), *Hippophae rhamnoides* L., Van Houtte's spiraea (*Spiraea vanhouttei* (Briot.) Zab.), the common lilac (*Syringa vulgaris* L.), the sweet mock-orange (*Philadelphus coronarius* L.), the common snowberry (*Symphoricarpos rivularis* Suksdorf.), the common barberry (*Berberis vulgaris* L.), the European elderberry (*Sambucus nigra* L.), the alpine currant (*Ribes alpinum* L.), the guelder rose Roseum (*Viburnum opulus* ‘Roseum’), and the rugosa rose (*Rosa rugosa* Thunb.). Plant material was collected during the vegetative period (May-October) in 2014. Samples were taken from lower branches of adult trees with an indication of the sampling site, species, three diameter, and sample heights. Composite samples of leaves from trees and shrubs of the same

species were used. Average samples were collected in dry weather [20]. Lithochemical samples were taken from the upper soil layer of a thickness of 0 — 10 cm using the envelope method [20, 21].

The iron content in samples was established by an X-ray fluorescence analysis using the Spektroskan Maks – G equipment (Spektron, Russia). Plant and soil samples were prepared according to [22]. The analysis was carried out in triple replication. The obtained data were statistically processed. The data in the charts and tables are presented as arithmetic means and standard errors of the mean. The statistical significance of a difference between variants was established using Student's t-test ($p \leq 0.05$). A correlation analyses was based on Pearson's chi-squared test.

3. Results and discussion

Soil is a natural barrier to metals. It inhibits metal uptake by plants and metal migration to contiguous environments. Therefore, special attention was paid to the quantitative parameters of element contents in soils – the first link of any food chain. When considering chemical element migration, of special importance are the anthropogenic conditions of studied urban landscapes. The content of iron and other biogenic elements was analysed in the accumulation horizon of major functional zones (ARZ, RZ, and ITZ). The landscape of recreational zones (RecZ) was used as the control.

The urban soils samples from humus horizon were named on particle size distribution as mostly sand or loamy sand. According to the redox conditions of migration of heavy metals the RecZ, RZ, ITZ presented geochemical landscapes with oxidizing conditions, and ARZ are landscapes with reducing conditions. According to the pH value the urban soils were alkaline (pH_{KCl} 7-8), and the soils from control area (RecZ) were neutral (pH_{KCl} 6-7). In view of geomorphological characteristics of test zones there were transeluvial geochemical (RZ), trans-accumulative (ITZ), and eluvial landscapes (RecZ, ARZ).

Environmental and climatic conditions of the landscape are also important in the metal accumulation. The climate of Kaliningrad oblast is a transitional temperate-continental one because of its being located on the seaside. The average annual temperature in the coastal areas (Kaliningrad) is 6–7°C. The frost-free period lasts 160–190 days, and the vegetation period lasts 200–205 days. The average annual amount of precipitation is 680–800 mm. The highest precipitation amounts fall in April–October (to 65–75%). The main form of precipitation is rain. Thus, the snow cover is not very deep. The duration of rainfall can be 65–70 days in some years. In cold winters, steady soil freezing is observed as early as the tenth of December, while thawing occurs in the last ten days of March. The soil's average annual surface temperature is only 1–1.5°C higher than the average annual air temperature [3; 16].

The natural level of iron in soils was established based on Fe content in the parent material. Background iron content estimated by VA Chernikov at 3800.0 mg/kg [16; 17] was used as the control.

An analysis of iron content in different functional zones shows that the maximum metal levels were observed in industrial and high-rise residential zones with heavy traffic (ITZs). The iron concentration was 2.3 times the control in the upper soil layer (RecZ) and 1.6 times the control in the accumulation horizon in residential zones (table 1). The content of iron in agricultural residential zones was slightly above the control (23.1%).

Table 1. Iron content in the accumulation horizon (0-10 cm) in different functional zones in the city of Kaliningrad, %

K*	Landscape types			
	RecZ	ARZ	RZ	ITZ
0.5-5	1.2±0.1	1.6±0.1	2.1±0.2	2.8±0.3

Comment: RecZ stands for recreational zones (control), ARZ for agricultural/residential zones, RZ for residential zones, ITZ for industrial and transport zones, and K* for the average element content according to [23].

Changes in iron accumulation in the studied soil horizon were analysed. The data obtain suggest that Fe contents changed within a calendar year. The maximum content was observed in November and the minimum in May. In April, the iron content in soil was gradually increasing to reach the maximum levels in November and the minimum in May (fig. 1).

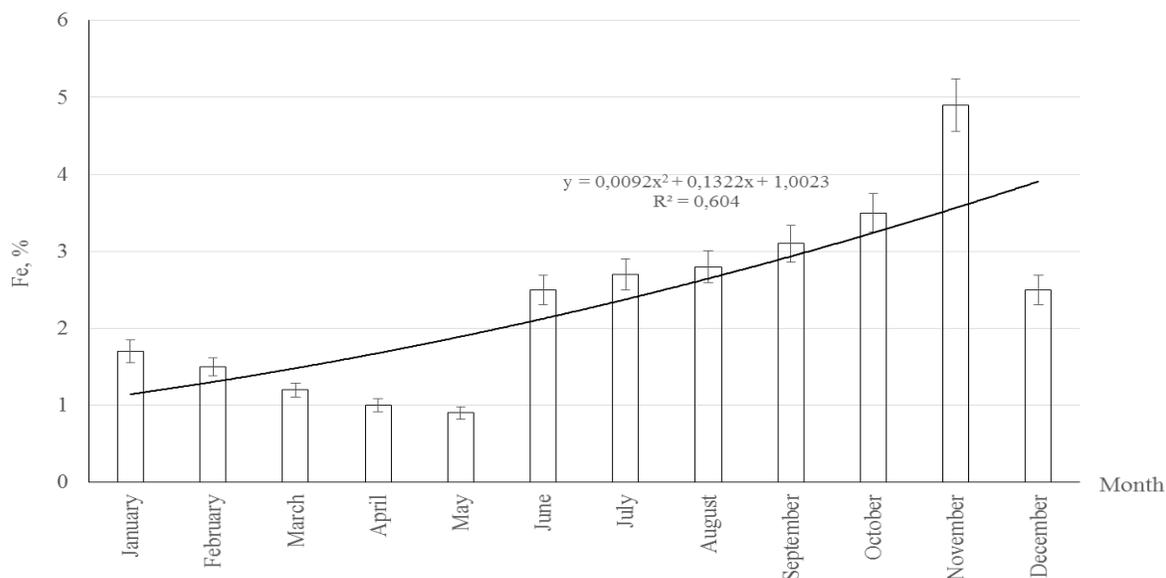


Figure 1: Changes in iron content in the accumulation horizon (0 — 10 cm) in Kaliningrad industrial/transport landscapes.

This study presents data on iron content in the samples of tree, shrub, and herb species. Iron is an essential heavy metal for plants. The average iron content in plants ranges from 0.02 to 0.08% (20-80 mg/kg of dry mass) [9]. In herbs, the normal Fe content in aboveground phytomass is 50.0 — 240.0 mg/kg of dry matter [6; 17; 24; 25]. The maximum permissible concentration of iron in herbs has not been established. The critical concentration occurs at 750.0 mg/kg (dry matter) [26]. Reactions of plants to iron deficiency or toxicity can vary and they depend on the genotype and species [17].

To estimate the human contamination of soils and vegetation with iron, it is essential to establish the natural background concentration of iron, which is used as a benchmark for identifying the level of element absorption. It has been shown that iron accumulation in plant leaves is irregular and it depends on the level of human contamination of soils and plant species. The highest background concentration of iron was observed in trees in the leaves of the Norway maple (249.5±25.1 mg/kg) and in shrubs in the leaves of the sweet mock-orange (225.4±21.8 mg/kg). The highest level of the metal was found in herbs in the leaves of the common yarrow (233.4±22.7 mg/kg), the common tansy (317.2±30/4 mg/kg), and the broadleaf plantain (485.3± 47.9 mg/kg) (tables 2-4).

Table 2. Iron content in tree leaves in different functional zones in Kaliningrad (P < 0.05).

Species	Fe, mg/kg		
	RecZ	RZ	ITZ
Tree species			
Black poplar	141.2±13.7	139.2±14.2	137.8±14.5
Silver birch	173.7±18.2	312.6±30.5	545.1±55.4
Norway maple	249.5±25.1	264.6±27.6	286.4±27.3
Small-leaved lime	184.3±17.9	427.8±43.3	647.5±63.9

Comment: RecZ stands for recreational zones (control), RZ for residential zones, and ITZ for industrial/transport zones.

Increasing contamination of urban ecosystems changes the balance of metal accumulation in the soil/plant system. Plants accumulate heavy metals in these conditions at a higher rate than similar species growing in an environmentally sustainable area do. The number of accumulated pollutants is determined by certain characteristics of a species — its biology, physiology, and biochemistry — as well as the properties and concentration of an element and the presence of metal antagonists in the plant and soil [9].

An analysis of data on iron content in plants growing in contaminated areas (RZ, ITZ) made it possible to identify species absorbing iron ions in greatest amounts. The iron content in the studied plants was 1.4 – 5.9 times the background. Critical concentration was observed in tree species in the leaves of the small-leaved lime and the silver birch (545.1-647.5 mg/kg), in shrubs in the sweet mock-orange and the rugosa rose (542.1-702.4 mg/kg), and in herbs in the leaves of the white clover (740.6 mg/kg), the cock's foot (379.4 mg/kg), and the common dandelion (290.8 mg/kg). In the leaves of the Norway maple, the black poplar, *Hippophae rhamnoides*, the European elderberry, the broadleaf plantain, the common yarrow, and the red clover growing in contaminated areas (ITZ), iron content did not differ significantly from the background.

Table 3. Iron content in the leaves of shrubs in different functional zones of Kaliningrad (P < 0.05).

Species	Fe, mg/kg		
	RecZ	RZ	ITZ
Shrubs			
European elderberry	179.3±17.5	198.3±18.6	217.6±20.1
Common snowberry	84.3±8.2	125.5±13.7	167.5±15.9
Common lilac	126.7±12.1	192.3±20.1	387.5±37.4
Guelder rose 'Roseum'	181.2±19.3	206.1±20.3	255.7±23.9
Wild privet	95.6±9.6	135.1±14.2	155.4±14.7
Sweet mock-orange	225.4±21.8	347.9±35.6	542.1±55.2
Alpine currant	163.6±16.7	215.4±20.9	330.9±34.4
<i>Vanhoutte Spirea</i>	110.7±11.3	163.8±17.2	253.8±24.2
Rugosa rose	119.5±12.4	289.6±26.3	302.4±28.4
Common barberry	95.2±9.1	143.6±14.2	197.8±19.3
<i>Hippophae rhamnoides</i>	134.3±13.5	129.7±13.5	132.2±13.4

Comment: RecZ stands for recreational zones (background), RZ for residential zones, and ITZ for industrial and transport zones.

Table 4. Iron content in the leaves of herbs in different functional zones in Kaliningrad (P < 0.05).

Species	Fe, mg/kg		
	RecZ	RZ	ITZ
Herbs			
Red clover	129.7±13.2	137.5±14.2	140.4±15.3
Broadleaf plantain	485.3±47.9	501.2±49.7	524.4±51.6
White clover	187.4±17.5	300.5±29.7	740.6±73.2
Common tansy	317.2±30.4	381.6±37.8	438.3±40.7
Common yarrow	233.4±22.7	247.5±23.9	288.3±27.5
Common dandelion	112.1±12.3	212.4±20.5	290.8±28.5
Cock's foot	139.4±14.6	269.7±27.3	379.4±38.5

Comment: RecZ stands for recreational zones (background), RZ for residential zones, and ITZ for industrial and transport zones.

A geochemical index of biological absorption of elements by plants – the biological absorption coefficient (BAC) – was calculated to describe biogenic migration of iron in the soil/plant system based on the total Fe content in soils and plant leaves.

In most studied plants, Fe demonstrated low absorption and average scavenging rates (CAB = 0.1 – 0.4). As iron contamination (iron content in the soil) increased, the CAB decreased in most species with the exception of those characterised by an iron absorption intensity above the background levels – the silver birch, the small-leaved lime, the common lilac, the white clover, and the cock's foot. The intensity of iron absorption in the common dandelion, the rugosa rose, the garland spirea, the sweet mock-orange, and the common snowberry did not change significantly.

Iron content was analysed in the leaves of the studied plants throughout the vegetative period. The minimum content of metal in leaves was observed at the beginning of vegetation (May). As the age and area of lamina

increased, iron concentration grew to reach its maximum in October. Fe concentration coefficient in the leaves of woody plants (May – October) was 1.5 – 3.0 (fig. 2). Iron content in the European elderberry, the rugosa rose, and *Hippophae rhamnoides* (October) was 3.3-9.9 times that of May (fig. 3). Fe concentration coefficient in the leaves of herbaceous plants (May – October) ranged from 2.7 to 5.4 (fig. 4).

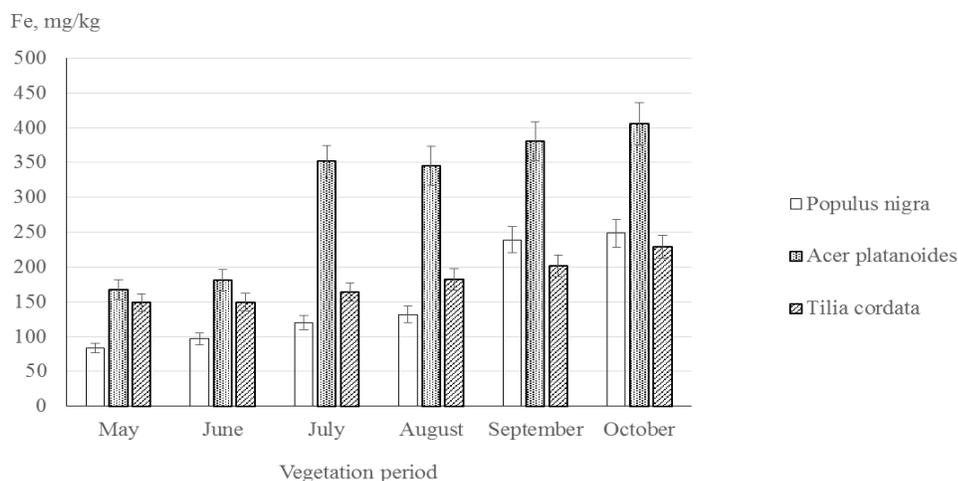


Figure 2: Iron content in the leaves of woody plants in Kaliningrad during vegetative period

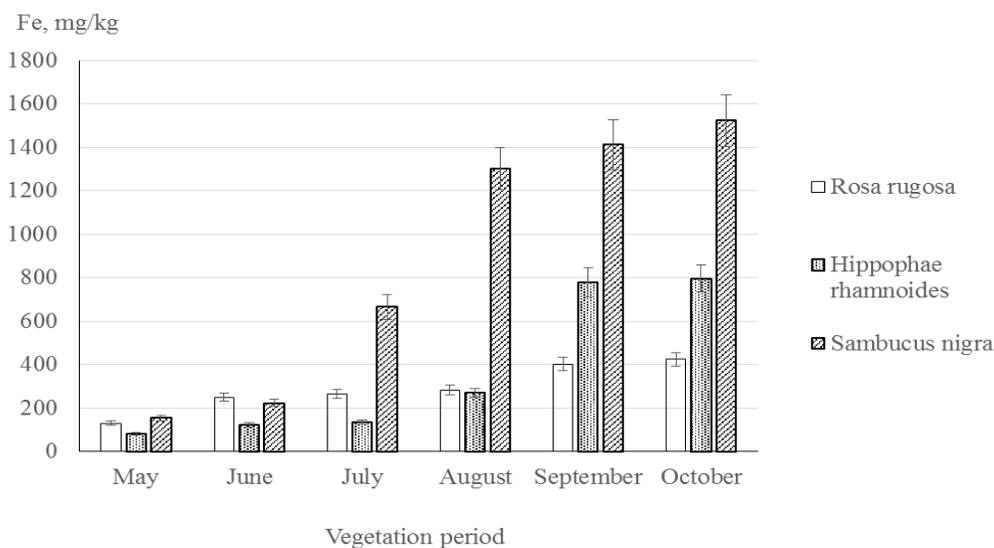


Figure 3: Iron content in the leaves of shrubs in Kaliningrad during the vegetative period

At the end of the vegetative period, a high iron concentration was observed in the leaves of the broadleaf plantain (1654.3 ± 146.2), the European elderberry (1524.3 ± 138.6), the common tansy (1013.2 ± 98.4), the common dandelion (802.4 ± 75.6), *Hippophae rhamnoides* (796.3 ± 71.3), and the white clover (736.2 ± 69.4). Fe concentration reached maximum levels in the European elderberry and *Hippophae rhamnoides* (9.93-9.95). An analysis of correlations between iron concentration in the soil and plants shows high contingency ($RZ=0.92-1.0$ $p<0.05$). The only exception was *Hippophae rhamnoides* ($RZ=-0.52$, $p<0.05$). In the black poplar, iron concentrations in the soil and leaves had a negative correlation ($RZ=-0.99$, $p<0.05$).

Antagonism between iron and other metals was observed in a number of agricultural plants. Recent studies suggest that chlorosis caused by the excessive heavy metal content in soils leads to iron deficiency [23; 26; 27].

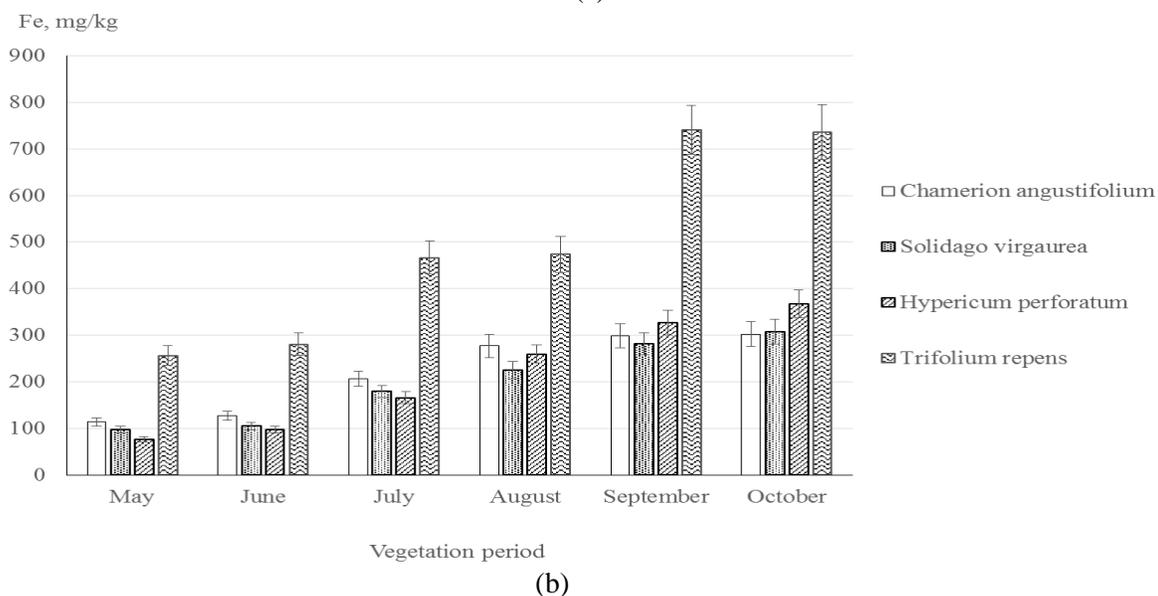
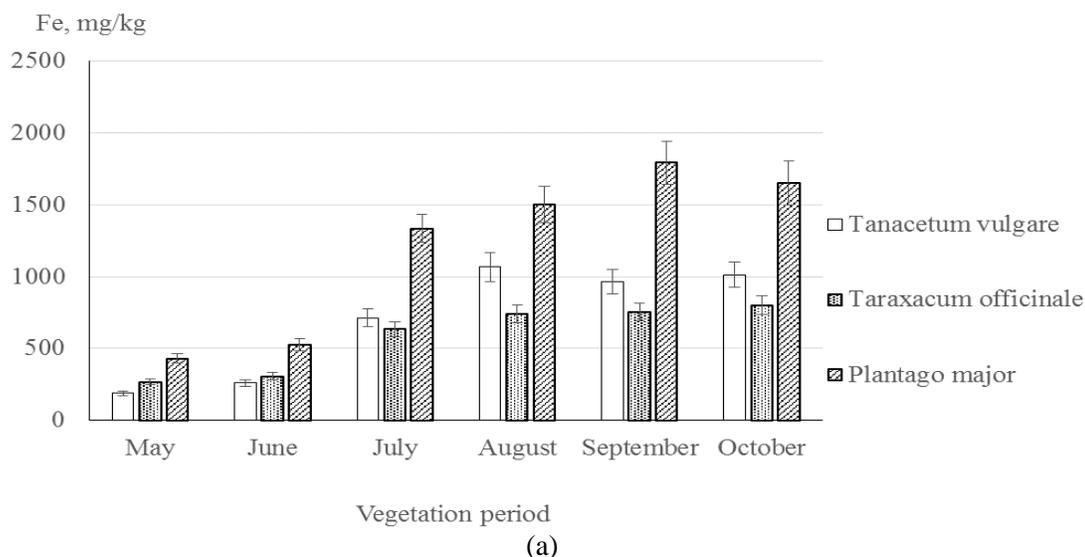


Figure 4: Iron content in the leaves of herbaceous plants in Kaliningrad during vegetation (a, b).

The excessive content of heavy metals, in particular, manganese, nickel, and cobalt decrease the rates of iron absorption and transportation in plants, which results in a reduced chlorophyll content. On the other hand, high concentrations of iron compounds in soils contribute to reduced absorption of microelements in plants. Table 5 contains data on correlations between certain elements affecting iron uptake by plants and iron (Mn/Fe; Ni/Fe; Co/Fe) in the soils of functional zones in Kaliningrad.

Table 5. Element/Fe correlation in soils in the studied areas

Landscape type	Element/Fe		
	Mn/Fe	Ni/Fe	Co/Fe
RecZ	0.20	0.007	0.003
AC	0.26	0.010	0.003
RZ	0.27	0.006	0.002
ITZ	0.23	0.008	0.002

Comment: RecZ stands for recreational zones (background); RZ residential zones, ITZ for industrial/transport zones.

An analysis of relevant data does not show significant changes in Mn/Fe, Ni/Fe, and Co/Fe ratios in the soils of different functional zones in Kaliningrad. This is indicative of the absence of processes accompanied by a selective manganese removal or supply (removal and supply of iron are much more seldom and they occur only in reducing environments). Elements contained in soils affect a plant collectively and they can either weaken or strengthen each other. The Fe/Mn correlation is crucial in assessing the resistance of plants to iron toxicity. Normal development of plants requires a Fe/Mn correlation of 1.5 — 2.5. Higher levels are associated with manganese deficiency and lower ones with irregular iron uptake (iron deficiency) [23-25; 27].

An analysis of the Fe/Mn ratio in the leaves of woody plants shows a reduction in iron content caused by an increase in human impact. The background values of Fe/Mn ranged from 2.4 to 13.2 (table 6). The Fe/Mn values in the leaves of the poplar and birch were 0.23 and 0.11 of the background respectively. In the leaves of the Norway maple, the Fe/Mn ratio fell below optimal values, which suggests irregular iron uptake in the plants.

Table 6. Fe/Mn correlation in the leaves of woody plants in different functional zones in Kaliningrad (P < 0.05).

Species	Fe/Mn		
	RecZ	RZ	ITZ
Tree species			
Black poplar	5.7	2.5	1.3
Silver birch	13.2	1.7	1.5
Norway maple	5.8	0.3	0.2
Small-leaved lime	2.4	2.6	3.1

Comment: RecZ stands for recreational zones (background), RZ for residential zones, and ITZ for industrial and transport zones.

Table 7. Fe/Mn correlation in the leaves of shrubs in different functional zones in Kaliningrad (P < 0.05).

Species	Fe/Mn		
	RecZ	RZ	ITZ
Shrubs			
European elderberry	3.5	4.0	4.3
Common snowberry	5.4	5.1	5.6
Common lilac	10.5	6.3	8.9
Guelder rose 'Roseum'	10.6	9.2	9.6
Wild privet	8.5	9.8	10.0
Sweet mock-orange	11.8	14.5	18.9
Alpine currant	5.6	4.3	5.2
Van Houtte's spiraea	8.9	8.3	10.2
Rugosa rose	9.4	14.9	12.9
Common barberry	7.9	7.8	8.5
<i>Hippophae rhamnoides</i>	7.8	3.4	2.8

Comment: RecZ stands for recreational zones (background), RZ for residential zones, and ITZ for industrial and transport zones.

In the leaves of the European elderberry, the wild privet, the sweet mock-orange, Van Houtte's spiraea, the rugosa rose, and the common barberry (ITZ), the Fe/Mn value was above the background. In the leaves of the common lilac and *Hippophae rhamnoides*, the Fe/Mn value was in inverse proportion to human impact.

The background Fe/Mn values in the leaves of shrubs ranged from 5.6 to 11.8 (table 7). In the leaves of the common snowberry, the guelder rose, and the alpine currant, this correlation did not show significant changes. A critical reduction in the Fe/Mn values was not observed. The maximum exceedance over the background level was 60% (in the sweet mock-orange).

In the leaves of herbaceous plants, the Fe/Mn background values ranged from 2.6 to 12.4 (table 8). In the leaves of the red clover, the broadleaf plantain, and the common yarrow growing in contaminated areas, it was 0.45 - 0.77

times that of background. It increased 1.3 – 2.5 times in the leaves of the white clover, the common dandelion, and the cock's foot and it did not show significant changes in the leaves of the common tansy.

There were no critical reductions in the Fe/Mn values in plants. The maximum exceedance over the background was observed in the leaves of the common yarrow and the white clover (2.2 – 2.5). In the leaves of the Norway maple, the Fe/Mn ratio was below optimal, which is indicative of irregular iron uptake. Plants with increased Fe/Mn values (the common yarrow, the white clover) may be affected by iron toxicity.

Table 8. Fe/Mn correlation in the leaves of herbaceous plants in different functional zones in Kaliningrad (P<0.05)

Species	Fe/Mn		
	RecZ	RZ	ITZ
Herbaceous plants			
Red clover	2.1	1.5	1.3
Broadleaf plantain	12.4	10.3	9.8
White clover	5.4	6.0	13.3
Common tansy	4.1	4.3	3.9
Common yarrow	4.6	2.0	2.1
Common dandelion	6.2	7.2	8.2
Cock's foot	2.6	3.4	4.4

Comment: RecZ stands for recreational zones (background), RZ for residential zones, and ITZ for industrial and transport zones.

Conclusions

In the accumulation horizon of soils in major functional zones (agricultural/residential, residential, and industrial/transport landscapes), iron levels were above the background. The maximum iron content was observed in industrial landscapes and high-rise residential zones with heavy traffic. Iron migration in the soil proved to be season-dependent. Iron migration increased during rainy periods and snowmelt; otherwise, the element tended to concentrate in the soil.

An analysis of iron content in plants growing in contaminated areas (RZ, ITZ) makes it possible to identify species that were most likely to accumulate iron ions. In tree species, Fe was actively accumulated by the silver birch and the small-leaved lime (545.1-647.5 mg/kg), in the shrubs by the sweet mock-orange (542.1 mg/kg), and in herbs by the white clover (740.6 mg/kg), the cock's foot (379.4 mg/kg), and the common dandelion (290.8 mg/kg). Iron concentration in the leaves of this species did not exceed the critical level (750-1000 mg/kg) during the vegetative period. These species can be used in the phytoremediation of areas contaminated with iron.

Most plants studied showed low iron absorption and average iron scavenging rates (BAC = 0.1–0.4). An increase in iron concentration resulted in a reduced BAC in most plants with the exception of species with a Fe absorption intensity above background values – the silver birch, the small-leaved lime, the common lilac, the white clover, and the cock's foot. The intensity of iron absorption in the common dandelion, the rugosa rose, the garland spirea, the sweet mock-orange, and the common snowberry did not show significant changes.

An analysis of correlations between iron concentrations in the soils and plants shows high contingency (RZ=0.92-1.0 p<0.05). However, this does not hold true for *Hippophae rhamnoides* (RZ=-0.52, p<0.05). There was a negative correlation between iron concentrations in the soil and the leaves of the black poplar (RZ=-0.99, p<0.05). Iron content in the leaves of studied plants was analysed throughout the vegetative period. The minimum iron content was observed at the beginning of vegetation (May) and it grew as the age and areas of the lamina increased. The maximum concentration was reached in October.

The Norway maple, the wild privet, *Hippophae rhamnoides*, the European elderberry, the broadleaf plantain, the red clover, and the common yarrow proved to be particularly resistant to the iron contamination of soils.

An analysis of relevant data does not show significant changes in the Mn/Fe, Ni/Fe, and Co/Fe ratios in the soils of different functional zones, which suggests the absence of processes accompanied by selective removal or supply of these elements. The Fe/Mn ratio is key in assessing plant resistance to iron toxicity. In the leaves of the Norway maple, the Fe/Mn ratio was below optimal values, which is indicative of irregular iron uptake. Plants with a high Fe/Mn ratio (the sweet mock-orange, the common yarrow, and the white clover) may be affected by iron toxicity.

References

1. Chupakhina G.N., Maslennikov P.V., Skrypnik L.N., Chupakhina N.Y., Poltavskaya R.L., Feduraev P.V., *Russ. Chem. Bull.* 9 (2014) 1946.
2. Chupakhina G.N., Maslennikov P.V., *Russ. J. Ecol.* 5 (2004) 290.
3. Maslennikov P.V., Chupakhina G.N., Skrypnik L.N. *Biol. Bull. Russ. Acad. Sci.* 2 (2014) 133.
4. Maslennikov P.V., Chupakhina G.N., Dedkov V.P., Kurkina M.V., Sadovnikov P.V., Melnik A.S., *Rastitelnye Resursy* 4 (2014) 83.
5. Maslennikov P.V., Skrypnik L.N., *Russ. J. MPSE* 1 (2015) 32.
6. Matveev P.M., Pavlovskiy V.L., Prokhorova T.M., Ecology of heavy metal accumulation by agricultural plants in the forest/steppe and steppe zone of the Volga region, Samara State University Press, (1997).
7. Orlov D.S., Malinina M.S., Motuzova G.V., Sadovnikova L.K., Sokolova T.A., Chemical pollution of soils and soil protection, Agropromizdat, (1991).
8. Agarwal S., Sairam R.K., Meena R.C., Tyagi A. Srivastava G.C., *J. Plant Sci.*1 (2006) 86.
9. Kopylova L.V., *Uchenye zapiski ZAbSPU* 1 (2012) 70.
10. Nozoye T., Nagasaka S., Kobayashi T., Takahashi M., Sato Y., *J. Biol. Chem.* 286 (2011) 5446.
11. Priyadarsini A., Sahoo S., Rout G.R., *IJAEB* 8 (2015) 285.
12. Rout G.R., Sahoo S. *RAS* 3 (2015) 1.
13. Vigani G., Maffi D., Zocchi G. *New Phytol.* 182 (2009) 127.
14. Wintz H., Fox T., Vulpe C. *Biochem. Soc. Trans.* 30 (2002) 766.
15. Yadav S.K., *S. Afr. J. Bot.* 76 (2010) 169.
16. Chernikov V.A., Aleksakhin R.M., Golubev A.M., Gringof I.G., Agroecology, Kolos, (2000).
17. Yanturin I.Sh., Amineva A.A., *Russ. J. Fund. Research* 6 (2013) 1456.
18. Yagafarova G.A., Buskunova G.G., Amineva A.A., Yanturin S.I., An ecological assessment of raw material obtained from the genus *Achillea* L. in the geochemical province of Southern Urals: A monograph, Bashkir State University Press, (2012).
19. Bgatov A.V., *Russ. J. Phil. Sci.* 2 (1999) 80.
20. Stanchenko L. Yu., *Vestnik IKBFU* 1 (2009) 81.
21. Vashcheykin A.S., Sadovnikov P.V., Kurkina M.V., Dedkov V.P., *Vestnik IKBFU* 1 (2014) 86.
22. Methodology for measuring the mass fraction of metals and metal oxides in soil powder samples using the X-ray fluorescence imaging, Spektron, (2010).
23. Kabata-Pendias A., Pendias H., Microelements in soils and plants, Mir, (1989).
24. Amineva A.A., Buskunova G.G., *Vestnik OS* 6 (2009) 532.
25. Starova M.V., Ecology: Finding solutions in Southern Urals, Nauka, (2003)
26. Ilyin V.B. Heavy metals in the soil/plant system, Nauka, (1991).
27. Ilyin V.B., Syso A.I., Microelements and heavy metals in soils and plants, Russian Academy of Sciences Press, (2001).

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