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GEOECOLOGICAL FEATURES OF ZINC ACCUMULATION IN THE SOIL - PLANTS SYSTEM OF URBAN ECOSYSTEMS

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Abstract: The study aims to determine zinc accumulation in urban soil and in common urban landscape species of woodlands, bushes and herbaceous plants (22 species). Maximum metal concentration was observed in the soil of landscapes of industrial-utility and in residential multistore areas with increased transport load (125.7-154.7 mg/kg^{-1}). Zinc (Zn) content of plant leaves in urban areas depended on its concentration in soil ($r = 0.86–0.99$, $p<0.05$) and the vegetation period. The minimum Zn content in plant leaves was observed at the beginning of the growing season (May), and later with increasing age and leaf blade area, the metal concentration increased, reaching a maximum in October. The highest rates of metal bioaccumulation were found in *Syringa vulgaris* (1.24 %), *Rosa rugosa* (1.17 %) and *Populus nigra* (1.1 %). These species will be useful for phytoremediation of areas moderately polluted with Zn. A decrease in Zn BAC and an increase in its concentration in the soil were identified in the majority of plant species. Plant species capable of limiting the entry of Zn from the environment were also identified.

Keywords: Environmental contamination, zinc, phytoindication, phytourbocenosis, phytoremediation.

Introduction

One of the main environmental problems nowadays is pollution associated with rapid growth of cities. The concentration of industrial enterprises, heavy traffic and activities of public utilities have resulted in large industrial cities standing out against the natural background and becoming centers of environmental contamination (Chupakhina *et al.*, 2017; Maslennikov *et al.*, 2018). Each city is a unique techno-ecosystem, the components of which are under various anthropogenic pressures. The most dangerous environmental pollutants in cities are heavy metals (HMs) — when entering the biological cycle, they impose a number of negative effects on all natural components of the urban ecosystem's "air-soil-water-plants" (Clemens *et al.*, 2002; Brezinova & Vymazal, 2015; Chupakhina *et al.*, 2017).

HMs can be subdivided into biogenic and toxicants. Such subdivision of is nominal, since different concentrations can cause both positive and negative effects on the body. Zinc (Zn) is an important nutrient that also belongs to the group of HMs. It plays a role in the metabolism of nucleic acids and proteins, besides stimulating and inhibiting the growth of plants (Rout & Das, 2003; Lopez, 2005; Gupta *et al.*, 2016). Zn acts as a cofactor for more than 300 proteins, the majority of which are zinc finger proteins, and also RNA and DNA polymerases (Lopez, 2005). It is the only metal present in all six enzyme classes (oxidoreductase, transferase, hydrolases, lyases, isomerases and ligases) (Nielsen, 2012; Gupta *et al.*, 2016).

Zn is involved in a number of physiological processes of plants, such as hormone regulation (e.g. the synthesis of IAA precursor, tryptophan), signal transduction via mitogen-activated protein kinases (Lin *et al.*, 2005; Broadley *et al.*, 2007; Hansch & Mendel, 2009; Gupta *et al.*, 2016), repair processes of the PS II complex during photoinhibition (Bailey *et al.*, 2002; Hansch & Mendel, 2009; Gupta *et al.*, 2016) and maintenance of CO_2 concentration in mesophyll. Peck and McDonald (2010) confirmed the participation of Zn in the regulation of Rubisco activity, along with the reduction of adverse effects of heat stress on wheat (Peck *et al.*, 2010; Sadeghzadeh, 2013).

There is a great difference between the required amount of Zn and its toxic level (Hambidge, 2000; White, 2012; Gupta *et al.*, 2016). On one hand, lack of the element is a main agricultural problem today. In particular, 50 % of the soil for cereal cultivation have Zn deficiency (Hotz & Brown, 2004; Das & Green, 2013). On the other hand, the accumulation of excess Zn will negatively affect soil processes. It changes the physical and physico-chemical properties of the soil and reduces its biological activity. Zn also inhibits vital activity of microorganisms (Hani & Pazira, 2011; Olaniran *et al.*, 2013; Sadeghzadeh, 2013), which leads to the disruption of organic matter formation in soil. Excess Zn in the soil cover hampers cellulose fermentation, respiration and urease activity (Vymazal & Brezinova, 2015; Gupta *et al.*, 2016).

The natural level of Zn in soil is determined primarily by its content in soil-forming rocks. The gross content of Zn in parent rocks of the Kaliningrad region is 9.7– 46.5 mg/kg^{-1} and its average content in the Earth's lithosphere amounts to 83 mg/kg^{-1} (Kabata-Pendias, 2011; Gupta *et al.*, 2016; Chupakhina *et al.*, 2017; Maslennikov *et al.*, 2018). The content in soil is also affected by their type and mechanical composition (Kabata-Pendias, 2011; Gupta *et al.*, 2016; Chupakhina *et al.*, 2017; Maslennikov *et al.*, 2018). Zn content in sod-light podzolic soil ranges from 29.8 mg/kg^{-1} in sandy to 48.4 mg/kg^{-1} in light loamy and 67.9 mg/kg^{-1} in medium loamy soils. Gross Zn amounts to 49.9 - 68.8 mg/kg^{-1} in light loamy and medium loamy soils. In humus-peat lowland and floodplain sod soils, it is 86.5 - 96.7 mg/kg^{-1} (Kabata-Pendias, 2011; Gupta *et al.*, 2016; Chupakhina *et al.*, 2017; Maslennikov *et al.*, 2018).

In addition to soil, Zn can also accumulate in plants. Some fractions in soil exist either as an insoluble complex, or in adsorbed and exchangeable forms. However, other fractions exist in water-soluble form and are freely available to plants. Root activity also makes the exchangeable form partially available for uptake via ion exchange and release of organic acids etc. Insoluble Zn comprises > 90 % of the metal in soil that cannot be utilized by plants, while the exchangeable form ranges from 0.1 to 2 µg Zn g^{-1}. Concentrations of water-soluble Zn range between 4 x 10^{-10} and 4 x 10^{-6} M in bulk soil solution (Gupta *et al.*, 2016). Soil moisture is another physical factor that affects Zn uptake by plant roots via diffusion. Role of soil moisture is very crucial in soil with low Zn availability (Gupta *et al.*, 2016). Solubility of Zn and the ratio of Zn^{2+} to organic-Zn ligand complexes will especially increase at low pH for low soluble organic matter soil. Higher levels of soil organic matter will enhance the entry of phytoavailable Zn in soil (Catlett *et al.*, 2002; Obrador *et al.*, 2003). In addition to soil pH, soil redox potential (i.e. Eh) strongly influences the speed and intensity of humification process, redox status of the rhizosphere and the mobility of Zn. In conclusion, soil type, mineral and clay types, soil biota and plant uptake will collectively determine Zn distribution in soil-root-plant fluxes.

A number of researchers have shown that the accumulation of Zn in the soil-plant system is a good tool for assessing environmental risk (Romero-Freire *et al.*, 2016; Lago-Vila *et al.*, 2017). Other authors suggest that mapping of the spatial distribution of zinc-polluted soil is necessary for human and ecological risk assessment (Hani & Pazira, 2011; Delavar & Safari, 2016; Baran *et al.*, 2018). Guo *et al.* (2012) reported that information about the pattern of heavy metal distribution in soil with different land use may assist in developing strategies to protect the environment and human health against long-term accumulation of HMs.

Urbanized territories are under strong technogenic pressure and all natural components of the urban ecosystem undergo a number of changes and acquire features that distinguish them from their natural counterparts. This leads to deterioration in environmental quality (Chupakhina *et al.*, 2017; Maslennikov, 2020). In the Russian Federation, monitoring studies are being conducted in many cities to assess the ecological status of natural components in the urban ecosystem. In the Kaliningrad region, such studies are sporadic in nature, lacking a common methodological base and certainly are in need of updating. For these reasons, studies assessing the ecological state of the natural vegetation of the urban ecosystem have a particular scientific and practical significance and relevance. The purpose of this study is to investigate the geoecological features of Zn accumulation in the soil system — plants in urban phytourbocenoses of the city of Kaliningrad, Russia. This study investigated the accumulation of Zn in the accumulative horizon of urban soil and in the most common types of trees, bushes and herbaceous plants in urban landscapes.

Materials and Methods

Area Characterization

The area under study comprised the main geochemical landscapes of Kaliningrad city, which were recreational zones (RecZ, control), agricultural/residential zones (ARZ), residential zones (RZ) and industrial/utility/transport zones (IUTZ) (Figure 1). Recreational landscapes within 40-50 km away from large industrial sources of pollution, and least affected by human and pollutants (Svetlogorsk), were used as the control area.

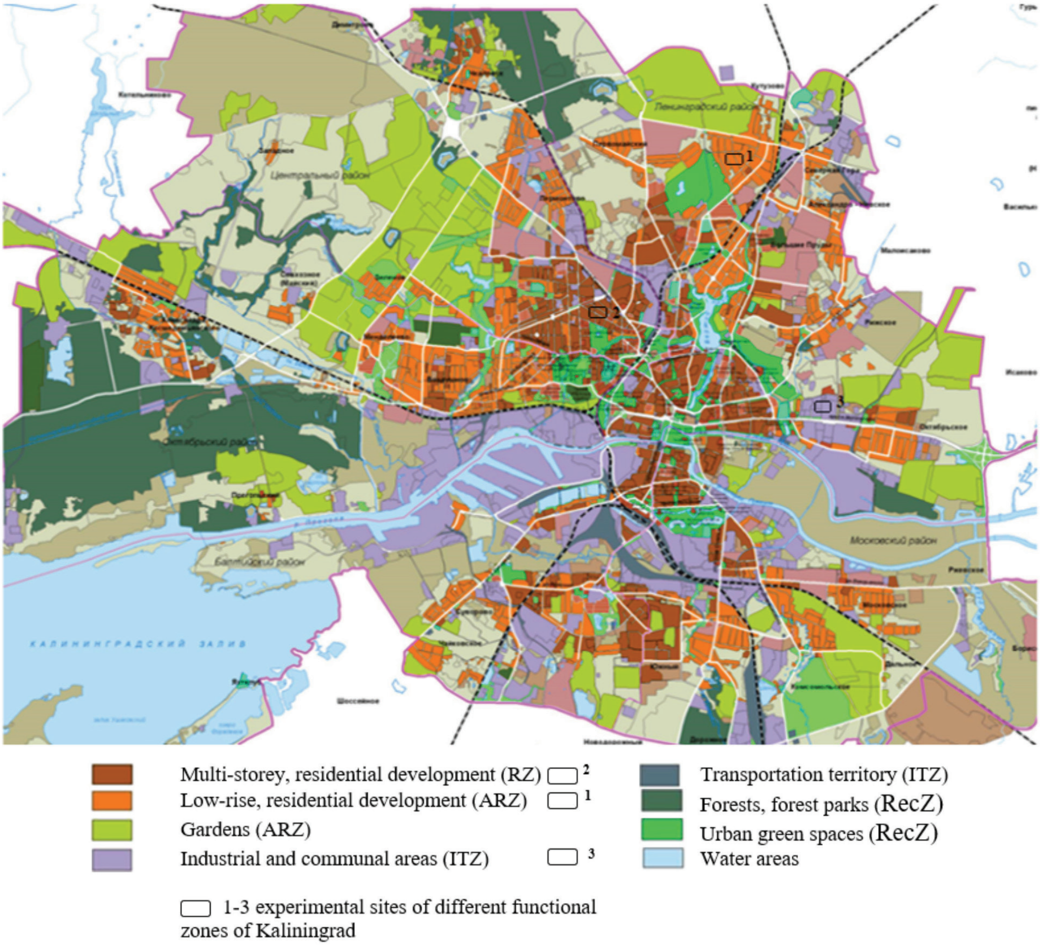

Figure 1: Functional zoning of Kaliningrad

Residential areas occupied up to 27 % of the city's territory (2,833 ha). Technogenic pedogeochemical anomalies were formed there, their contrast depending on the height and location of the facilities. Residential buildings served as a mechanical barrier to airflow and directly affected the characteristics of entry, movement, accumulation and removal of polluting chemicals (Maslennikov *et al.*, 2018). The agro-residential landscape (ARL) included individual buildings combined with household plots (summer cottages, garden and kitchen-garden plots), and its share in the structure of urban areas was quite significant, which amounted to 15 % (2,398 ha) of the city's landscape (Maslennikov *et al.*, 2018). IUTZs occupied 15 % of the urban area (2,430 ha). Landscapes of enterprises were characterized by an extensive degradation of the biological cycle of substances and served as the source of anthropogenic emission and accumulation of pollutants (Maslennikov *et al.*, 2018). RecZ landscapes were the least subjected to atmotechnogenic impact, since the role of biogenic migration in them was still profound. They amounted to 16 % of the territory and were located in the city center and on the outskirts.

According to the redox conditions of HMs. RecZ, RZ and IUTZ sites were represented by geochemical landscapes with oxidative conditions, whereas ARZ sites were represented by landscapes with reducing conditions. The acid-base conditions of urban soil was slightly alkaline (pH_{KCl} 7-8), but it was neutral in the control area (RecZ) (pH_{KCl} 6-7) (Maslennikov *et al.*, 2018). As per geomorphological features of research sites, RZ soil was represented by transeluvial geochemical landscapes, IUTZ by trans-accumulative, and RecZ and ARZ by eluvial landscapes. Samples of the humus-accumulative horizon, which were selected around the city, were mainly sand or sandy loam by granulometric composition (Maslennikov *et al.*, 2018).

Material Collection and Heavy Metal Analysis

Zn concentration was analysed in the tissues of the most common urban plant species (Table 2). Plant material was collected during the growing season from May to October 2018. In each functional zone, plant and soil samples were taken from three sites. Soil samples were collected from the topsoil at a depth of 0-10 cm, using the envelope method (Chupakhina *et al.*, 2017; Maslennikov, 2020). In the study areas, we established permanent research sites with an area of 100 m^2. The size of the zone from which the plant samples were collected corresponded to 1 km^2. Zn concentration in the soil and plant samples was measured by X-ray fluorescence with the help of a Spektroskan Maks–G spectrometer (SPECTRON, Russia). Soil samples were prepared according to Chupakhina *et al.* (2017). Plant leaves were dried to a constant weight and ground to powder in a quartz mortar. The content of Zn in averaged samples was determined and expressed in µg/g of dry weight (Chupakhina *et al.*, 2017; Maslennikov, 2020). "Averaged" means that combined plant material was collected from six to nine individual plants at each of the three experimental sites in a functional zone under study. Each combined sample was analysed in triplicates.

In order to characterize the migration of biogenic zinc in the soil-plant system, the coefficient of biological absorption (CBA) was calculated on the basis of Zn gross content in soil and leaves. CBA is a biogeochemical indicator of the elements' biological absorption intensity by vegetation. According to the biological absorption intensity, all elements can be divided into the following categories: vigorous absorption elements (CBA = 10-100); strong absorption elements (CBA = 1-10); elements of weak absorption and average capture (CBA = 0.1-1.0); and, elements of weak capture (CBA = 0.01-0.10). When estimating the intensity of biogenic migration, plants were assumed to accumulate elements with a CBA of >1, as elements were only captured by plants with a CBA <1 (Chupakhina *et al.*, 2017; Phetsombat et al., 2006).

In the course of the study, 378 plant and 12 soil samples were analysed. Charts and tables were used to present the data in arithmetic means and standard errors of the mean. Statistical significance of differences between variants was established using Student's t-test ($p \leq 0.05$). The figures show polynomial trend lines, degree - 2. Correlation analysis was conducted using Pearson's chi-squared test.

Results

Zinc Content in Soil of Different Functional Zones

Analysis of zinc content in the soil of various functional areas of the city showed that maximum metal concentration was observed in IUTZ landscapes and in residential multistore areas with increased transport load (154.7±11.8 mg / kg-1). The concentration of zinc in the upper soil layer of such sites exceeded the background indicator 3.1 times. In ARZ and RZ, zinc content in the accumulative soil horizon exceeded the background indicator by 2.2 and 2.5 times, respectively (Table 1.). In general, the study revealed an excessive zinc accumulation in the accumulative soil horizon not only in relation to the background, but also to the approximate permissible concentration (APC) of metal (55 mg / kg-1). Samples of all urban sites exceeded the standard between 2.0 and 2.8 times.

Zinc Content in Plants of Different Functional Zones

Urban ecosystems in Kaliningrad (which were used for biogeochemical monitoring) consisted of parks, housing area landscapes, lawns and road landscapes. These were mainly man-made systems (semi-cultivated, cultivated and ornamental) that were subjected to human impact. Plant composition of urban ecosystems was not very diverse and it was represented by lawn grasses and weed species, trees and shrubs that were traditionally used in city gardening.

This study analyzed the background levels of Zn in tree leaves, shrubs and herbaceous plants — the accumulation of the metal in the leaves in polluted areas and its change during the growing season. Analysis of Zn background levels in plants did not reveal statistically significant differences among the types of plants (trees, shrubs and herbaceous). Maximum metal content was observed in leaves of *Populus nigra* (83.2±8.2 mg/kg-1) and *Betula pendula* (57.3±5.6 mg/kg-1) in woody plants, in leaves of *Sambucus nigra* (30.2±3.1 mg/kg-1) in shrubs and in leaves of *Trifolium pratense* (38.6± 2.7 mg/kg-1) among grass species (Table. 2).

Table 1: Zn concentrations in the topsoil (0–10 cm) in different functional zones of Kaliningrad, mg/kg -1

Landscape type				
K	RecZ	ARZ	RZ	IUTZ
9.7—46.5	49.4±0.5	108.2±10.5*	125.7±12.6*	154.7±11.8*

Note: RecZ stands for recreational zones (background), ARZ for agricultural/residential zones, RZ for residential zones, and IUTZ for industrial/utility/transport zones. K is the average element content in maternal rocks of the Kaliningrad region according to (Chupakhina *et al.*, 2017; Maslennikov *et al.*, 2018). Data are expressed as mean values ± standard deviations. * Significantly different from control values (RecZ) ($p<0.05$, Student's t-test). The content of elements was determined in mixed samples from three research sites of each functional area. Each combined sample was analysed using three analytical replications. Due to insignificant discrepancy between the analytical replicates, statistical processing of data was carried out only by taking into account biological replications (n=3).

Table 2: Zn concentrations in the leaves of woody, shrub and herbaceous plants in different functional zones of Kaliningrad.

Species	**Zn, mg/kg $^{-1}$**		
	RecZ	**RZ**	**IUTZ**
Tree species			
Populus nigra L.	83.2±8.2	122.9±13.1*	148.6±14.3*
Betula pendula Roth	57.3±5.6	74.3±7.2*	81.2±8.1*
Acer platanoides L.	33.1±3.1	35.5±3.6	37.8±3.7
Tilia cordata Mill.	22.1±2.0	24.2±2.3	26.6±2.5
Shrubs			
Sambucus nigra L.	30.2±3.1	34.2±3.3	32.4±3.3
Symphoricarpos rivularis Suksdorf.	24.6±2.5	31.8±3.1	37.8±3.8*
Syringa vulgaris L.	24.2±2.3	79.4±8.1*	94.5±9.3*
Viburnum opulus ´Roseum´	24.4±2.4	48.2±4.8*	69.7±6.8*
Ligustrum vulgare L.	20.2±2.1	23.7±2.2	26.8±2.5*
Philadelphus coronarius L.	19.7±1.8	24.7±2.5	30.9±2.9*
Ribes alpinum L.	19.6±1.9	27.3±2.8*	38.5±3.8*
Spirae vanhouttei (Briot.) Zab.	18.5±1.9	20.3±1.8	19.8±1.8
Rosa rugosa Thunb.	17.3±1.8	63.7±6.4*	85.4±8.6*
Berberis vulgaris L.	17.1±1.7	20.5±1.9	24.6±2.4*
Hippophae rhamnoides L.	14.1±1.4	18.6±1.9	21.6±2.1*
Herbs			
Trifolium pratense L.	38.6±3.8	58.1±5.7*	62.4±6.2*
Plantago major L.	34.5±3.5	36.3±3.5	33.4±3.2
Trifolium repens L.	28.0±2.7	34.7±3.4	38.2±3.8*
Tanacetum vulgare L.	27.2±2.7	42.4±4.1*	57.6±5.7*
Achillea millefolium L.	25.4±2.5	41.0±4.1*	49.3±4.9*
Taraxacum officinale Wigg.s.l.	23.1±2.3	30.2±3.1	34.7±3.4*
Dactylis glomerata L.	20.3±2.1	23.2±2.4	29.8±2.8*

Note: RecZ stands for recreational zones (background), RZ for residential zones, and IUTZ for industrial/utility/transport zones. Data are expressed as mean values ± standard deviations. * significantly different from control values (RecZ) ($p<0.05$, Student's t-test). The content of elements was determined in three mixed plant samples in three analytical replicates. Due to the insignificant discrepancy between the analytical replicates, statistical processing of data was carried out only by taking into account biological replications (n=3).

Zn content in plants at contaminated zones (eg. IUTZ) varied from 19.8 to 148.6 mg/kg. Metal content in the leaves of *Syringa vulgaris* under conditions of severe soil pollution in industrial-utility and transport landscapes (IutL) exceeded the background by 3.9 times, and in *Rosa rugosa* leaves by 4.9 times. In the leaves of *Achillea millefolium*, *Ribes alpinum*, *Tanacetum vulgare* and *Viburnum opulus*, Zn content was 1.9 to 2.9 times higher than in the background. Metal concentration exceeded the background by 1.3 to 1.8 times in the leaves of *Ligustrum vulgare*, *Trifolium repens*, *Betula pendula*, *Berberis vulgaris*, *Dactylis glomerata*, *Hippophae rhamnoides*, *Taraxacum officinale*, *Symphoricarpos rivularis*, *Philadelphus coronarius*, *Trifolium pratense* and *Populus nigra*. Zn accumulation was insignificant in the leaves of *Tilia cordata*, *Acer platanoides*, *Spirae vanhouttei*, *Sambucus nigra* and *Plantago major*.

The zinc content in the leaves of plants of urban ecosystems was studied during the growing season (May to October). The analysis of the metal accumulation dynamic showed that minimum Zn content in leaves was observed at the beginning of the season (May), and later increasing with the increase of age and leaf blade area, reaching its maximum in October. At the end of the season, in the leaves of woody plants (*Populus nigra*, *Tilia cordata, Acer platanoides*), Zn content had exceeded its initial level by 1.6 to 2.3 times (Figure 2).

In the leaves of shrubs (*Sambucus nigra*, *Rosa rugosa* and *Hippophae rhamnoides*), Zn content increased by an average of 2.5 to 3.7 times at the end of the growing season (Figure 3).

Among the herbaceous plants, zinc content in *Tanacetum vulgare* and *Taraxacum officinale* leaves exceeded the similar indicator in October by 2.6 to 3.2 times compared with the level in May. In the leaves of *Trifolium repens,* the increase was 1.5 times higher in the same period. It was only in *Plantago major* leaves that the metal content did not have significant changes during the growing season (Figure 4).

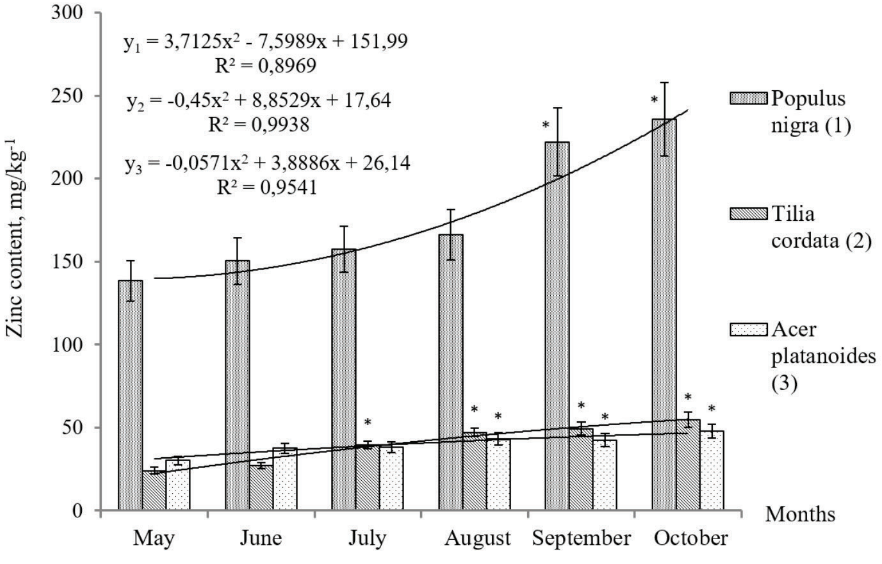

Figure 2: The zinc content in the leaves of woody plants during the growing season in 2018 (industrial/ transport landscapes). The abscissa axis shows the growing season, months; the ordinate indicates zinc content, mg/kg^{-1}; — is a polynomial trend lines, degree - 2. Data are expressed as mean values ± standard deviations. The content of elements was determined in three mixed plant samples in three analytical replicates. Due to the insignificant discrepancy between the analytical replicates, statistical processing of data was carried out only by taking into account biological replications (n=3). * Significantly different from control values (May) (p<0.05, Student's t-test).

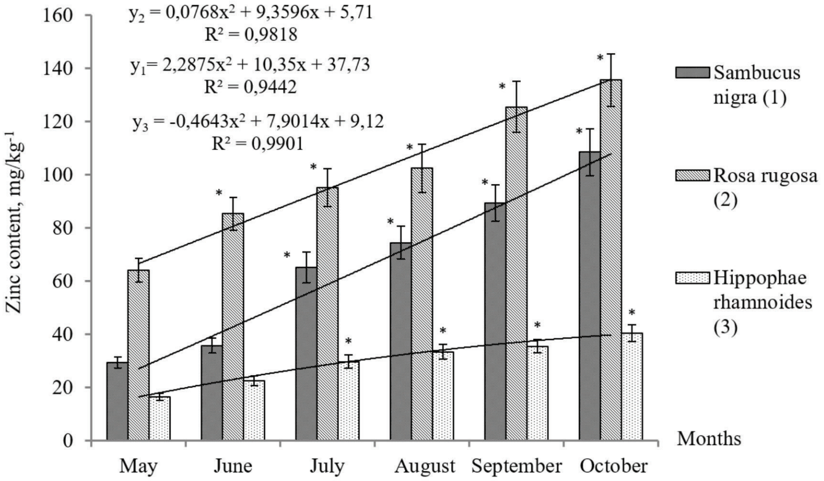

Figure 3: The zinc content in the leaves of shrub plants during the growing season in 2018 (industrial/ transport landscapes). The abscissa axis shows the growing season, months; the ordinate indicates zinc content, mg/kg^{-1}; — is a polynomial trend lines, degree - 2. Data are expressed as mean values ± standard deviations. The content of elements was determined in three mixed plant samples in three analytical replicates. Due to the insignificant discrepancy between the analytical replicates, statistical processing of data was carried out only by taking into account biological replications (n=3). * significantly different from control values (May) (p<0.05, Student's t-test).

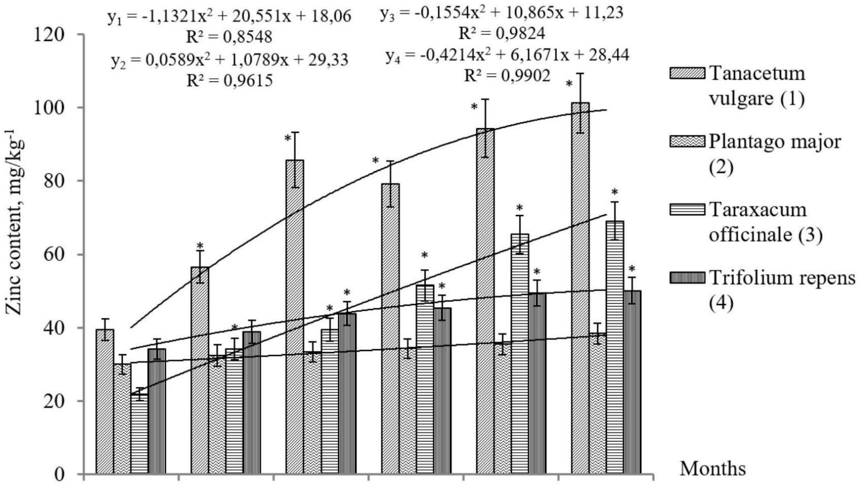

Figure 4: The zinc content in the leaves of herbaceous plants during the growing season in 2018 (industrial/ transport landscapes). The abscissa axis shows the growing season, months; the ordinate indicates zinc content, mg/kg^{-1}; — is a polynomial trend lines, degree - 2. Data are expressed as mean values ± standard deviations. The content of elements was determined in three mixed plant samples in three analytical replicates. Due to the insignificant discrepancy between the analytical replicates, statistical processing of data was carried out only by taking into account biological replications (n=3). * Significantly different from control values (May) (p<0.05, Student's t-test).

Discussion

Zinc Content in Soil

Analysis of Zn content in the soil of various functional areas of the city showed that metal concentration was observed in the range from 108.2 to 154.7 mg/kg^{-1}. Maximum concentrations in soil samples were registered in trans-accumulative geochemical landscapes with oxidative conditions of soil formation and a weak alkaline reaction of the soil solution (IUTZ). Main reasons for Zn accumulation in the surface soil horizons of trans-accumulative landscapes included the proximity of the bedrock and the ability of trans-accumulative landscapes to absorb mineral and organic components with the formation of stable compounds (Maslennikov *et al.*, 2018).

In general, the reasons for a rather strong pollution of soil grounds in urban ecosystems in Kaliningrad might be different, but the main factors were atmotechnogenic emissions from enterprises, road transport and peat fires (Maslennikov *et al.*, 2018). Metal entry is also observed via precipitation (1 litre of rain and snow water accounted for 0.004–0.210 mg of Zn). Some Zn had entered the soil from mineral and organic fertilizers. One kg of mineral fertilizer contained a few to hundreds of milligrams of zinc, while in organic fertilizer, the amount ranges from tens to hundreds of milligrams (Maslennikov *et al.*, 2018).

Another factor that increased the accumulation of Zn in urban soil was their alkalinization. A total of 88.0 % of the urban area in Kaliningrad had been characterized by a weak alkaline reaction of the soil solution (pH 7.5–8.0). And only 10.0 % of urban soil had slightly acidic pH (5.5–6.5) and 2.0 % of the soil were neutral (Maslennikov *et al.*, 2018). Moreover, at a pH range of 5.5–7.0, Zn concentration in soil solution (soluble Zn) decreased significantly by 30- to 45-fold for each unit with an increase in soil pH (Gupta *et al.*, 2016). In this regard, the removal and migration of many HMs, including Zn, would be severely disrupted, which might lead to their accumulation in the upper soil horizon, causing the transformation of the soil geochemical structure in urban ecosystems of Kaliningrad.

Zinc Content in Plants of Different Functional Zones of Kaliningrad

A strong technogenic impact was manifested not only in the soil, but also in the vegetation of the city. Plants are one of the most sensitive indicators of technogenic pollution of the urban environment and are the first line of protection from precipitation deposition, including metal-containing aerosols (Chupakhina *et al.*, 2017; Maslennikov, 2020).

A quantitative analysis of metal content in the soil-plant system made it possible to reveal a number of accumulation patterns. An increase in the degree of urban ecosystem pollution had led to a change in the balance of metal accumulation in the soil-plant system. Under these conditions, plants were able to accumulate heavy metals in much larger quantities than similar species growing in an ecologically clean area. The number of pollutants absorbed by plants depended on the species' peculiarities, like biology, physiology and biochemistry, as well as on specificity of the elements, their concentration and the presence of antagonist metals (Gupta *et al.*, 2016). Soil conditions, such as redox, geomorphological conditions and acid-base features of the upper soil layer, were also important for plant growth (Gupta *et al.*, 2016).

An analysis of the ecological and geochemical characteristics of Zn accumulation in plant leaves had allowed us to identify the main factors contributing to an increase in its content in plant tissues, which were technogenic and geomorphological factors. With an increase in the atmo-technogenic pollution in the studied landscapes, there was an increase of metal content in plant tissues. Maximum level of Zn in leaves had been identified in IutL. For the majority of plants under study, the analysis of correlations between Zn concentrations in the soil and plants revealed a highly reliable degree of conjugacy between the levels of metal accumulation in soil and leaves (r=0.86–0.99,

$p<0.05$). With the exception of *Sambucus nigra* ($r=0.74$, $p< 0.05$) and *Plantago major* ($r=-0.13$, $p=0.05$) (Table 3).

The accumulation of Zn in the studied plants was also significantly influenced by geochemical conditions of the territories. An increase of heteropolar and complex-heteropolar compounds of Zn with organic matter was observed in the soil content of trans-accumulative landscapes (IutL) (Chupakhina *et al.*, 2017; Gupta *et al.*, 2016). Data analysis of Zn content in plants growing in polluted areas (RZ, IutL) had allowed us to identify species which accumulated metal ions the most. *Syringa vulgaris* and *Rosa rugosa* were among species which actively accumulated Zn. Metal content in the leaves of the former under conditions of severe soil pollution (like in IutL) exceeded the background by 3.9 times, and in the latter by 4.9 times. Seven out of 22 studied plant species showed an excess of Zn content in crop production. But in general, metal content in studied plants leaves did not reach maximum permissible values for their vital activity. For example, none of the plant samples exceeded critical (150–200 mg/kg^{-1}) and phytotoxic (400 mg / kg^{-1}) Zn concentrations (Chupakhina *et al.*, 2017; Gupta *et al.*, 2016).

Despite the crucial role of Zn in metabolic reactions, elevated levels of this heavy metal ion can be phytotoxic. By replacing other divalent cations, Zn toxicity could interrupt vital metabolisms like photosynthesis, glycolysis and the electron transport chain (Cakmak, 2000; Cakmak, 2008; Disante *et al.*, 2010). Excess Zn might interfere with genetic material through basic modifications, DNA breakage, rearrangements, depurination and epigenetic modifications. Crosstalk between Zn and other ions (mainly Fe, Ca, P) could also modify physiological and molecular functions of both Zn-stressed and Zn-deficit plants. In order to maintain a balance under Zn-excess conditions, several homeostatic mechanisms are activated at genetic, cellular, organ and whole plant levels.

At genetic level, controlled expression of specific transport proteins in different cell layers of root and shoot made them act as check points in regulating the concentration of metal cations in relevant cell types. At cellular level, several low molecular weight metal chelators and metal-binding proteins participated in homeostatic regulation of species charged with Zn via cytosol and their subsequent storage in intracellular compartments. These metal chelators mainly included phytochelatins and metallothioneins. Furthermore, there had been reports on the sequestration of Zn as an organic acid complex in subcellular compartments (vacuole, cell wall, vesicles) (Verbruggen *et al.*, 2009; Kramer, 2010; Sinclair & Kramer, 2012; Samardjieva *et al.*, 2015). The storage of Zn in vacuoles provided resistance to Zn toxicity.

Zinc content in plant leaves of urbo-ecosystems would change during the vegetative period (May – October). The analysis of metal accumulation dynamics showed a minimum Zn content in leaves at the beginning of the growing season (May), which later increased with age and expansion of leaf blade area, reaching its maximum in October. The maximum Zn concentration was observed in the leaves of *Populus nigra* in October (235.8 ± 22.1 mg / kg^{-1}). In the leaves of other plants, the metal level was much lower. The metal content in the leaves of the studied plants at the end of the growing season did not exceed its phytotoxic level (400 mg / kg^{-1}). The reason for the higher concentration of zinc in plant leaves at the end of the growing season was a significant contamination of soil with this metal and its gradual accumulation in plant tissues. The amount of metals in plants was influenced by seasonal dynamics, and their content at the beginning of the growing season could exceed two to three times the same indicator at the end of the growth period (Ilyin & Syso, 2001). Thus, an analysis of the metal storage capacity in 10 species of woody plants showed that in most species growing under polluted conditions, the Zn content increased by the end of the growing season. The content of other metals, on the contrary, might decrease (Sidorova, 2014). Other studies had shown that the dynamics of metal accumulation in the leaves of balsamic poplar (*Populus balsamifera*

L.) was affected by proximity to the source of industrial emissions (Sterlitamak industrial site). Under these conditions, the Zn content in the leaves did not change until the middle of the growing season, but then intensified sharply. At the same time, under conditions of a relatively clean area (background), the Zn concentration in the leaves of these plants decreased by the end of the growing season (Sidorova, 2014).

Each element has a special physiological function in a plant, therefore the intensity of their absorption would not be the same. Plants, as they were well known, had a selective ability to accumulate elements. According to the type of chemical elements, mineral absorption could be divided into barrier-free (concentrating) and barrier (non-concentrating) plants (Chupakhina *et al.*, 2017). Metal content in the ashes of barrier-free plants increased in proportion to its content in the environment. Barrier plants had a concentration threshold above which the absorption of elements would stop despite an increase in their content in the environment. The analysis of Zn absorption intensity in the background area showed that for the majority of plants under study, it was the element of weak absorption and average capture (CBA = 0.3–0.8). For plants like *Betula pendula* (CBA = 1.16) and *Populus nigra* (CBA = 1.68), Zn was strongly absorbed (Table. 3). For the majority of plant species, it was established that increasing Zn soil contamination had resulted in a significant decrease of the metal's CBA. There was an exception for *Rosa rugosa* and *Syringa vulgaris*, in which the intensity of element absorption was higher than in the background area (Table 3).

Plants had developed certain protective mechanisms to prevent an excessive supply of elements to their vegetative and generative organs. Barrier type element absorption involved a decrease in the intensity of metal absorption and an increase in its concentration in the soil (Chupakhina *et al.*, 2017). Barrier-free plants would undergo an increase of CBA and a higher concentration threshold, beyond which there was no more absorption of the element.

The accumulation of HMs in plants depended not only on their species and physicochemical properties of the metal, but also on the mode of entry into the plants. The increase of atmotechnogenic pressure would cause the existing relationship between heavy metal content in soil and plants to be disrupted. Apparently, the growth of atmotechnogenic load would reinforce the importance of the foliar rout of pollutants entering the plants, and this increased the concentration of metals in plant leaves in contaminated zones (Chupakhina *et al.*, 2017). The relationship between Zn content in the accumulative horizon of urban soil and in plant leaves could be described with linear equations. Corresponding linear regression coefficients, which were calculated by the least squares method, indicated an average increase in the Zn content in plants (in mg / kg^{-1}) with an increase in its concentration in the soil by 1 mg/kg^{-1}. The corresponding regression Zn coefficients for trees, shrubs and herbaceous plants are given in Table 4.

The correlation of regression coefficients with zinc APC allowed us to estimate the average efficiency of metal bio-adsorption among typical representatives of the city's synanthropic flora. Thus, in woody plants, bioaccumulation efficiency was 0.07 % for *Tilia cordata*, 0.08% for *Acer platanoides*, 0.41 % for *Betula pendula*, and 1.1 % for *Populus nigra*. As for shrubs, Zn bioaccumulation efficiency was 1.24 % for *Syringa vulgaris*, 1.17 % for *Rosa rugosa*, 0.74 % for *Viburnum opulus*, 0.30 % for *Ribes alpinum*, 0.22 % for *Symphoricarpos rivularis*, 0.18 % for *Philadelphus coronarius*, 0.13 % for *Hippophae rhamnoides*, 0.12 % *Berberis vulgaris*, 0.11 % for *Ligustrum vulgare,* 0.05 % for *Sambucus nigra* and 0.03 % for *Spirae vanhouttei*. Values for herbaceous plants were the following: *Tanacetum vulgare* (0.49 %), *Trifolium pratense* (0.42 %), *Achillea millefolium* (0.41%), *Taraxacum officinale* (0.19 %), *Trifolium repens* (0.17 %), *Dactylis glomerata* (0.15 %), *Plantago major* (0.01 %).

Table 3: The intensity of zinc absorption by leaves of trees, shrubs and herbaceous plants in various functional zones in Kaliningrad

Species	The coefficient of biological absorption (CBA)		
	RecZ	**RZ**	**IUTZ**
Tree species			
Populus nigra L.	1.68	0.97	0.96
Betula pendula Roth	1.16	0.59	0.52
Acer platanoides L.	0.67	0.28	0.24
Tilia cordata Mill.	0.45	0.19	0.17
Shrubs			
Sambucus nigra L.	0.61	0.27	0.21
Symphoricarpos rivularis Suksdorf.	0.50	0.25	0.24
Syringa vulgaris L.	0.49	0.63	0.61
Viburnum opulus ´Roseum´	0.49	0.38	0.45
Ligustrum vulgare L.	0.41	0.19	0.17
Philadelphus coronarius L.	0.40	0.20	0.20
Ribes alpinum L.	0.40	0.22	0.25
Spirae vanhouttei (Briot.) Zab.	0.37	0.16	0.13
Rosa rugosa Thunb.	0.35	0.50	0.55
Berberis vulgaris L.	0.35	0.16	0.16
Hippophae rhamnoides L.	0.29	0.15	0.14
Herbs			
Trifolium pratense L.	0.78	0.46	0.40
Plantago major L.	0.70	0.29	0.22
Trifolium repens L.	0.57	0.28	0.25
Tanacetum vulgare L.	0.55	0.34	0.37
Achillea millefolium L.	0.51	0.33	0.32
Taraxacum officinale Wigg.s.l.	0.47	0.24	0.22
Dactylis glomerata L.	0.41	0.19	0.19

Note: RZ stands for recreational zones (background), RZ for residential zones, and IUTZ for industrial/utility/transport zones.

The correlation of linear regression coefficients with the metal APC might be useful in a preliminary assessment of soil phytoremediation effectiveness, since it suggested the proportion of metal APC that was utilized by plants during one growing season. Such analysis would help to initiate the development of phytoremediation technologies that could be adapted in the Kaliningrad region, i.e. the selection of plants - remediators from the representatives of local phytophlora. This would also offer prospects for experimental development of phytoremediation technologies in the region.

Conclusion

High Zn content was found in the accumulative horizon of soil in main functional zones of the city (ARZ, RZ, and IUTZ). Maximum metal

Table 4: The relationship between zinc content (x) in the soil and plant leaves (y)

Species	Linear regression equation	R^2*	R**
Tree species			
Populus nigra L.	$y = 0.6034x + 52.045$	0.9816	0.99
Betula pendula Roth	$y = 0.2273x + 45.998$	0.9996	0.99
Acer platanoides L.	$y = 0.0421x + 30.846$	0.9404	0.97
Tilia cordata Mill.	$y = 0.0398x + 19.935$	0.9141	0.96
Shrubs			
Syringa vulgaris L.	$y = 0.6828x - 8.8695$	0.9965	0.99
Rosa rugosa Thunb.	$y = 0.6421x – 14.972$	0.9972	0.99
Viburnum opulus ´Roseum´	$y = 0.4078x + 2.6959$	0.9482	0.97
Ribes alpinum L.	$y = 0.1641x + 10.47$	0.8723	0.93
Symphoricarpos rivularis Suksdorf.	$y = 0.1196x + 18.285$	0.9579	0.98
Philadelphus coronarius L.	$y = 0.0984x + 14.304$	0.9006	0.95
Berberis vulgaris L.	$y = 0.066x + 13.488$	0.9053	0.95
Hippophae rhamnoides L.	$y = 0.069x + 10.525$	0.9794	0.99
Ligustrum vulgare L.	$y = 0.0595x + 17.039$	0.9507	0.98
Sambucus nigra L.	$y = 0.0276x + 29.241$	0.5548	0.74
Spirae vanhouttei (Briot.) Zab.	$y = 0.0148x + 17.915$	0.7383	0.86
Herbs			
Tanacetum vulgare L.	$y = 0.2716x + 12.609$	0.9344	0.97
Achillea millefolium L.	$y = 0.2235x + 14.051$	0.9929	0.99
Trifolium pratense L.	$y = 0.2334x + 27.432$	0.9911	0.99
Taraxacum officinale Wigg.s.l.	$y = 0.1072x + 17.576$	0.9831	0.99
Trifolium repens L.	$y = 0.0955x + 23.158$	0.9936	0.99
Dactylis glomerata L.	$y = 0.0798x + 15.678$	0.7866	0.89
Plantago major L.	$y = -0.0034x + 35.107$	0.0158	-0.13

Note:* Approximate reliability value. ** Correlation coefficient.

content was observed in IutL and residential multistore areas with increased transport load. Background content of Zn in plant leaves did not depend on their life form. In natural conditions, active accumulators of include *Betula pendula* and *Populus nigra*, *Sambucus nigra* (among shrubs), and *Trifolium pratense* (among herbaceous plants). The highest absorption rates in plants growing in polluted areas were typical for *Syringa vulgaris, Rosa rugosa* and *Populus nigra.* These species might be useful for the potential phytoremediation of areas moderately polluted with Zn. The majority of plants under study showed an increase of Zn content in the leaves by the end of the growing season, and they demonstrated a highly reliable correlation between the levels of metal accumulations in the soil and leaves ($r = 0.86–0.99$, $p < 0.05$). Plant species capable of limiting the entry of Zn from the environment were identified. To conclude, the study of Zn content in the soil-plant system was an important step in assessing the risk of potential transfer in the soil–plant–human chain, and the results could be used to improve the ecosystem and human health, beside planning, assessing risks and making decisions on environmental management in the region.

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