Bioavailability of selected trace and rare earth elements to *Juncus effusus* L.: the potential role of de-icing chlorides in the roadside environment

Sabina Dołęgowska · Agnieszka Gałuszka ·
Zdzisław M. Migaszewski · Karina Krzciuk

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Abstract

Background and aim The presence of chlorides in soils, e.g., from de-icing salts may change metal availability to plants.

Methods To assess the role of de-icing chlorides on bioavailability of metals, the samples of the rhizosphere soils, roots and shoots of *Juncus effusus* L. were collected monthly from April to June of 2019 in the vicinity of roads and analyzed for trace (Ag, Cd, Co, Cu, Pb, Zn) and rare earth elements (from La to Lu).

Results Concentrations of Cl^- were distinctly higher in the shoots than in the roots. Apart from Cd, the concentration sequence of the other metals was as follows: rhizosphere soils > roots > shoots. The bioaccumulation and translocation factors indicated that Cd was the most preferably transported to the shoots as opposed to Ag, Co, Pb and REEs that showed a very low translocation potential. Negative correlations, which were noted between Cu and Co in the shoots

and Cl^- in soils, revealed their role in salinity stress alleviation. All soil samples showed a positive anomaly of Ce and a negative anomaly of Eu, whereas the shoots showed in turn a negative anomaly of Ce and a distinct positive anomaly of Eu. The lowest salinity factors (K/Na, Ca/Na) of the shoots resulted from an increase of salinity in *J. effusus* by higher sodium concentrations derived from de-icing NaCl.

Conclusions De-icing agents may change the uptake of other elements. In natural habitats, the factors affecting this process include: type of element, soil metal concentrations and interactions, and individual plant features.

Keywords *Juncus effusus* L. · De-icing salts · Trace metals · Rare earth elements · Bioavailability

Introduction

Low concentrations of chlorides have a beneficial effect on plant growth and development (White and Broadley 2001). In contrast, an excess of this anion is an environmental stress factor. High salinity may lead to disturbances of photosynthesis and cellular water balance, but also to mobilization of trace metals (Cd, Cu, Pb, Zn) in soil (Li et al. 2010; Wang et al. 2020). Chlorides enter the environment with rainfall, fertilizers, sea spray or air pollution. In most countries of the temperate climate zone, chloride salts, e.g., sodium chloride (NaCl), calcium and magnesium chlorides

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S. Dołęgowska (✉) · A. Gałuszka · Z. M. Migaszewski · K. Krzciuk
Analytical Chemistry and Environmental Geochemistry
Department, Institute of Chemistry, Jan Kochanowski
University, 7 Uniwersytecka St, 25-406 Kielce, Poland
e-mail: sabina.dolegowska@ujk.edu.pl

(CaCl_2 , MgCl_2) have been used as de-icing agents of road maintenance (Gałuszka et al. 2011). Unfortunately, this practice has many detrimental effects leading to degradation of roadside soils and vegetation (Bäckström et al. 2004; Czerniawska-Kusza et al. 2004; Ordóñez-Barona et al. 2018). Sodium chloride, which is the most often used de-icing salt, reaches soil releasing metals bound by organic matter, clay minerals and Fe- and Mn-oxyhydroxides. The abundance of Na^+ , Ca^{2+} and Mg^{2+} ions causes the cation exchange due to competition between major and trace metal ions, or in the presence of chlorides leads to formation of inorganic complexes (Cheng et al. 2018; Li et al. 2010).

Chloride complexes have a direct impact on metal bioavailability, for example, soluble cadmium complexes ($\text{CdCl}_n^{(n-2)}$) increase Cd bioavailability leading to a direct uptake of these compounds or enhanced mass transport of Cd^{2+} ions (Cheng et al. 2018 and references therein; Wang et al. 2016). This process and its efficiency depend on several factors, including plant species, initial concentrations of Cd and NaCl, and the type of habitat (soils, hydroponics). Co, Cu and Zn also form soluble chloride complexes, therefore in the presence of Cl^- ions, their bioavailability and content in plants may increase. Bäckström et al. (2004) found that concentrations of free Cu^{2+} in soil solutions increased during the winter season, suggesting that the Cu^{2+} ion exchange process can be highlighted by the presence of higher chloride contents derived from de-icing agents. However, most of the released Cu^{2+} ions are immediately bound by organic ligands, so there is no relationship between a soil chloride concentration and Cu accumulation by plants. It is noteworthy that the presence of chloride ions does not increase complexation of zinc, which occurs in soil mainly as Zn^{2+} ion (Usman et al. 2005 and references therein).

Ag and Pb form insoluble salts with chlorides (AgCl , PbCl_2) and soluble polychloride complexes ($\text{AgCl}_n^{(n-1)}$, $\text{PbCl}_n^{(n-2)}$). According to the free-ion model, the occurrence of chloride ions in aqueous solutions reduces silver bioavailability due to formation of insoluble AgCl salt, but bioavailability of chloride silver complexes differs both in soils and aquatic environments (Fortin and Campbell 2000; Langdon et al. 2015; Wang et al. 2016) observed that higher concentrations of chlorides in soils resulted in increased accumulation of Ag in the shoots of wheat (*Triticum aestivum* L. cv. Sunbrook).

This relationship was explained by formation of soluble and colloidal chloride complexes, and AgCl which is taken up by passive diffusion. The addition of NaCl also increases the availability of Pb due to formation of soluble complexes, and massive transport of Pb^{2+} ions. It was shown that the amount of insoluble PbCl_2 is too small to significantly reduce the bioavailability of Pb and to decrease its content in plant tissues (Li et al. 2010; Usman et al. 2005).

A recent review of the literature on this issue indicates that there are no studies describing the effect of salinity and chloride ions on the bioavailability of rare earth elements in plants. Complexation of these metals affects their diffusion from the soils to the root surfaces where they are blocked by lateral transfer pathway configuration. This suggests that the presence of organic and inorganic ligands may change their bioavailability and concentrations in plants (Liang et al. 2008). Considering the molar mass, light rare elements (LREE – from La to Eu) are favoured by plants, but their uptake depends on several environmental and biological factors, including climate, topography, soil taxonomy, hydrology, physiology and genetics (Ding et al. 2007; Migaszkowski and Gałuszka 2015).

Most studies on the effect of de-icing salts on trace metal mobilization are laboratory-based (Cheng et al. 2018; Fortin and Campbell 2000; Ghallab et al. 2007). Previous investigations, conducted in natural habitats, have mainly centered on accumulation of major ions (Na^+ , Ca^{2+} , Mg^{2+} , Cl^-) and their effect on soil and plant conditions (Czerniawska-Kusza et al. 2004; Devitt et al. 2014; Gałuszka et al. 2011; Ordóñez-Barona et al. 2018). Only a few researchers (Bäckström et al. 2004) have addressed this issue to trace metals. The main objectives of the present study were: (i) to examine seasonal changes in concentrations of selected trace and rare earth elements in the shoots, roots, and rhizosphere soils of *Juncus effusus* L. collected from roadsides exposed to de-icing salts (NaCl), and (ii) to explain whether and how chloride concentrations affect the bioavailability of these metals.

Materials and methods

Study area

The city of Kielce is the capital of the Świętokrzyskie province (south central Poland). It is located in the

central part of the Holy Cross Mountains (HCM) – a region that belongs to a separate climatic unit on the climatic map of Poland. Mean annual temperature in the Holy Cross Mountains is 1–2 °C lower than the mean temperature of the surrounding regions, whereas the mean annual precipitation is higher and exceeds 750 mm per year. The city lies within hills and valleys surrounded by forests. The geology of the region includes two main geologic units: the Łysogóry (north) and the Kielce (south). The latter encompasses several rock formations from the Lower Cambrian to the Lower Carboniferous. The study area is characterised by a high variability of soil types including rankers, cambisols, rendzinas, arenosols, podzols, fluvisols and chernozems (Dołęgowska et al. 2021).

The city of Kielce is located at a junction of major communication routes: Warsaw-Kraków and Łódź-Rzeszów (Fig. 1). Numerous local roads connect the surrounding villages with the city, allowing their residents to commute to work. The maintenance of main and local roads during the winter needs using chemical de-icers. In Poland the most commonly used road salt is a mixture of sodium chloride (97% NaCl), calcium chloride (2.5% CaCl_2) and potassium hexacyanoferrate(II) (0.5% $\text{K}_4[\text{Fe}(\text{CN})_6]$), which is added to avoid salt clumping. Road services are reluctant to use alternative salts (CaCl_2 and MgCl_2)

due to their higher price and hygroscopicity. Of these two salts, calcium chloride is more commonly used, although it is also considered less environmentally friendly than magnesium chloride (Gałuszka et al. 2011).

The winter of 2018/2019 preceding the sampling year was quite mild. January was the coldest month, with an average temperature of around -5 °C. The average temperatures of December and February were around 0 and 4 °C, respectively. Snowfall was also below average (Weatheronline.pl/weather/maps/city).

Fieldworks

The basic criterion for the selection of sampling sites was the occurrence of *J. effusus* in roadside ditches. Therefore, two sampling sites (#4 and 5) were located within the city, sites #1, 6 and 7 were situated by main roads toward Warsaw, Opatów and Nowa Słupia, whereas sites #2 and 3 by rural roads (Fig. 1). The shoots, roots, and rhizosphere soils of *J. effusus* were collected during three sampling campaigns, in April, May and June of 2019, respectively.

Samples were taken from roadside ditches with trapezoidal cross-section extending along roads except for the sample from site #5 collected from a roadside open space, about 3 m from the road

Fig. 1 Sketch map of the study area

shoulder. The ditches reached about 0.5 m in depth. Their profile was uneven and variable, they were also steeply sloped and covered with vegetation along almost their entire length. Light grey-brown and grey-brown sandy soil predominated at sites #1–4 and 7, 8, whereas grey-brown sandy loam soil was found at sites # 5 and 6.

Plants (shoots and roots) and soils were collected according to the methodology described earlier by Kovacheva et al. (2000) and Krzciuk (2019, 2020). The mean height of the plants was 30 cm in April and 40–50 cm in May and June. The composite shoot samples (from 3 to 5 increments depending on the sampling site) were collected about 3–4 cm above the soils cover. The weight of single sample was about 100 g. Soil surrounding the *J. effusus* roots (from a depth of 0.15 to 0.20 m) was carefully separated from the roots to avoid their mechanical damages. Subsequently, each soil sample weighing about 500 g was *in situ* cleaned from external material, oversized particles ($\varnothing > 2$ mm), and mixed. The roots were carefully cleaned from a remaining adhered material and mixed. Afterward, the cleaned samples were separately packed in a polyethylene bags and transported to the laboratory.

Why *Juncus effusus*?

Juncus effusus L. is a widely distributed perennial macrophyte preferring humid habitats and wetlands. The preference for water-logging conditions has resulted in formation of an aerenchyma tissue that contains enlarged gas spaces as a response on abiotic stress caused by hypoxia. Due to this characteristic, the plant can release oxygen into the rhizosphere, thus changing redox conditions and bioavailability of metals (Syranidou et al. 2017). *J. effusus* has also a wide ecological tolerance, which is evidenced by a high resistivity to several toxic metal(loid)s. Due to this ability, it has been widely used in phytoremediation for removal trace metal(loid) and organic pollutants (Bouldin et al. 2006; Rahman et al. 2014; Syranidou et al. 2017; Wiessner et al. 2013; Zare et al. 2020). This high tolerance makes *J. effusus* like halophytes, salt-tolerant plants growing on soils or waters of high salinity (Krzciuk and Gałuszka 2019, 2020; Peng et al. 2018). Analysis of the *Juncus* sp. shoots growing on contaminated wetland in the margin of a saline lake in Iran (Zare et al. 2020) confirmed that this

plant can accumulate and stabilize trace metals in tissues under high salinity conditions. Studies from the Holy Cross Mountains (Krzciuk and Gałuszka 2019, 2020) have shown that Mn, Zn, and Cd are most efficiently transferred from the root to the shoot, in contrast to Pb and REEs whose transfer is constrained.

Sample preparation

As mentioned before, the samples were transported to the laboratory and prepared for further analysis. The process of sample treatment is presented in Fig. 2.

Analysis of total Cl in shoots and roots of *J. effusus*

The shoots and roots were analyzed for the total chlorine content using a portable XRF analyser (model Thermo Scientific NITON XL3t 960 GOLDD+) with an excitation source 50 kV X-ray tube with Ag anode. The detection mode was set on “ALL GEO”. The time of FPXRF analysis was 120 s. Measurements were done in triplicates and precision was expressed as 2 standard deviations of the mean values. The emission spectra were transferred to the PC and appropriately processed with the use of the Niton Data Transfer software. The Apple leaves (CRM-1515) and Tobacco leaves (CTA-VTL-2) as certified reference materials were used to ensure the quality control. The recovery values were in the range of 92 to 111%.

Fig. 2 Details of sample preparation procedure

Analysis of pH, EC, and exchangeable chlorides in rhizosphere soil water extracts

Soil samples weighing 10 g each were placed in beakers, mixed with 25 mL of deionized water, and agitated for 24 h (~140 mph). Subsequently, the samples were filtrated, and the obtained extracts were used for measurements of pH (model SP 300, Slandi, Poland), EC (model SC300, Slandi, Poland) and chloride concentrations (portable spectrophotometer, model LF300, Slandi, Poland).

Analysis of major, trace and rare earth elements

The shoot and root samples weighing 0.5 g were digested in a closed microwave system (Multiwave 3000, Anton Paar, Austria) with 8 mL of HNO₃ (1:1) (Suprapur®) and 1 mL of 30% H₂O₂ (Suprapur®). The rhizosphere soil samples (0.5 g each) were digested in 8 mL of *aqua regia* (6 mL of 30% HCl Suprapur® and 2 mL of 65% HNO₃ Suprapur®) solution. After digestion, the samples were diluted to 25 mL with deionized water and filtered to disposable Falcon tubes (Dołęgowska and Migaszewski 2013; Krzciuk and Gałuszka 2019, 2020; Loell et al. 2011). The digestion parameters are presented in Table 1 of ESM. To ensure the quality control, blank samples and certified reference materials were prepared using the same digestion procedures. The glassware was prepared by washing with a detergent, rinsing, and soaking in 5% HNO₃ for 1 week. Subsequently, it was rinsed with deionized water and dried. The digested solutions were analyzed for major (Na, K, Ca, Mg), trace (Ag, Cd, Pb, Co, Cu, Zn) and rare earth elements using the FAAS (model iCE 3000, ThermoScientific) and ICP-MS techniques (model ELAN DRC II, Perkin Elmer). Prior to the analysis, the AAS instrument was optimized and calibrated with Certipur® Single-Element Standards for Atomic Absorption Spectroscopy. The ICP-MS instrument was optimized with a standard daily procedure and the calibration was done with Perkin Elmer Multielement Calibration Standards. Iridium and rhodium internal standards were added to all samples to control instrument drift. Moreover, for Nd, Sm, Gd, Dy, and Yb the correction equations were introduced to eliminate individual interferences. The average percentage recovery (range of 80 to 110%) was calculated using the following certified reference materials: for soils – GSS4, GSS7 (Chinese Academy of Geological Sciences),

Montana I Soil (2710a), for shoots and roots – Tomato leaves (1573a) and Peach leaves (1547).

Statistical analysis

Data analysis was performed by using STATISTICA StatSoft® and Microsoft® Excel. The Kruskal-Wallis test ($p < 0.05$) was done to find differences between sampling sites and sampling seasons. In turn, Spearman's rank coefficients ($p < 0.05$) were computed to find correlations between all parameters examined (Table 2 of ESM).

Bioconcentration, translocation and salinity factors

Bioaccumulation (BAF) and translocation (TF) factors were calculated according to the following equations:

$$BAF = c_{shoot}(mg \cdot kg^{-1}) / c_{soil}(mg \cdot kg^{-1}) \quad (1)$$

$$TF = c_{shoot}(mg \cdot kg^{-1}) / c_{root}(mg \cdot kg^{-1}) \quad (2)$$

Where:

c_{shoot} – the metal concentration in shoot,

c_{soil} – the metal concentration in rhizosphere soil,

c_{root} – the metal concentration in root.

The salinity factors were expressed as K/Na and Ca/Na ratios, and computed in relation to the K, Ca and Na concentrations in soils and shoots (Table 3 of ESM).

Normalized patterns and anomalies of REE

To eliminate the Oddo-Harkins effect occurring in the group of rare earth elements, the results were normalized to North American Shale Composite (NASC), which is used as a standard material for normalization (Bau et al. 2018). The normalized patterns are presented in Fig. 3. The individual anomalies were computed using double-sided elements showing no anomalies (Dołęgowska et al. 2017) and are compiled in Table 2.

Results

pH, EC and Cl

Table 1 presents the summary statistics (ranges, means, standard deviations) for pH, EC and elements

in the rhizosphere soils, roots, and shoots of roadside *J. effusus* collected within three sampling campaigns, in April, May and June of 2019. The pH of rhizosphere soil solutions ranged from 6.0 to 7.9, with mean values of 7.3 (April), 7.2 (May), 7.3 (June). The electric conductivity (EC) of soil extracts varied from 198 to 2982 $\mu\text{S}\cdot\text{cm}^{-1}$ with the lowest mean value in April (501 $\mu\text{S}\cdot\text{cm}^{-1}$) and the highest in June (994 $\mu\text{S}\cdot\text{cm}^{-1}$). The concentrations of Cl^- in the rhizosphere soil solutions varied from 8.60 to 49.6 $\text{mg}\cdot\text{L}^{-1}$. The mean Cl^- contents in samples collected in different months were as follows: April – 21.0 $\text{mg}\cdot\text{L}^{-1}$, May – 23.8 $\text{mg}\cdot\text{L}^{-1}$, June – 22.0 $\text{mg}\cdot\text{L}^{-1}$. Chloride concentrations in the roots ranged from 973 to 9420 $\text{mg}\cdot\text{kg}^{-1}$, whereas in the shoots from 3598 to 12,672 $\text{mg}\cdot\text{kg}^{-1}$. Statistically significant differences between the concentrations of Cl^- in samples collected are marked in Table 1.

Major and trace elements

Concentrations of Cd in our samples were in the range of 0.170 $\text{mg}\cdot\text{kg}^{-1}$ (shoots) to 6.35 $\text{mg}\cdot\text{kg}^{-1}$ (roots) and varied according to the sampling sites and the type of sample. The lowest mean values were noted in the rhizosphere soils (0.771 $\text{mg}\cdot\text{kg}^{-1}$) and the highest in the roots (2.00 $\text{mg}\cdot\text{kg}^{-1}$). Zn contents ranged from 17.7 $\text{mg}\cdot\text{kg}^{-1}$ (shoots) to 341 $\text{mg}\cdot\text{kg}^{-1}$ (rhizosphere soils), with mean values of 43.6 $\text{mg}\cdot\text{kg}^{-1}$ (shoots), 90.2 $\text{mg}\cdot\text{kg}^{-1}$ (roots) and 152 $\text{mg}\cdot\text{kg}^{-1}$ (soils). The mean concentrations of Cu were 4.15 $\text{mg}\cdot\text{kg}^{-1}$ (shoots), 10.3 $\text{mg}\cdot\text{kg}^{-1}$ (roots), and 20.4 $\text{mg}\cdot\text{kg}^{-1}$ (rhizosphere soils), whereas the concentrations of Co varied from 0.033 (shoots) to 23.0 $\text{mg}\cdot\text{kg}^{-1}$ (rhizosphere soils) with the lowest mean levels in April (9.65 $\text{mg}\cdot\text{kg}^{-1}$ rhizosphere soils, 1.33 $\text{mg}\cdot\text{kg}^{-1}$ – roots) and in June (0.089 $\text{mg}\cdot\text{kg}^{-1}$ – shoots). In our research the mean concentrations of Ag were: 0.109 $\text{mg}\cdot\text{kg}^{-1}$ (rhizosphere soils), 0.072 $\text{mg}\cdot\text{kg}^{-1}$ (roots) and 0.009 $\text{mg}\cdot\text{kg}^{-1}$ (shoots), whereas the concentrations of Pb in shoots varied from 0.006 to 1.20 $\text{mg}\cdot\text{kg}^{-1}$ and were much lower than those in the roots (2.56–32.1 $\text{mg}\cdot\text{kg}^{-1}$) and soils (17.7–104 $\text{mg}\cdot\text{kg}^{-1}$) (Table 1).

The obtained mean values of REE were as follows: 0.018 $\text{mg}\cdot\text{kg}^{-1}$ for shoots, 1.12 $\text{mg}\cdot\text{kg}^{-1}$ for the roots and 6.45 $\text{mg}\cdot\text{kg}^{-1}$ for the rhizosphere soils. The $\text{La}_{\text{NASC}}/\text{Yb}_{\text{NASC}}$, $\text{La}_{\text{NASC}}/\text{Sm}_{\text{NASC}}$ and $\text{Sm}_{\text{NASC}}/\text{Yb}_{\text{NASC}}$ ratios were in the ranges of 1.09–2.85,

0.57–2.64, 0.52–17.5, respectively (Table 2). The computed $\text{Ce}/\text{Ce}_{\text{NASC}}$ and $\text{Eu}/\text{Eu}_{\text{NASC}}$ values indicating the predominant positive anomaly of Ce in the rhizosphere soils (1.09–1.27) and the negative anomaly in the shoots (0.11–1.01) and the prevailing negative anomaly of Eu in the soils (0.71–1.03) and the strong positive anomaly in the shoots (1.36–13.7).

Spearman's rank correlation coefficients

The influence of Cl^- on metal availability was assessed by the Spearman's rank correlation coefficients (Table 2 of ESM). Taking into consideration the type of sample and the month of collection, statistically significant coefficients were recorded for the following pairs: in April – $\text{Cd}_{\text{roots}}-\text{Cl}_{\text{roots}}$ -0.86, $\text{Co}_{\text{soils}}-\text{Cl}_{\text{roots}}$ -0.79; in June – $\text{Cd}_{\text{soils}}-\text{Cl}_{\text{shoots}}$ -0.79, $\text{Cd}_{\text{roots}}-\text{Cl}_{\text{soils}}$ -0.82, $\text{Cu}_{\text{roots/shoots}}-\text{Cl}_{\text{soils}}$ -0.86, -0.89, $\text{Pb}_{\text{soils}}-\text{Cl}_{\text{shoots}}$ -0.79, $\text{Pb}_{\text{roots}}-\text{Cl}_{\text{soils}}$ -0.72. As for REE, significant correlations were obtained: in April between La, Ce, Ho, Er and Tm in roots and Cl^- in soils (the range of coefficients varied from 0.79 to 0.86); in May between Tb and Yb in the shoots and Cl^- in the roots (0.79 in both cases), and in June between Ce, Pr, Nd, Gd, Tb, Tm and Lu in the shoots and Cl^- in shoots (0.82–0.96). Bioavailability of metals depends also on their interactions, which in turn are directly related to their role in plant and content in soil. Relationships between metals in all samples examined, expressed as the significant Spearman's coefficients were as follows: in April – $\text{Cu}_{\text{soils}}-\text{Ag}_{\text{soils}}$ 0.93, $\text{Cu}_{\text{roots}}-\text{Ag}_{\text{roots/shoots}}$ 0.93, 0.82, $\text{Cu}_{\text{shoots}}-\text{Cd}_{\text{shoots}}$ 0.89, $\text{Cu}_{\text{soils}}-\text{Co}_{\text{soil}}$ 0.82, $\text{Zn}_{\text{soils/roots}}-\text{Cd}_{\text{roots}}$ 0.89, 0.93; in May – $\text{Cd}_{\text{soils}}-\text{Ag}_{\text{soils}}$ 0.78, $\text{Cd}_{\text{shoots}}-\text{Ag}_{\text{shoots}}$ 0.95, $\text{Cd}_{\text{roots}}-\text{Cd}_{\text{soils}}$ 0.93, $\text{Co}_{\text{soils/roots}}-\text{Ag}_{\text{soils}}$ 0.86, 0.78, $\text{Co}_{\text{roots/shoots}}-\text{Ag}_{\text{roots}}$ 0.86, 0.86, $\text{Co}_{\text{roots}}-\text{Co}_{\text{shoots}}$ 0.93, $\text{Cu}_{\text{soils/shoots}}-\text{Cd}_{\text{soils/shoots}}$ 0.86, 0.82, $\text{Pb}_{\text{shoots}}-\text{Ag}_{\text{shoots}}/\text{Pb}_{\text{roots}}$ 0.78, 0.86, $\text{Pb}_{\text{roots}}-\text{Cu}_{\text{roots}}/\text{Pb}_{\text{soils}}$ 0.82, 0.93, $\text{Zn}_{\text{soils}}-\text{Cd}$, Cu_{soils} 0.82, 0.89, and in June – $\text{Cd}_{\text{soils}}-\text{Ag}_{\text{soils}}$ 0.61, $\text{Cd}_{\text{shoots}}-\text{Ag}_{\text{shoots}}$ 0.93, $\text{Cu}_{\text{soils}}-\text{Ag}_{\text{soils}}$ 0.82, $\text{Cu}_{\text{shoots}}-\text{Ag}_{\text{shoots}}$ 0.82, $\text{Pb}_{\text{soils}}-\text{Ag}_{\text{soils}}$ 0.96, $\text{Pb}_{\text{roots}}-\text{Cu}_{\text{roots}}$ 0.93, $\text{Zn}_{\text{soils}}-\text{Cd}$, Cu_{soils} 0.89, 0.79. Significant correlations between individual REEs and other elements ranged from -0.86 to 0.96 (Table 2 of ESM) and depended on the element and the type of sample.

Table 1 The pH, electric conductivity (EC) and element concentrations in rhizosphere soils, roots, and shoots of roadside *J. effusus*

Month of collection	April	May	June	April	May	June	April	May	June
Parameter	Rhizosphere soils			Roots			Shoots		
pH	6.0-7.9	6.4-7.6	6.8-7.8	-	-	-	-	-	-
$\bar{x} \pm \sigma$	7.3±0.6	7.2±0.4	7.3±0.4	-	-	-	-	-	-
EC ($\mu\text{S}\cdot\text{cm}^{-1}$)	236-928	209-1194	198-2982	-	-	-	-	-	-
$\bar{x} \pm \sigma$	501±258	631±345	994±943	-	-	-	-	-	-
Cl ($\text{mg}\cdot\text{L}^{-1}$)	10.7-30.2	12.0-49.6	8.60-43.3	-	-	-	-	-	-
$\bar{x} \pm \sigma$	21.0±9.31	23.8±13.5	22.0±11.7	-	-	-	-	-	-
$\text{mg}\cdot\text{kg}^{-1}$									
Cl	-	-	-	973-9420	1769-6516	2532-9180	3598-12672	3849-9403	7031-12674
$\bar{x} \pm \sigma$	-	-	-	3601±2776**	4389±1692**	4909±2387**	7083±2810**	7240±1838**	9479±2347**
Ag	0.060-0.185	0.066-0.142	0.065-0.224	0.025-0.168	0.022-0.240	0.013-0.215	0.004-0.042	0.002-0.003	0.003-0.002
$\bar{x} \pm \sigma$	0.102±0.044	0.09±0.028	0.127±0.058	0.052±0.052	0.071±0.080	0.093±0.088	0.015±0.013	0.008±0.001	0.006±0.006
Cd	0.410-1.08	0.420-1.83	0.376-2.01	0.752-1.64	0.832-5.72	0.805-6.35	0.272-3.06	0.269-2.84	0.170-0.863**
$\bar{x} \pm \sigma$	0.628±0.222	0.857±0.518	0.829±0.587	1.17±0.299	2.55±1.99	2.29±2.03	1.26±1.17	1.25±0.874	0.415±0.261
Co	5.25-16.5	6.08-23.0	5.19-22.1	1.33-8.06	2.12-14.2	1.59-7.27	0.034-0.465	0.033-0.280	0.048-0.148
$\bar{x} \pm \sigma$	9.65±4.34	10.1±5.96	10.7±5.54	4.01±2.40	5.71±4.01	5.21±2.04	0.128±0.157	0.117±0.081	0.089±0.035**
Cu	9.06-26.6	9.73-27.9	10.7-43.4	4.67-13.7	6.74-20.2	3.62-16.4	1.30-6.03	1.46-6.72	1.64-7.06
$\bar{x} \pm \sigma$	18.2±7.27	19.1±7.53	23.9±11.9	9.27±3.02	11.6±5.00	9.91±5.17	3.50±1.74	4.47±2.16	4.46±1.63
Pb	17.7-104	18.2-73.8	19.0-89.4	3.95-16.4	7.04-25.1	2.56-32.1	0.259-0.752	0.175-0.752	0.006-1.20
$\bar{x} \pm \sigma$	45.9±31.0	47.5±23.8	52.8±32.4	9.86±4.31	15.2±6.42	11.5±10.2	0.396±0.173	0.332±0.203	0.222±0.432
Zn	95.1-218	100-291	106-341	38.6-102	52.3-245	48.6-197	30.2-97.8	24.8-82.5	17.7-40.6
$\bar{x} \pm \sigma$	123±44.2	168±76.5	166±83.1	58.3±22.8	117±71.3	95.6±50.4	54.2±22.7	54.8±20.9	29.8±8.60**
$\mu\text{g}\cdot\text{kg}^{-1}$									
La	12.7-29.9	12.6-27.4	12.5-29.4	1.78-6.15	1.55-4.36	0.734-5.021	19.6-248	12.8-349	<0.500-130
$\bar{x} \pm \sigma$	21.3±5.69	19.0±4.46	19.2±6.09	3.33±1.60	3.22±1.07	2.41±1.58	58.6±84.1	125±115	37.4±24.6*
Ce	32.8-63.5	33.2-58.6	32.49-62.5	3.27-15.7	2.97-9.94	1.09-11.4	12.7-417	6.57-368	12.5-169
$\bar{x} \pm \sigma$	46.0±10.9	41.4±8.50	42.7±11.3	7.45±4.42	6.78±2.39	5.24±0.686	88.3±146	129±131	47.3±57.3
Pr	2.90-5.50	2.99-5.13	2.91-5.39	0.36-1.45	0.347-1.10	0.119-1.31	0.550-47.0	0.57-40.5	3.39-18.1
$\bar{x} \pm \sigma$	4.14±0.963	3.72±0.709	3.80±0.916	0.825±0.398	0.801±0.291	0.580±0.416	9.68±16.6	14.1±14.4	4.95±6.15
Nd	8.82-16.7	9.12-15.9	8.75-16.4	1.44-5.02	1.39-4.50	0.449-5.37	1.65-176	0.67-143	1.48-69.6
$\bar{x} \pm \sigma$	12.8±3.08	11.5±2.20	11.8±2.87	3.19±1.36	3.23±1.23	2.33±1.69	32.7±63.5	49.8±54.2	17.0±24.2
Sm	2.12-4.34	2.22-4.10	2.14-4.19	0.277-1.19	0.269-0.936	0.111-1.14	1.29-39.7	1.91-32.41	<0.500-16.4
$\bar{x} \pm \sigma$	3.23±0.857	2.90±0.621	2.98±0.774	0.703±0.349	0.660±0.262	0.489±0.349	8.96±13.7	12.2±11.2	5.32±5.51*
Eu	0.321-0.907	0.334-0.843	0.325-0.863	0.053-0.252	0.059-0.215	0.039-0.228	2.40-11.3	2.77-13.6	2.71-6.33
$\bar{x} \pm \sigma$	0.601±0.234	0.509±0.170	0.549±0.186	0.160±0.082	0.143±0.063	0.110±0.067	4.42±3.15	5.59±4.07	3.98±1.34
Gd	2.00-4.17	2.08-4.02	2.06-4.05	0.261-1.15	0.288-0.968	0.106-0.1089	1.06-34.4	1.91-35.4	1.32-16.8
$\bar{x} \pm \sigma$	3.15±0.845	2.81±0.637	2.88±0.762	0.717±0.356	0.664±0.271	0.402±0.329	8.37±11.7	12.2±12.1	4.27±5.72
Tb	0.273-0.554	0.278-0.528	0.280-0.540	0.037-0.158	0.039-0.129	0.015-0.153	0.540-5.22	0.360-5.45	<0.500-2.41*
$\bar{x} \pm \sigma$	0.424±0.111	0.378±0.082	0.394±0.101	0.099±0.049	0.092±0.037	0.067±0.046	1.46±1.68	2.05±1.83	1.139±0.721
Dy	1.39-2.87	1.45-2.68	1.44-2.66	0.195-0.817	0.205-0.678	0.080-0.787	1.26-24.8	2.53-26.8	1.07-11.8
$\bar{x} \pm \sigma$	2.14±0.537	1.93±0.414	1.99±0.481	0.510±0.252	0.478±0.193	0.346±0.234	6.81±8.09	10.1±8.45	4.17±3.58
Ho	0.256-0.555	0.274-0.499	0.269-0.485	0.036-0.162	0.038-0.133	0.014-0.147	<0.500-5.05	0.590-5.55	<0.500-2.11
$\bar{x} \pm \sigma$	0.402±0.105	0.359±0.078	0.372±0.086	0.098±0.050	0.091±0.037	0.066±0.043	1.78±1.62*	2.16±1.65	1.08±0.598*
Er	0.727-1.60	0.777-1.39	0.768-1.39	0.099-0.464	0.101-0.375	0.034-0.419	1.13-14.1	1.29-14.4	<0.500-6.79

Table 1 (continued)

Month of collection	April	May	June	April	May	June	April	May	June
Parameter	Rhizosphere soils			Roots			Shoots		
$\bar{x} \pm \sigma$	1.13±0.295	1.02±0.208	1.05±0.246	0.268±0.144	0.254±0.107	0.181±0.122	3.89±4.59	5.31±4.62	2.98±2.17*
Tm	0.101-0.216	0.108-0.186	0.104-0.187	0.014-0.065	0.014-0.051	0.005-0.058	<0.500-1.73*	0.210-2.53	<0.500-1.09
$\bar{x} \pm \sigma$	0.151±0.039	0.140±0.027	0.142±0.031	0.037±0.021	0.034±0.014	0.025±0.017	0.968±0.661	0.960±0.830	0.609±0.322*
Yb	0.621-1.35	0.685-1.12	0.637-1.09	0.081-0.362	0.072-0.302	0.029-0.332	0.81-11.6	0.850-13.3	0.550-5.37
$\bar{x} \pm \sigma$	0.937±0.241	0.849±0.154	0.859±0.174	0.213±0.117	0.200±0.084	0.143±0.097	3.33±3.87	4.87-4.32	1.98±1.63
Lu	0.098-0.218	0.109-0.177	0.107-0.176	0.012-0.058	0.011-0.047	0.045-0.052	<0.500-2.18	<0.500-2.66	<0.500-1.20
$\bar{x} \pm \sigma$	0.151±0.039	0.136±0.024	0.141±0.027	0.033±0.019	0.031±0.013	0.022±0.015	0.918±0.712*	1.13±0.785*	0.636±0.342*

$\bar{x}$ - arithmetic mean, σ - standard deviation, * - arithmetic mean computed for data above the limit of quantification, ** - results significantly different ($p < 0.05$) from the others

BAF, TF and salinity factors

Bioaccumulation factor (BAF) is used to quantify the effectiveness of a plant in the trace elements uptake from soil. The BAF below 0.01 means no accumulation, between 0.01 and 0.1 indicates low accumulation, between 0.1 and 1.0 medium accumulation and above 1.0 high bioaccumulation Aladesanmi et al. 2019; Pachura et al. 2016 and references therein). The BAF of examined metals varied from <0.001 to 7.5 and were strongly element and site dependent (Fig. 4A). The lowest values were obtained for REEs (<0.001-0.03) and the highest for Cd (0.13-7.5). For Zn and Cu, the BAF values were in the ranges of 0.094-1.03 and 0.07-0.69, respectively, whereas for Ag, Co and Pb were as follows: 0.02-0.23, 0.002-0.07, <0.001-0.05.

The translocation factor (TF) is employed to assess the effectiveness of an element transport from the root to the shoot. For this factor, the values lower than 1 indicate that metals are accumulated by plants but stored in the roots. The values higher than 1 indicate translocation to the aerial parts (Mellem et al. 2009). The TF values, for all the metals examined varied from <0.001 to 3.7, and similar to BAF with the lowest for REE (<0.001-0.10) and the highest for Cd (0.02-3.7) (Fig. 4B).

The K/Na and Ca/Na ratios, known as salinity factors were computed to compare the levels of soil and plant salinity. In our study, they varied from 1.8 to 110, with the lowest values in the roots (mean of 8.3), and from 0.34 to 58, with the lowest in the shoots (mean of 4.5), respectively (Table 3 of ESM). The mean Ca/Na ratio values of the roots and shoots

collected in June (1.9, 0.97) were up to 7 times lower than those recorded in April (9.7, 5.7) and May (5.8, 6.7).

Discussion

pH and Cl

Metals may be present in soil solution in three major states, as free (non-complexed) ions, inorganic and organic soluble or insoluble complexes. Their bio-availability depends on a binding capacity of soil and a number of factors, like pH, redox potential, soil texture, clay and organic matter content, occurrence of iron and manganese oxyhydroxides, presence of different anions and cations, and activity of microorganisms (Schlesinger and Bernhardt 2020; Singh et al. 2014). According to the literature, bioavailability of trace metals and element transfer from the soil solution to the root depend on this parameter (Singh et al. 2014). However, no significant correlations were found between the pH of soil solutions and trace element contents in soils and individual parts of plant.

In soils, chlorine occurs mainly in the form of simple Cl^- ions. In the temperate climate zone, soils have a net negative charge, therefore their anion adsorption capacity is low. It is also less efficient in the presence of organic ions which can block anion binding sites (Schlesinger and Bernhardt 2020). Lower concentrations of chlorides in soil solutions (sites #2, 3) corresponded to higher ones in the roots and shoots, but these correlations were not significant ($p > 0.05$). Between April and June, a gradual increase

Table 2 NASC-normalized REE concentration ratios in rhizosphere soils, roots, and shoots of roadside *J. effuses* collected within three sampling campaigns

Month of collection	Sampling site	La _{NASC} /Yb _{NASC}			La _{NASC} /Sm _{NASC}			Sm _{NASC} /Yb _{NASC}			Ce/Ce _{NASC}			Eu/Eu _{NASC}		
		Soil	Roots	Shoots	Soil	Roots	Shoots	Soil	Roots	Shoots	Soil	Roots	Shoots	Soil	Roots	Shoots
April	1	2.76	2.15	2.07	1.32	0.99	1.19	2.09	2.17	1.74	1.14	1.23	0.89	0.97	0.98	1.36
	2	1.88	0.82	2.00	1.16	0.57	1.28	1.62	1.45	1.56	1.11	0.99	0.73	0.85	1.01	7.38
	3	2.05	2.20	1.47	1.15	1.24	1.21	1.78	1.78	1.21	1.26	0.95	0.92	0.71	0.90	3.27
	4	2.52	1.98	2.00	1.41	1.13	3.85	1.79	1.75	0.52	1.11	0.94	0.5	0.73	0.91	13.7
	5	2.82	2.50	1.30	1.28	0.95	1.67	2.21	2.64	0.78	1.12	0.99	0.69	1.03	1.04	3.39
	6	1.88	1.32	2.20	1.27	0.88	1.06	1.48	1.50	2.08	1.17	1.07	0.63	0.84	1.06	2.63
	7	2.14	1.48	0.75	1.27	0.97	1.44	1.68	1.52	0.52	1.10	0.93	0.84	0.73	1.17	2.72
May	1	2.45	1.65	1.72	1.29	0.89	1.05	1.91	1.84	1.64	1.14	1.06	1.01	0.95	1.03	1.87
	2	2.14	1.27	1.36	1.19	0.76	1.06	1.80	1.67	1.28	1.16	1.09	1.01	0.85	0.98	1.91
	3	1.84	2.00	3.30	1.09	1.05	2.12	1.69	1.90	1.56	1.27	1.03	0.65	0.71	0.89	1.67
	4	2.53	1.57	1.55	1.39	1.04	1.99	1.82	1.50	0.78	1.09	1.00	0.6	0.74	0.96	6.10
	5	2.49	2.16	1.30	1.30	1.11	1.25	1.92	1.95	1.04	1.11	0.94	0.38	0.81	0.97	6.86
	6	1.94	1.41	17.5	1.27	0.91	11.2	1.53	1.55	1.56	1.16	0.83	0.11	0.81	1.05	2.29
	7	2.23	1.87	1.30	1.28	1.03	1.25	1.74	1.82	1.04	1.10	0.95	0.91	0.74	0.93	1.71
June	1	2.85	1.90	1.80	1.35	0.89	1.73	2.11	2.13	1.04	1.15	1.05	0.9	0.96	1.00	5.71
	2	2.23	1.51	1.00	1.22	0.85	0.96	1.83	1.78	1.04	1.16	1.04	n.d.	0.89	0.94	9.27
	3	1.92	2.07	1.45	1.13	1.07	1.86	1.71	1.93	0.78	1.26	1.07	0.83	0.71	1.06	4.57
	4	2.33	1.43	1.35	1.33	0.99	1.73	1.75	1.44	0.78	1.10	1.02	0.76	0.79	0.97	6.10
	5	1.99	2.53	n.d.	1.09	1.27	n.d.	1.83	1.99	n.d.	1.25	0.84	n.d.	1.00	1.64	n.d.
	6	1.95	1.32	2.90	1.22	0.93	1.39	1.60	1.42	2.08	1.15	1.07	0.75	0.84	1.26	3.94
	7	2.16	1.59	2.60	1.26	0.97	1.56	1.71	1.64	1.67	1.10	0.99	0.78	0.76	1.06	1.66
	$\bar{x}$	2.24	1.75	2.42	1.25	0.98	2.04	1.79	1.78	1.18	1.15	1.00	0.69	0.83	1.04	4.41
	Min	1.84	0.82	0.75	1.09	0.57	0.96	1.48	1.42	0.52	1.09	0.83	0.11	0.71	0.89	1.36
	Max	2.85	2.53	17.5	1.41	1.27	11.2	2.21	2.64	2.08	1.27	1.23	1.01	1.03	1.64	13.7

Fig. 3 NASC-normalized REE concentration patterns of all the examined *J. effusus* samples collected within three sampling seasons

Fig. 4 Box-plots of: A - bioaccumulation (BAF) and B - translocation (TF) factors computed for *J. effusus* samples

in Cl^- content was observed in the shoots and roots from site 1 and in the shoots from sites 3 and 5, but only in samples from the first site this increase correlated with a gradual decrease in soils. Despite the gradual increase, the Cl^- content of the shoots from site 5, was still the lowest in comparison to its content in the shoots from the other sites. It can be explained by the fact that at this location (Fig. 1), samples were taken from a roadside open space, about 3 m from the road shoulder.

Chloride ions supports plant growth, therefore, it dominates in above ground organs (shoots, leaves) and its accumulation can be limited only in salinity

sensitive plants. Differences ($p < 0.05$) in Cl^- concentrations between various parts of the plant are not surprising and have been noted by several authors (White and Broadley 2001 and references therein). The distribution sequence obtained (shoots>roots) backs up previous findings (Chen et al. 2010). About 45% lower concentrations in the roots in comparison to the shoots, and the average translocation factor (TF) of 2.3 (Fig. 4B), clearly indicate that Cl^- is easily transported from the roots to the shoots. According to the literature, the average Cl^- content in plants varies from 1000 to 20,000 $\text{mg} \cdot \text{kg}^{-1}$, but the plant requirement for optimal growth is much lower, in

the range of 200 to 400 mg•kg⁻¹ (Chen et al. 2010; Wang et al. 2020). The obtained values (Table 1) are in the medium range, but are higher than the optimum values recorded for plants of the temperate climate zone, e.g., corn (10–20 mg•kg⁻¹), sugar beet (100–200 mg•kg⁻¹) and higher than concentrations found in the shoots of *J. effusus* (2914 mg•kg⁻¹) collected from sites located in the HCMs (Krzciuk and Gałuszka 2019), but not exposed to de-icing salts (unpublished data). The reason for this is the exposure of examined plants to de-icing agents, which are an additional source of Cl⁻.

Cd, Co, Cu and Zn

Formation of chloride complexes in soils changes the mobility of trace metals and their availability to plants (*vide* 1 section). Ghallab et al. (2007) and Weggler et al. (2004) noted that the addition of chlorides to different types of soil increased Cd concentrations in plants due to formation of CdCl_n⁽ⁿ⁻²⁾ complexes. Further research (Cheng et al. 2018) gave the opposite results. The authors found that the addition of NaCl reduces Cd accumulation in *Carpobrotus rossii* shoots and inhibits the Cd uptake by roots and its translocation from the root to the shoot. The order of the average Cd contents: Cd_{roots} > Cd_{shoots} > Cd_{soils} confirms the previous findings (Benavides et al. 2005) that Cd easily penetrates the roots and then passes to the aboveground parts. The mean value recorded in the shoots (0.960 mg•kg⁻¹) was higher than that noted in *Juncus* sp. (0.674 mg•kg⁻¹) collected from the vicinity of saline Maharlu Lake in Iran (Zare et al. 2020), but lower than in the *J. effusus* shoots from the Holy Cross Mountains (2.35 mg•kg⁻¹) (Krzciuk and Gałuszka 2019). The shoots taken in June were depleted in Cd in comparison to those from April and May and this difference is significant ($p < 0.05$) (Table 1). This may indicate three aspects: (i) activation of mechanisms that limit the entry of Cd from the root to the xylem during the growing season as evidenced by Lux et al. (2011) (positive correlations were recorded in May and June for the Cd_{roots}-Cd_{soils} pair; Table 2 of ESM), (ii) reduction in Cd contents as an effect of dilution due to an increase in plant biomass, or (iii) inhibition of Cd accumulation in the presence of higher Cl⁻ contents. The reduction in Cd, but also in Pb, Co and Zn contents observed from May to June was not recorded in our previous

studies (Krzciuk and Gałuszka 2019). In contrary to our results, samples of *J. effusus* collected monthly from May to November within the HCM area showed an increase in Co and Zn, and in some cases in Pb. The reduction was noted for Cd and Ag. In both studies, the concentration of Cu was higher in the shoots from June than in the shoots from May. Considering the inhibition of Cd uptake by Cl⁻ ions, in April and May, the concentrations of Cd in the roots and soils were positively correlated with the Cl⁻ content in the rhizosphere soil solutions. At that time, this correlation was negative for the shoots. In June these relationships changed to positive for the shoots and negative for the roots and soils. The observed change suggests that chlorides may affect Cd availability, but this process is not observed before the growing season when the biomass growth of plant is negligible (Lux et al. 2011). Zn, Cu and Co form similar complexes with chlorides as Cd, but their behavior in the soil differs due to different affinity to Cl⁻ ions and role in plants (Du et al. 2020; Ghallab et al. 2007; Usman et al. 2005). Both Zn and Cu do not change their form in the presence of chloride ions and occur mainly as M²⁺ ions. Complex compounds (MCl_n⁽ⁿ⁻²⁾) account for about 2% (Usman et al. 2005). In April and May the content of Zn in the shoots was slightly and negatively, but insignificantly, correlated with the content of Cl⁻ in the soils, while in June this correlation was positive. The lack of significant correlations between Zn and Cl (Table 2 of ESM), confirms that Cl⁻ ions, even in higher concentrations, do not affect the accumulation of this metal, which in the soils occurs mainly as a divalent ion or a complex with organic ligands (Matthews et al. 2004; Tsonev and Lidon 2012).

The concentration order of Zn was as follows: soils > roots > shoots ($p < 0.05$). Concentrations recorded in the shoots collected in April and May were almost twice as high as those in June ($p < 0.05$) (Table 1). This suggests that Zn is taken up by the *J. effusus* shoots more effectively at the beginning of the growing season. The content of Zn in the roots and soils was positively and significantly correlated with the content of Cd in the same samples (Table 2 of ESM). Such correlations were found regardless of the time of sampling. The negative correlations obtained for the Zn_{soils}-Cd_{shoots} pair may indicate inhibition of Cd uptake and its translocation in the presence of Zn (Du et al. 2020).

Concentrations of Cu were typical for samples from uncontaminated sites (Table 1). Regardless of the time of sampling, we found a strong and positive correlation between Cu and Cd in the shoots. According to the literature (Murtaza et al. 2017), the presence of Cu suppresses the Cd uptake. The synergistic effect for those two metals can be observed, but only at low metal concentrations (Mwamba et al. 2016). Significant and negative correlations between $Cu_{shoots/roots}-Cl_{soils}$ were found in June. Such negative, although insignificant, relationships were also noted for Co (Table 2 of ESM). This similarity can be explained by the fact that these two metals are known to alleviate salinity stress (Hejazi Mehrizi et al. 2012; Yadav et al. 2020), which in the case of our study is due to the presence of higher Cl^- concentrations from de-icing salts. Co belongs to microelements responsible for the plant growth, metabolism, and development of root nodules (Nagajyoti et al. 2010). In our study, the concentrations in the shoots were even 400 times lower than those in the soils and 130 times lower than in the roots. These results are in complete agreement with Kosiorek and Wyszowski (2020) and further support the concept of the presence of Co tolerance mechanism (Mahey et al. 2020). We also found higher concentrations ($p>0.05$) in May and June than in April which may result the Co release from insoluble forms by biologically produced chelating ligands during the growing season (Palit et al. 1994).

Ag and Pb

Silver and lead belong to elements which in the presence of chloride ions form both insoluble and stable salts ($AgCl$; $PbCl_2$) and soluble complexes. We did not find statistically significant correlations between Ag and Cl (Table 2 of ESM), even though a characteristic trend was observed. Regardless of the time of sampling, concentration of Ag in the shoots and roots corresponded to Cl^- content in roots, while an opposite relationship was noted for Cl^- content in soil solutions. This suggests that the presence of chlorides in soil solutions may reduce Ag uptake by plants (Fortin and Campbell 2000 and references therein), especially at low concentrations of Ag (Cruzado-Tafur et al. 2021).

The concentration order of Ag was as follows: rhizosphere soils>roots>>shoots with significant

differences between the shoots and the other samples ($p<0.05$). The above order is consistent with our previous findings (Krzciuk and Gałuszka 2019), but in this study, the concentration of Ag in the shoots was almost nine times lower than in the roots, whereas the shoots and roots of *J. effusus* from the Holy Cross Mountains did not reveal such a big difference (results compared for samples collected in May) (Krzciuk and Gałuszka 2019). This may confirm the relationship related to reduced Ag uptake in the presence of higher Cl^- concentrations. According to the literature, the amount of Ag absorbed by plants depends on its concentration in soils (Cruzado-Tafur et al. 2021 and references therein), but in our study Ag concentrations in the shoots were on average 17 times lower than those in the soils. The similar relationship was noted by Tyler and Olsson (2001) for *A. capillaris* planted in Ag-saturated soils. The authors obtained much lower concentrations in the above-ground parts than in the soils and roots. This phenomena can be explained by the fact that plant roots act as a barrier against many less essential elements, but the influence of Cl^- on this process needs further investigations.

The possible co-occurrence of Ag, Cd, Cu and Pb in the shoots collected at the beginning and during the growing season (May and June), as shown by the correlation coefficients (Table 2 of ESM), is due to the fact that these metal ions (Ag^+ , Cu^{2+} , Cd^{2+} , Pb^{2+}) activate the biosynthesis of phytochelatins – trace metal binding peptides (Schmoger et al. 2000).

Significant and negative correlations obtained for the $Pb_{roots/soils}-Cl_{soils/shoots}$ pairs (Table 2 of ESM) suggest that Pb may limit the bioaccumulation of Cl^- , especially during the growing season. According to the literature data, the addition of Cl^- ions to the soil solution changes a process of Pb accumulation. This change depends on the pH and chloride concentrations (different types of complexes are formed) and a low concentration of NaCl inhibits Pb accumulation (Xiong and Feng 2001). However, the efficiency of this process is also dependent on the soil type (Usman et al. 2005).

The mean values of Pb in the shoots and roots were higher than those in *J. effusus* from the Holy Cross Mts. (Gałuszka et al. 2015; Krzciuk and Gałuszka 2019). Only in May the significant correlations were found between the content of this metal in the samples analyzed.

REEs

According to the literature, REEs form chloride complexes, but the efficiency of this process and stability of compounds depend on several factors, including temperature (Gammons et al. 1996). Stability of REE chloride complexes increases with temperature which in our study can be confirmed by correlations with Cl^- recorded in the shoots from June (Table 2 of ESM). The most interesting positive correlations ($p < 0.05$) were recorded in the samples taken in May between the following pairs of elements: Ag-REE, Cd-REE, and Co-REE. Such correlations have not been found by Krzciuk and Gałuszka (2019), which may suggest a possible chloride role in the process of metal accumulation, however, in-depth investigation is needed.

The typical REE concentrations in soils vary from 10 to 100 $\text{mg}\cdot\text{kg}^{-1}$ (Dołęgowska and Migaszewski 2013), whereas in plants they are much lower, ranging from <0.05 to 2.58 $\text{mg}\cdot\text{kg}^{-1}$ (Hu et al. 2013). The same relationship has been observed in our study (Table 1). La and Ce predominated in all the samples examined. The concentration order in the shoots ($\text{Ce} > \text{La} > \text{Nd} > \text{Pr} > \text{Sm} > \text{Gd} > \text{Dy} > \text{Eu} > \text{Er} > \text{Yb} > \text{Ho} > \text{Tb} > \text{Lu} > \text{Tm}$) differed from that in the roots and rhizosphere soils, which is like total concentrations in the Earth's crust ($\text{Ce} > \text{Nd} > \text{La} > \text{Pr} > \text{Sm} > \text{Gd} > \text{Dy} > \text{Er} > \text{Yb} > \text{Eu} > \text{Ho} > \text{Tb} > \text{Lu} > \text{Tm}$) (Greenwood and Earnshaw 1997). The calculated $\text{La}_{\text{NASC}}/\text{Yb}_{\text{NASC}}$, $\text{La}_{\text{NASC}}/\text{Sm}_{\text{NASC}}$ and $\text{Sm}_{\text{NASC}}/\text{Yb}_{\text{NASC}}$ ratios (Table 3) indicate a characteristic change in element enrichment in the samples examined. The rhizosphere soils are enriched in light rare elements (LREE), the roots in medium rare earth elements (MREE), while both light and in some cases heavy rare elements (HREE) prevail in the shoots. The observed predominance of LREE over HREE in the soils has been noted by several authors (Brioschi et al. 2013; Wang et al. 2005) and relates to the LREE higher mobility in this matrix. The values of $\text{La}_{\text{NASC}}/\text{Sm}_{\text{NASC}}$ and $\text{Sm}_{\text{NASC}}/\text{Yb}_{\text{NASC}}$ ratios obtained for the roots point to preferential accumulation of MREE by this part of the plant species (Ding et al. 2005; Brito et al. 2020), whereas the possible translocation of HREE from the roots to the shoots may be associated with specific organic complexation in xylem vessels during the accumulation process (Ding et al. 2005). A characteristic change in shape of the REE-normalized

patterns (Fig. 3) is in line with the previous findings (Dołęgowska and Migaszewski 2013; Krzciuk and Gałuszka 2020). The suppression in the roots of the soil-occurring Ce (+) and Eu (-) anomalies (Fig. 3; Table 2) and their subsequent enhancement in the shoots (Ce (-), Eu (+)) is related to the change in the redox conditions within the root zone of *J. effusus*.

BAF, TF and salinity factors

The lowest BAF values indicating a lack of accumulation were obtained for REEs and for Co. These values show a good correlation with those documented by Krzciuk and Gałuszka (2019) and indicate that transfer of these metals to the shoots of *J. effusus* is limited. Pb shows low accumulation, while Cu, Zn and Ag the medium one. The BAF values of Cd point to medium and high accumulation, which does not support the previous research in this area (Krzciuk and Gałuszka 2019) and is scarce in non-hyperaccumulative plants. In most cases, cadmium bioaccumulation factors found in the literature pinpoint to low and medium accumulation (Aladesanmi et al. 2019). Higher values (0.4 to 5.8) are recorded for plants growing on soils contaminated with this metal (Mganga 2014; Retamal-Salgado et al. 2017) or for hyperaccumulative plants used in remediation of Cd-polluted sites (Li et al. 2018). These unexpected results may be due to the occurrence of higher Cl^- concentrations (from de-icing salts), and are confirmed by the statistically significant correlation between the BAF of Cd and Cl^- content in the *J. effusus* roots. The BAF of Cd was also correlated with the BAF of Cu, Zn and Ag, which confirms their co-occurrence in the shoots at different levels (Table 1) (Schmoger et al. 2000). Taking under consideration differences between the sampling seasons, the BAF of Zn from April and May differed significantly from the BAF noted in June, when the lowest values were recorded. In regards to Ag, such differences occurred during all three sampling seasons with the highest BAF values in April. Depending on the sampling location, the highest BAF values were recorded in the samples from sites #2 and 3, but no correlation was found between these values and Cl^- content in samples from these sites.

The TF values obtained are strongly element and dependent (Fig. 4b). The lowest values were recorded for REEs, while higher than 1.0 were obtained for

Zn and Cd. These findings are in good agreement with the results of Krzciuk and Gałuszka (2019). It is worth noting that the TF of Eu, Ho, Er, Yb and Lu were negatively correlated ($p < 0.05$) with the content of Cl^- in the *J. effusus* roots.

The K/Na ratios (Table 3 of ESM) are comparable with those obtained for urban soils and roadside tree leaves collected in Kielce in 2010, while the Ca/Na ratios are much lower than those from 2010 (Gałuszka et al. 2011). A decrease in these ratios indicates an increase in salinity, caused by elevated sodium concentrations from additional source of this metal, e.g., de-icing salts. The variability of the computed ratios is related to the type of sample, sampling time and site location. In the roots, the lowest K/Na mean value was recorded for samples collected in June. Regardless of sampling time, for both shoots and soils, the K/Na ratio was significantly higher. In general, the Ca/Na ratio of soils was higher than that of roots and shoots. The exception is the soil from site 5, which is in complete agreement with the lowest Cl^- concentrations in samples from this location (Table 2 of ESM). It is interesting to note that the differences between the following pairs: $\text{K/Na}_{\text{roots(April/May)}} - \text{K/Na}_{\text{roots(June)}}$; $\text{Ca/Na}_{\text{tissues(May)}} - \text{Ca/Na}_{\text{tissues(June)}}$ were statistically significant. Both ratios indicate enhanced accumulation of sodium at the beginning of the growing season.

Conclusions

The presence of chlorides in soils, e.g., from de-icing salts, leads to formation of complex compounds with various trace metals. This process changes metal mobility making them accessible to plants. The assessment of the potential effect of de-icing agents on metal bioavailability to roadside plants in their natural habitats is more problematic than in the laboratory-based conditions. This process depends on the type of element, soil metal concentrations and interactions, and individual plant features.

The computed salinity factors indicate risen concentrations of Na and its origin from de-icing salt. The comparison of Cl^- concentrations in the rhizosphere soil, roots and shoots of roadside *J. effusus* showed that Cl^- ions are easily transported to the aboveground parts hence its concentrations were the highest in the shoots and up to 8 times higher compared to the roots. The concentrations

of Cl^- in the shoots were up to 3 times higher than those in the shoots of *J. effusus* collected from the sites not exposed to de-icing agents. The concentration order of examined elements (excluding Cd) was: rhizosphere soils > roots > shoots, indicating their controlled uptake. Almost reversed (roots > shoots > rhizosphere soils) for Cd may suggest that this metal is much easier taken up by the roots and transported to the shoots, however, this process is inhibited in the growing season. The computed BAF and TF values showed that Cd was taken up most easily, followed by Zn and Cu. The bioaccumulation and translocation of Ag, Co, Pb and REEs were very low. This suggests that at a low metal concentration, chlorides may reduce the efficiency of these processes. However, confirmation of the potential role of Cl^- ions in these processes requires further research.

Strong negative correlations found in June between Cu and Co in the shoots/roots and Cl^- in the rhizosphere soils may suggest their role in salinity stress alleviation due to the presence of an additional source of Cl^- , i.e. de-icing salts. The MREE exhibited higher concentrations than LREE and HREE in the roots as opposed to soils and the shoots that showed LREE enrichment. Significant correlations between some REEs and Cl^- recorded for the shoots collected in June may indicate the influence of temperature on the stability of REE chloride complexes, however, it is the first insight into this issue which needs more studies. As in the previous studies, we noted the characteristic change in the Ce and Eu anomalies observed in the soil-root-shoot system, i.e., from Ce (+) and Eu (-) in the soils to Ce (-) and Eu (+) in the shoots. This relation resulted from *J. effusus* features and changes in the redox conditions within the root zone of this plant species.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships

that could have appeared to influence the work reported in this paper.

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