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Review Paper

LITHIUM IN THE ENVIRONMENT AND ITS EFFECTS ON HIGHER PLANTS

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*RUDOLF KASTORI, IVANA MAKSIMOVIĆ, MARINA PUTNIK-DELIĆ**

University of Novi Sad, Faculty of Agriculture, Trg D. Obradovića 8, 21000 Novi Sad, Serbia
**Corresponding author*: putnikdelic@polj.uns.ac.rs

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SUMMARY

Lithium (Li) is present in low concentrations in all parts of the biosphere, including living organisms. It reaches the terrestrial environment primarily through natural processes to which parent substrate was subjected during pedogenesis, and due to anthropogenic activities. Individual soil types differ regarding Li content; for example saline and loamy soils have higher Li content. It is found in low concentrations primarily in ionic form in aquatic environments in surface and groundwater. It is mobile in the soil and thus soil contamination with Li can lead to its higher concentration in groundwater. In the environment, Li reaches the atmosphere from Li-emitting sources. It is widely used in many industries, lately in the Li-ion batteries in electronic goods, due to which it may be a potential risk for the environment. Terrestrial plants take up Li largely via roots from the soil, but also via shoots from the atmosphere. In the soil, Li is mostly bound by clay fraction and organic matter. During the uptake, transport and distribution in plants it behaves like an alkaline earth ion, not like an alkali ion. The fact that Li is immobile in the phloem supports this claim. Its ascendent transport mainly depends upon the transpiration intensity. More Li is taken up by plants from acid soils than from alkaline soils. Li is non-essential for plant growth and development. In low concentrations it can be stimulative and affect chemical composition and organic production of plants. Li plays an important role in the metabolism of halophyte species. It is increasingly regarded as an essential trace element for animals and humans, and used in human medication to treat dementia, suicidal ideation, aggression and violence. High levels of Li are toxic to all plants, but uptake and sensitivity to Li are species-dependent. Some representatives of the Ranunculaceae, Solanaceae and Asteraceae families are characterized by increased Li accumulation, while Poaceae, Liliaceae, Brassicaceae, Caprifoliaceae show low accumulation. High concentrations of Li have adverse effects on many physiological and biochemical processes in plants (DNA, RNA and protein pathways, water relations, content of photosynthetic pigments, photosynthesis, production of reactive oxygen species, lipid peroxidation of the cell membranes etc.), which is further manifested as stunted growth, developmental disorder, visual symptoms, interveinal necrosis and necrosis along the leaf margins. Hyperaccumulator plants extract significant amounts of Li and are therefore used in phytoremediation. Better understanding of the effects of beneficial and phytotoxic concentrations of Li on metabolism and plant growth and development remains vital for the improvement of the knowledge about biological activity of Li in higher plants.

Key words:
lithium, environment, plants, beneficial effects, toxic effects

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INTRODUCTION

Lithium (Li) has become a very important element in the last few decades due to its economic, geopolitical, environmental and scientific relevance, as well as its global strategical significance. The element Li (from Greek *lithos*, stone) was discovered in petalite in 1817 by the Swedish chemist Johan August Arfwedson. It is widely present in nature in low concentrations. According to its abundance, Li is the 25th element in the Earth's crust, where it is present to an extent of about 0.006 wt% (Aral & Vecchio-Sadus, 2008; Bibienne et al., 2020), and is likely to be concentrated in acidic igneous rocks and sedimentary aluminosilicates. The mean Li content in magmatic rocks (0.5-40 ppm) is lower than in sedimentary rocks (5-75 ppm) (Kabata-Pendias & Pendias, 2000). The presence of Li is detected in primary and sedimentary mountains, marbles, granites, syenties, gneisses and calcareous rocks (Steinkoenig, 1915; Hayyat et al., 2021). The average concentrations in shale and granitic rocks are 5 to 10 times higher than in carbonate-based rocks. Li reacts with other elements, most commonly it is found in some silicates and phosphates, and exists as salts or minerals. Li does not occur freely in nature; it is an alkali metal with atomic number 3. Out of all alkali metals, Li has the highest heat capacity, the smallest ionic radius and the least density; it is the lightest metal and has the largest hydration shell. Despite certain similarities in chemical and physical properties between Li and other alkali metals, it is very different from sodium (Na) and potassium (K) regarding its importance for living organisms. Some Li compounds, such as LiOH, Li_2CO_3, LiF, and Li_3PO_4, are significantly less soluble in water than the corresponding Na and K compounds. In Li compounds, bonds have more covalent properties than in Na and K compounds (Kőrösi, 1980). Li does not usually form complex ionic species, but can be bound in some organometallic compounds and chelates.

Li-containing materials are widely used in the Li-ion batteries in electronic goods in portable electronic devices and electric vehicles; in the ceramics and glass industry and metallurgy; in production of aluminium, pharmaceuticals and certain weapons, and in its elemental form as a nuclear reactor coolant and catalyst in rubber manufacturing (Kszos & Steward, 2003; Mohr et al., 2012). Li is also a compound of mood stabilising drugs (Aral & Vecchio-Sadus, 2008), greases (Hao et al., 2017) and sometimes in the manufacture of methamphetamine (Person et al., 2005). However, only 2% of Li is used in the pharmaceutical sector (Franzaring et al., 2016). Its compounds are used to increase viscosity of oils and fats, and can also be applied as antifreeze (LENNTECH, 2007). Significant Li production started after the Second World War. From 1955 to 1980, average annual production was approximately 5 kt Li/y. Since 1980, this production has been increasing at an annual rate of 5.1%, reaching 25 kt Li/y in 2008 (Mohr et al., 2012). According to Ober (2018), the worldwide Li production in 2017 was 43 kt Li/y. Increased needs for Li have resulted in its higher price.

The first legitimate medical application of Li was introduced in the middle of the 20th century when Li_2CO_3 was found to be beneficial for bipolar disorder, previously known as manic depression (Cade, 1949). More recently, it has found other applications, notably in dermatological disorders, such as herpes virus infections, seborrheic dermatitis and in oncology. Li has antimanic, antidepressant, antipsychotic, antiaggressive, antisuicidal and antineurotic effects (Schafer, 2012). Concentrations above 0.015 mg Li/L are protective against dementia (Kessing et al., 2017). Increased Li intake reduces levels of aggression and violence (Goldstein & Mascitelli, 2016). Schrauzer (2002) discussed Li essentiality for rats and goats and Li deficiency in humans. Average worldwide Li intake ranges widely from 10 to 1,900 µg/d. Metallic Li is mildly toxic. Li toxicity primarily affects the central nervous system. Since Li is almost immobile in the phloem tissues, leafy vegetables are the largest source of Li in foods, especially the lower leaves (Robinson et al., 2018). Medicinally-used Li partially reaches the environment and thus may enter the food chain (Franzaring et al., 2016).

Li mining, ore processing and industrial and pharmaceutical applications are potential risks for the environmental contamination with Li and consequently its entry into the food chain (Robinson et al., 2018). Li is a non-essential microelement, but an occasionally beneficial element for organisms (Schafer, 2012). However, in higher concentrations it is toxic to humans (Aral & Vecchio-Sadus, 2008) and plants (Franzaring et al., 2016). Owing to its diverse applications, studying Li mobility in the soil-plants-humans system and its biological activity is receiving more environmental and research focus.

LITHIUM IN THE ENVIRONMENT

Parent material and soil

Li enters the environment through natural processes from the parent material, such as minerals, clays, salt lakes, underground brine reservoirs, as well as anthropological activities. Rock Li sources include minerals such as Li micas, jadarite, lepidolite, eucrytite, spondumene, pentalite, amblygonite, as well as clay sources such as hectorite. A significant portion of Li occurs in the soil as a component of minerals including spodumene. Content of Li in typical

mineral deposits ranges widely from 0.5 to 2%, depending on the deposit location and the presence of Li mineral type (Mohr et al., 2010). In rock deposits in different parts of the world, Li content (%) in spondumene ranges from 0.5 to 1.9, in pentalite around 0.7, in lepidolite around 2, in jadarite 0.84, in hectorite 0.33, and various others from 0.37 to 1.4 (Mohr et al., 2010, 2012). Brine sources include Li found in salt water deposits, and include salars, lakes, oilfield brines and geothermal brines. Li content varies from 20 to 1500 mg/L in natural brines. Li exploitation from brines is environmentally and economically much more favourable than its mining from ore.

During weathering, the basic soil-forming process, in oxidizing and acid media Li is relatively easily released from the parent material and then incorporated in caly minerals, fixed by organic matter or by some other mineral oxides and ultimately accumulated in phosphate rocks (Hayyat et al., 2021). Precipitation primarily dissolves Li from acidic igneous rocks. Li sorption increases with increasing soil pH and decreases with increasing Li concentrations (Robinson et al., 2018). It is considered that Li content in soil depends more on the pedogenetic processes during soil formation than its initial content in parent rocks. Agricultural land is fortified with Li through fertilizers and composts of different origins. Li content in the soil ranges widely depending on the physical and chemical properties of the soil and Li presence in the parent material.

Naturally, Li concentration ranges between 2 and 200 mg/kg in the soil (Bernard, 2015). Light sandy soils, especially in humid climates, have lower Li content, while heavy loamy soils have higher Li content. On average, light organic soils contain 1.3 mg/kg, and limestone soils contain 56 mg/kg. Saline and arid soils contain relatively higher concentration of Li. In arid conditions, Li moves upwards with the soil solution and deposits in the upper soil layers in the form of easily soluble salts, such as borates, sulphates and chlorides.

Like Na, Li is found on the surface of soil colloids in the easily exchangeable form. Anderson et al. (1988) found a positive correlation between clay content and total and exchangeable Li contents in the soil, but a negative correlation between clay content and water-soluble Li. A significant correlation between clay content and exchangeable Li in the soil was also found. A strictly positive correlation between clay soil fraction and Li content was found by Robinson et al. (2018). The clay fraction of soil contains higher Li concentrations than the organic soil fraction. Schrauzer (2002) reported the range of Li content in clay fraction to be 7 to 200 mg/kg. In the soil, Li can be found as Li oxide (Li_2O), Li chloride (LiCl) and Li carbonate (Li_2CO_3) in all types of soils primarily in the clay fraction, and to a lesser extent in the organic soil fraction.

Due to various edaphic and climatic conditions during formation, and different chemical and physical properties, individual soil types differ significantly in Li content. Means of total content of Li in surface soils calculated on the world scale (mg/kg) is as follows: podzols (sandy soils) 22, cambisoils (silty and loamy soils) 46, rendzinas 56, kastanozems and chernozems 53, and histosols (organic soils) 1.3 (Kabata-Pendias & Pendias, 2000). Negrel et al. (2017) studied the concentration of Li extracted with hot water in agricultural soils (0-20 cm) and grazing land soils (0-10 cm) in 33 European countries at an area of 5.6 million km^2 and found Li concentration in the European agricultural soil to be on average 11.4 mg/kg, which is about four times lower than in the Earth's upper crust (41 mg/kg). Distribution of Li extracted in hot water shows that its concentration in agricultural soils of northern Europe is dominantly lower (6.4 mg/kg) than in southern Europe where it is significantly higher (15 mg/kg). Soil texture and organic matter substantially determine Li behaviour in the soil. Organic matter plays a crucial role in metal immobilization in the soil (Sastre et al., 2007). According to Hayyat et al. (2021), Li has an overall negative impact on the soil, due to the observed loss of important nutrients (K, Na, N) in leachate after Li application. Organic matter addition (10%) to the soil reduces negative impacts of Li on the soil and minimizes the loss of nutrients. Distribution of Li in the soil profile differs from that of some other elements, since approximately the same Li concentration is found in the topsoil as in the subsoil, but in most cases its higher content is found in the underlying layers (Merian, 1991; Steinkoenig, 1915).

Aquatic environments

Li is present in surface and groundwater of larger bodies of waters in seawater, oceans, saline and mineral waters (Steinkoenig, 1915). According to Aral & Vecchio-Sadus (2008), typical background concentrations of Li in the fresh water are 0.07-40 µg/L and in seawater 170-190 µg/L. Li concentrations of the world's major lakes range from 0.014 to 14.0 mg/L in the Dead Sea (Huh et al., 1998). Li in water in primarily found in its ionic form. Reaction between metal Li and water produces Li hydroxide and hydrogen:

$$2Li + 2e^- + 2H_2O \rightarrow 2LiOH + H_2$$

At higher temperatures, Li reacts with hydrogen to form Li hydride (LiH). Li compounds such as Li chloride, phosphate, carbonate, fluoride and hydroxide in water are more or less soluble (LENNTECH, 2007).

Increase in population density and anthropogenic activities are accompanied by a large enrichment in aqueous Li in river and tap water (Choi et al., 2019). Increased Li content has a toxic effect on the aquatic organisms (LENNTECH, 2007). Most of natural bodies of water have higher Na content, which alleviates toxic Li effects (Kszos & Stewart, 2003; Kszos et al., 2003). Kugimiya et al. (2020) reviewed the literature data and concluded that Li content in drinking water ranges from 0 to 219 µg/L depending on the location and environmental conditions. Li found in drinking water is completely bioavailable. The findings of the mentioned authors reconfirm the inverse association between Li levels in drinking water and suicide rates particularly in the male population. In some geologically exposed areas, Li concentration in drinking water can be so high that it contributes to extremely high Li intake of 30 mg/L into body which approximately corresponds to the dosage used in the treatment of mood disorders. Li-chloride and Li-sulphate have high water solubility, and the compounds will dissociate in aqueous environment. In natural bodies of water, higher Na concentration protects from Li toxicity. Long-term use of drinking water with low Li content is considered to be a risk factor for higher incidences of suicides, homicides and crimes, as shown in several studies (Schafer, 2012). Drinks such as tea, coffee, beer, wine can contain significant amounts of Li, therefore it is important to consider those as Li sources when examining its body intake. On average, mineral water contains 0.05 to 1 mg/L Li, but remarkably higher contents can be found in natural mineral waters, up to 100 mg/L (Schrauzer, 2002). Li isotopes can also be found in drinking water and river water (Huh et al., 1998). The influx of Li isotopes predominantly comes from anthropogenic sources, more than from local weathering inputs, in such bodies of water in the urban areas (Choi et al., 2019).

Plants, and drinking water to some extent, are the main source of Li in the food chain, and both largely depend on Li dynamics in the soil (Franzaring et al., 2016; Szklarska & Rzymski, 2019). Pollutant mobility in the soil greatly depends on the soil physical and chemical properties, pollutant solubility in water and the present concentration. Li content in drinking water also depends on the soil type (Schafer, 2012). Physical properties of the soil, such as porosity, permeability, bulk density and texture, play an important part in promoting the conditions for the interaction between the pollutants and soil or water particles, and consequently their migration in the soil (Huang et al., 2019). Li which enters the soil by contamination or otherwise can easily become mobile and can reach groundwater often used as a source of drinking water or for irrigation of plants. Li concentration in leachate ranges from 0 to 95 mg/L, but the standard value is below 2.5 mg/L. Irrigating with water which has elevated content of Li can result in its accumulation in plants and cause toxic symptoms on plant leaves. Few crops tolerate up to 5 mg/L concentration of Li in irrigation water (Hayyat, 2021). Li-chloride and Li-sulphate are particularly easily water-soluble salts and they easily enter groundwater and aqueous environment in general. Based on much literature data, Li concentration in groundwater ranges within very wide limits, from 0.5 mg /L to 500 g/L, depending on the location (Shahzad et al., 2016).

Atmosphere

Li is present in the atmosphere in trace amounts, and it enters the atmosphere through emissions during the production processes which utilize Li, such as manufacturing of ceramics, glasses or lubricants. From the atmosphere, Li reaches soil surface, water and plants as liquid or solid deposit. In the vicinity of sources which emit Li into the atmosphere, Li deposits on the soil surface can exceed its content leached from the soil, which consequently increases its content in the soil (Anderson, 1990). According to Aral & Vecchio-Sadus (2008), typical background concentration of Li in the atmosphere is 2 ng/m^3. Plants can accumulate Li from the atmosphere as well, for example in the vicinity of a Li-emitting source (Anderson, 1990). Therefore, vegetation near a Li-emitting source may be affected by Li from the air as well as the soil. Robinson et al. (2008) reported on Li accumulated from dust particles into the cuticular wax of plant leaves.

LITHIUM UPTAKE, TRANSLOCATION AND ACCUMULATION IN HIGHER PLANTS

Uptake

Despite its low concentration in the environment, plants assimilate and accumulate Li easily. Li distribution in flora was studied as early as the late 19th century (Focke, 1872). Plants take up Li in the form of monovalent cation Li^+. The precise mechanism of Li uptake is not fully understood (Shahzad et al., 2016). Based on the similarities in physical and chemical properties between Li ions and ions of other alkali metals, such as Na and K, it is assumed that Li uptake follows a similar mechanism. Kabata-Pendias & Mukherjee (2007) stated that Li can use the same pathway and the same transport carrier through the cell membrane as K ion, which is why it is easily taken up. There is a view that plants are unable to regulate Li uptake since there is, to a certain extent, direct proportionality between Li content in plant tissue and Li content in the soil. Most of geogenic Li in the soil is insoluble and therefore

inaccessible to plants. However, if Li is introduced into the soil, it binds to a small extent and thus becomes accessible to plants (Robinson et al., 2018).

The intensity of Li uptake depends on many environmental and internal factors, primarily on its concentration in the nutrient medium (Li et al., 2009; Hawrylak-Nowak et al., 2012). Kavanagh et al. (2018) reported a positive linear dependence between Li content in plants and quantity of Li introduced into the soil in all species in the trial: *Brassica napus* at r^2=0.73, *Brassica oleracea* at r^2=0.73 and *Helianthus annuus* at r^2=0.86. Li in plants reflects well amount present in the soil. According to Antonkiewicz et al. (2017), depending on Li concentration in the nutrient solution, maize utilized between 2 and 24% of Li present in the nutrient medium. The presence of plant-accessible Li increases when soil pH is lower due to decreased negative surface charge and cation-binding sites, which leads to a more intense Li uptake by plants (Aral & Vecchio-Sadus, 2008). Soil moisture and intensity of transpiration also affect Li uptake. According to Makus et al. (2006), lighter textured soil and reduced light intensity improved Li uptake. Intensive Li uptake was observed in plant species that grow on solonetz and solonchak, and other soil types with increased content of alkali metals (Kabata-Pendias & Pendias, 2000). Intensity of Li uptake from its salts depends on their water solubility. Li uptake is more intense from Li-chloride than from Li-carbonate which is less water soluble. Many studies discussed the possibility of applying chelating agents in order to induce metal accumulation in plants (Nowack et al., 2006). The application of chelating agents EDTA and EDDS significantly increased Li uptake in *Brassica oleracea* and *Helianthus annuus* and especially in *Brassica napus*.

Li had specific synergistic and antagonistic effects on the uptake of other macro- and microelements (Robinson et al., 2018; Török et al., 2021). Many authors have studied and showed the interaction of Li and other alkali and alkaline earth metals during uptake. Kabata-Pendias & Mukherjee (2007) reported that Li interacts with Na and K ions and enzymes which require a magnesium (Mg) ion. This could explain the effect of Li on the activity of Mg-containing enzymes (Brich, 1988). It is considered that Li effect on Na and K content can be partially explained as a result of interaction of the stated ions, and partially as a result of Li effect on the active transport of K and Na through the membrane. K ion is able to fully reverse Li effects in many cases (Bodot, 1992). Li concentration in plants directly and significantly correlated with the presence of heavy metals in the soil as soil acidity increased, since their solubility increased with lowering of pH (Lambert et al., 1983). Franzaring et al. (2016) reported that the levels of Ca, Mg and K significantly decreased in maize leaves on Li-treated soil, while it had no effect on the levels of iron, nickel and cobalt. Ca concentration in maize leaves decreased from 8,000 ppm in control to 2,000 ppm in plants grown on soil treated with 400 ppm Li in the form of Li-chloride. Due to the antagonism between Li and Ca during their uptake by roots, high Ca level in the soil reduces the possibility of phytotoxic effects of high Li concentrations. Strontium (Sr) affected Li uptake similarly as Ca. The level of interactions between Li and other elements also depends on the genotype (Makus et al., 2006).

Li uptake intensity also depends on the internal factors. Plants take up Li more intensely in the early phases of growth and development than in the later phases. K uptake in young plants under optimal environmental conditions was much more intense than Li uptake. However, in older plants under unfavourable conditions (shading, lack of oxygen etc.) K uptake was much more reduced than Li uptake. Plant species and genotypes differ greatly in Li uptake and accumulation (Hawrylak-Novak et al., 2012; Robinson et al., 2018).

Many researchers explored the possibility of K replacement with Li. It has long been known that elements of similar physical and chemical properties could partially replace the function of another related element, predominantly in the non-specific processes. For example, Na can replace the non-specific part of K in different plant species to a greater or lesser extent (Marschner, 2012). Brinner & Lucaaus (1866) were among the first to attempt K replacement with Li when growing clover and oats. Their results showed that plants were not able to develop normally in the event of such a replacement. According to Scharrer and Schropp (1933), not only that Li was unable to replace K fully, but even the smallest amounts of K were unable to be replaced by Li. Replacement of K by Li was impossible in lower plants as well. Contrary to this, Codina et al. (1983) reported that Li can replace 50% of K in plants. Additionally, other studies also indicated that Li can replace K or Na in plants, including Na-loving plants (Yalamanchali, 2012).

Translocation

Based on its mobility in the phloem, Li translocations in plants are more similar to alkaline earth metals Ca, Sr and barium (Ba) than alkali metals (Hinz & Fischer, 1976), as well as its distribution and accumulation in the root and shoot. Namely, coefficient of accumulation of Ca, Sr and Li in plant roots is often higher than in the case of alkali metals K, rubidium (Rb) and caesium (Cs). Ca and other divalent and trivalent ions are able to stimulate the uptake of monovalent cations and anions, which is known in plant physiology as Viets-effect. In this regard, Li is also very similar to Ca since both elements stimulate Rb uptake.

As mentioned before, during transport Li ion behaves more like an alkaline earth ion than an alkali ion. Zeller & Feller (2000) applied Li to wheat flag leaf and the largest portion was present in that leaf, while only a small amount

was found below or above the application location. Applying Li on the leaf did not greatly affect its content in the grain; therefore, it can be concluded that there was only some Li translocation, if any, from the leaf through the phloem, which means its mobility in the phloem was low. Transport in the stem through the xylem was possible for all tested elements, while transport from leaf to grain was possible only for the elements which are mobile in the phloem, such as Na, Cs, K and Rb. Transport and distribution of Li is consistent with the elements with limited mobility in phloem which are mostly transported in xylem (Evangelou et al., 2016). Li accumulation in older leaves and its lower concentration in the seeds or fruits also indicate its low translocation or mobility in the phloem. Due to this, growing fruit or seed crops on Li-contaminated soils decreases the risk of its entry into the food chain. Immobility of Li in the phloem can be interpreted and explained in different ways. Some authors consider that Li does not reach phloem at all, but is immobilized before it reaches sieve tubes. This view is often employed to explain low mobility of other ions in the phloem, such as Ca. Kastori et al. (1976) reported on a more intensive Ca transport in the phloem, or translocation, which happens only after the tissue, or binding sites in the cells, are saturated with this element. One of the preconditions for the transport of organic and mineral matter through the sieve tubes is water solubility. Li ion is similar to alkaline earth ions, and because Li-carbonate and Li-phosphate have poor water solubility, their creation could be one of the causes for low mobility in the phloem. Creation of Li-carbonate and Li-phosphate in the phloem prevents Li transport. Li transport in the cortex is very slow, just like in the parenchymal tissue, and its intensity does not exceed the order of magnitude of diffusion.

Ascending transport of Li occurs in the xylem. Translocation of Li from root to shoot increases with the increase of its concentration in the nutrient medium, which indicates a relatively easy translocation of this metal through the plant. Kalinowska et al. (2013) found that Li concentration in lettuce root was 3.5 to 4 times higher than in shoot under low Li concentration in the nutrition medium. Translocation factor increased with increased Li concentration in the nutritive medium, which has lead to similar Li levels in both plant parts. Li concentration was the highest in the roots, lower in the stems and leaves, and the lowest in the inflorescences in maize grown under hydroponic conditions (Antonkiewicz et al., 2017). Li binding in the root can be important regarding the protection from its phytotoxic effect (Aral & Vecchio-Sadus, 2008). Ascending Li transport in the xylem is under the influence of the transpiration stream.

Accumulation

Li uptake and accumulation under the same environmental conditions vary significantly across plant families and genotypes. Plants from the families *Asteraceae*, *Rosaceae* and *Solanaceae* are highly able to accumulate Li, just like halophilic plants, which also have a high tolerance to Li (Schrauzer, 2002; Kabata-Pendias & Mukherjee, 2007). Some members of the family *Solanaceae* can accumulate > 1.000 mg Li/kg DM in the leaves. Kabata-Pendias & Pendias (2000) reported on Li concentrations in certain plant families based on many other studies: the highest Li concentration (ppm DW) was found in *Rosaceae* (2.9), *Ranunculacea* (2.0) and *Solanaceae* (1.9), lower in *Urticaceae* (0.24) and *Poaceae* (0.24), and the lowest in *Polygonaceae* (0.10). Species within a family may differ significantly regarding Li concentration. Franzaring et al. (2016) analyzed Li concentration in thirteen plant species collected in the field, and found the highest concentration (ppm) in *Ranunculus sardous* Crantz (2.16) and *Plantago laceolata* L. (0.42), and the lowest in *Vitis vinifera* L. (0.05) and *Hypericum perforatum* L. (0.05). According to Török et al. (2021), *Lolium* sp. had on average 4.30, *Mentha* sp. 1.70 and *Urtica* sp. 0.66 mg Li/kg DW in karst areas. *Cirsium arvense* and *Solanum dulcamera* accumulate Li three to six times more than other plants. Additionally, *Chenopodiaceae* plants are considered to have high ability to accumulate Li. Li concentration in fungi is lower than in higher plants, on average 0.189 ppm, and dicots reach higher levels than monocots (Vetter, 2005). Halophilic plants, such as *Holoschoenus vulgaris* and *Carduus arvense*, can reach Li concentrations of 99.6 to 226.4 µg/g (Tölgyesi, 1983). According to Jiang et al. (2014), Li accumulator, medicinal herb *Apocynum venetum*, accumulated > 1,800 mg Li/kg in leaf tissue, and owing to this the plant has antidepressant and anxiolytic effects. Application of increasing Li concentrations in lettuce in the forms of Li-chloride and Li-hydroxide resulted in its accumulation in shoots and roots, and the form of Li did not have a significant effect (Kalinowska et al., 2013).

Li concentration in the edible parts of the cultivated species ranges widely and depends on the plant species and plant organ. Primary dietary sources of Li are vegetables and grains, which contain 0.5 to 3.4 mg Li/kg and contribute between 60% and 90% of the total Li intake (Schrauzer, 2002). Meat products have very low Li concentration, only about 0.012 mg/kg. According to Macholz & Lewerenz (1989), the leaves of leafy vegetables have higher Li content than seed, which indicates solid ascending translocation of Li in the xylem through the transpiration stream and its immobility in the phloem. Li concentration in lettuce fresh matter was 0.3-0.6, in cabbage 1.2, in green onion 1.8, and in spinach 4.6 mg/kg (Shahzad et al., 2016). Kabata-Pendias & Pendias (2000) listed Li concentrations for a larger number of plant foodstuffs. The values indicate significant differences among individual foodstuffs, as well as low Li concentration in corn grains, onion bulbs and carrot roots. Kavanagh et al. (2018) gave an overview of many

plant species which have higher Li accumulation, where *Brassica carinata* stands out with 8000 mg Li/kg. Generally speaking, grasses are considered to accumulate less Li than herbs, and Li concentration in young plants is higher than in older plants.

Unlike terrestrial plants, aquatic plants that live in seas have higher Li concentrations. According to Brovik-Romanov (1969), Li concentration in some sea plants in the Caspian Sea (*Zostera marina, Rupia spiralis*) ranges from 0.66 to 1 mg/kg fresh matter, but is lower in algae (*Laminariales, Fucales, Rhodymeniales* and *Charales*) and ranges from 0.18 to 0.45 mg/kg fresh matter. Coefficient of Li accumulation in aquatic plants is nevertheless quite lower than that of other alkali metals (coefficients of accumulation: Na 0.75, Li 0.95, Rb 18, K 19 and Cs 45).

Microorganisms (bacteria, fungi, yeasts, actinomycetes) also differ greatly regarding Li accumulation (Tsuruta, 2005). Strains of the bacteria *Arthrobacter nicotianae* and *Brevibacterium helvovolum* have great ability for Li accumulation, around 1.0 and 0.7 mg/g dry weight cells, respectively.

Understanding metal accumulation and more generally contaminant accumulation by plants is important considering their use in phytoremediation and agromining (phytomining). Agromining is considered to be an environmentally responsible approach to site remediation. The process of agromining is based on the use of plants to extract metals from soils. Plant species capable of remediation should have higher tolerance to the contaminant, form larger aboveground mass and accumulate metal to a larger extent, predominantly in the shoot. Plants that are not hyperaccumulators do not accumulate metal to a larger extent even in the case of its higher concentration in the nutrient substrate, while hyperaccumulator plants accumulate 100 to 1000 times higher levels than those in the substrate in which they grow. Li metal agromining industry may be wishful thinking right now (Kavanagh et al., 2018), especially because agromining technology is environmentally much more suitable than conventional mining methods (opencast, underground), but also energetically and cost-effectively more advantageous than hard rock mineral mining or extraction from mineral-rich brines. It is believed that Li agromining is a potentially viable process. Li et al. (2009) reported that brown-seeded *Brassica carinata* has some potential in phytoremediation of Li-contaminated water and soil. Hawrylak-Novak et al. (2012) and Antonkiewicz et al. (2017) supported the idea of using maize for rhizofiltration of contaminated water or soil remediation bay phytoextraction. Mycorrhiza is the most widespread association between microorganisms and higher plants (Smith & Read, 2008). Some fungi like *Aspergillus* or arbuscular mycorrhizal fungi can accumulate higher concentrations of Li and this contributes considerably to remediation of Li toxicity in soils (Shahzad et al., 2016).

BENEFICIAL EFFECTS OF LITHIUM IN PLANTS

Due to its concentration in plants, Li is regarded to be a microelement. According to the available data, plants can end their life cycle without the presence of Li; therefore, it is considered a non-essential microelement for plant growth and development. According to Török et al. (2021), Li plays an important role in the metabolism of halophyte species. Various studies show that small doses of Li can be beneficial to plant growth and development (Okhrimenko & Kuzmenko, 1975; Kastori, 1976; McStay et al., 1980; Schafer, 2012; Shahzad et al., 2016) (Tab. 1). Additionally, Li toxicity is highlighted as the primary effect on the plant life processes (Shahzad et al., 2016). Despite the fact that Li presence and its impact on the flora have been studied since late 19th century (Scharrer, 1955), the biological activity of Li in plants needs further research, because it is still debated and poorly understood whether plants even require Li (Kalinowska et al., 2013).

Ezdakova (1964) categorized plants into four groups depending on their reaction to Li presence. The first group comprises plants with elevated Li accumulation under all conditions and to an extent favour soils with high Li content, such as some plants from the families *Ranunculaceae, Solanaceae* and *Cirsium vulgare* from the family *Asteraceae*. The second group comprises plants which accumulate Li only if in excess in the soil, such as *Mentha longifolia, Phlomis thapsoides* and *Gossypium hirsutum*. The third group consists of plants that do not have high Li requirements and do not grow on soils with elevated Li content, such as *Brassicaceae, Caprifoliaceae, Liliaceae, Poaceae*. The fourth group consists of plants which do not have higher Li requirements but do not mind soils with elevated Li content, such as *Tamaricaceae, Zygophyllaceae* and *Alhagi crichisorum* from *Fabaceae*. There are transitional forms between these groups.

It is thought that Li^+ ion can exhibit a specific effect on the plant life processes based on its physical and chemical properties, as well as a non-specific effect based on the similarities with monovalent (K^+ and Na^+) and divalent (Ca^{2+} and Mg^{2+}) cations (Schafer, 2004). Small ionic radius (0.068 nm) of Li^+ ion gives it the highest electronegativity and the strongest polarization power among all ions of alkali metals, which largely determines its biological effect. Li has not been shown to act as a cofactor in any enzyme or enzymatic transportation system within plants (Kastori, 1976; Kastori et al., 1976; Kavanagh et al., 2018). However, similarly to other alkali metals, Li can regulate metabolism due to its affinity for Ca- and/or Mg-activated enzymes (Kabata-Pendias & Mukherjee, 2007). Effects of Li on

enzymatic, and consequently physiological processes in plants, most probably are due to the fact that Li ion has a very large hydration shell and the radius of the hydrated ion of 0.34 nm. Monovalent cations with a large hydrated radius are weakly sorbed via outer-sphere binding (Sposito, 2016). Hydrophilic Li ion especially increases the content of water bound in colloidal system and thus affects colloid-chemical properties of protoplasm, size and velocity of colloidal imbibition and cellular water content. Based on the available results, it can be assumed that the mechanism of Li effects on certain life processes in plants cannot simply be reduced to its effects on physical and chemical properties of protoplasm colloid, or hydration, despite the fact that it is indisputably very important. It cannot be ruled out that Li specifically affects certain physiological and chemical processes, although the mechanism of its effects in most cases is insufficiently understood.

Table 1. Overview of the beneficial effects of Li on higher plants

Li application	Plant species	Effect	Author
Seed immersion in 1% solution of LiCl	Wheat, barley, peas, clover	Growth stimulation	Voelcker (1903)
0.1 g $LiNO_3$/kg soil	Barley, pea	Growth stimulation	Nakamura (1904)
Hydroponic solution 12 ppm Li*	Cucumber	Increased fruit yield	Rusin (1979)
10 Ibs Li /Ac (Li_2SO_4)	Spinach, mustard	In reduced light increased plant fresh wt.	Makus et al. (2006)
Murashig and Skoog medium 30 mM Li*	*Brassica carinata*	Stimulated root length and fresh weight	Li et al. (2009)
Nutrient solution 5 mg Li/L*	Maize	Increased shoot fresh biomass	Hawrylak-Novak (2012)
Hydroponic culture 2.5 mg Li/L (LiOH), 2.5 and 20 mg Li*	Lettuce	Increased root fresh biomass	Kalinowska et al. (2013)
Hydroponic conditions 1-32 mg/Li/L (Li as LiCl)	Maize	Stimulating effect on the yield	Antonkiewicz et al. (2017)

Soviet researchers were the first to show beneficial effects of small Li doses on plant productivity and metabolism (Kastori, 1976; Kastori, 1978). According to Golovina (1964), Li affected carbohydrate turnover. It was found that Li significantly increased invertase activity in sugar beet leaves, especially in the period of sugar translocation from the leaves to the root. Using Li in field conditions, Vlasyuk et al. (1973) found an increase in potato tuber citric and malic acids. Vlasyuk et al. (1976) reported that Li increased phosphorylase synthesis in the leaves of young tomato and potato plants, as well as starch content in potato tubers. Rusin (1979) applied Li to cucumber plants and found increased fruit yield, fruit sugar and ascorbic acid content, but Li did not accumulate in the fruit. McStay et al. (1980) reported that Li use in beans significantly increased plant height, first trifoliate fresh weight and leaf area. Antonkiewicz et al. (2017) found increased maize yield when using different concentrations of Li under the conditions of nutrient solution to 22.3%.

Li can have an indirect beneficial effect on plants by reducing infections caused by fungi and bacteria. Many earlier studies dealt with plant infection control by using Li (Vidali, 1951; Darby & Westgatge, 1958). According to Takamatsu et al. (1979), 5 µM Li in *Erysiphe graminis* f. sp. *hordei* inhibited appressorial and haustoria development on barley. When applied to cucumbers, Li reduced the incidence of powdery mildew (Abood & Losel, 1991), and when applied to potatoes, it inhibited the winged form of aphids (Harrewijn, 1983). In general, application rates of Li controlling the infection were also phytotoxic and when rates were reduced to non-phytotoxic levels, the disease prevailed (Anderson, 1990).

PHYTOTOXICITY OF LITHIUM

Li phytotoxicity was first observed in 1871 in a trial where Li caused buckwheat death and rye biomass reduction (Nobbe et al., 1871). Li phytotoxicity predominantly occurs on Li-contaminated sites. Industrial applications of Li are the major sources of Li contamination, particularly with the disposal of Li-ion batteries (Gao et al., 2019). The applications pollute the environment, soil and water, and provide direct sources of Li phytotoxicity. After entering the cytoplasm, Li may directly attack various metabolic systems. Li phytotoxicity largely depends on its concentration and availability to plants, plant species and genotype, as well as the duration of the exposure and manner of application (Tab. 2). Individual plant organs show different levels of tolerance to Li. Maize roots were the most resistant organs to Li (Antonkiewicz et al., 2017). Bingham et al. (1964) listed a larger number of plant species which had varying sensitivity to Li, and reported that its concentration for normal growth was < 5-10, 6-70 at which 25% growth reduced, and >100 ppm at which growth completely reduced. Li concentration at which growth was completely reduced in slightly sensitive red beet was 2,500-4,000 ppm. It is considered that there might be a

similarity between plant tolerance to higher concentrations of Na and Li. Citrus fruits, pear, soybean, tomato and grapevine are particularly sensitive to high Li concentrations.

Li has a profound toxic effect on plants which have higher requirements for Ca, and a less profound effect on some algae and fungi which require less Ca. This is confirmed in studies where higher Li concentrations reduced Ca content in plants, and inversely where higher doses of Ca reduced Li uptake (Epstein, 1960). Based on this, Ca can be added to soils to prevent Li toxicity.

Higher Li concentrations cause numerous changes in plant metabolism, which are subsequently manifested during growth and development. The first plant organ to come in contact with Li is the root. Kabata-Pendias & Mukherjee (2007) reported damaged root tips in plants grown on Li contaminated soils, and Mulkey (2005) stated that excess Li altered root gravitropic growth in maize. Many studies showed Li toxicity on DNA, RNA and protein biosynthesis pathways (Kastori, 1976; Shahzad et al., 2016). Based on many other studies, Anderson (1990) found the primary effect of Li in influencing the stability and conformational state of DNA, which in turn affects the metabolism of RNA and proteins.

Toxic effects of Li are also evident in plant water regime. According to McStay et al. (1980), Li concentration above 4 mg/L led to stomatal closure and disturbed water regime in beans. Reduced stomatal conductance can be the result of turgidity loss, or decreased water content in plant tissues. Magalhaes et al. (1990) stated that Li stress reduced water retention in tissues. Alternatively, there is another view that low Li concentrations increase water adsorption by macromolecules, while high Li concentration competed for water and acted as a dehydrating agent (Shahzad et al., 2016). The effect of Li on stomatal movement could also be caused by antagonism between Li and K, since in most plant species K^+, associated with an anion, plays a major role in turgor changes in the guard cells during stomatal movement (Hawkesford et al., 2012).

High Li concentrations affect the content of photosynthetically active plant pigments, both directly and indirectly. Indirect effects include formation of necrotic lesions, spots and regions, primarily on older leaves (Naranjo et al., 2003; Kalinowska et al., 2013), which decreases chlorophyll content and photosynthetically active leaf area in plants. Direct cause of decreased chlorophyll content could be the increased catalytic action of chlorophyllase and other enzymes which are responsible for chlorophyll bleaching (Harpaz-Saad et al., 2007). Hawrylak-Nowak et al. (2012) showed that Li concentration of 50 mg Li/L significantly reduced the contents of chlorophyll *a* and *b*, and of carotenoids in maize, while it did not affect the content of photosynthetic pigments in sunflower. The same Li concentration increased the levels of lipid peroxidation in the cell membranes of the sunflower leaves by 68%, as determined by the production of melano-aldehyde in plants. Peroxidation of the membrane lipids leads to cell membrane damages, disturbances of membrane integrity and consequently their increased permeability. According to Li et al. (2009), Li stress decreased chlorophyll content and phenolic compound production in *Brassica carinata*. Li also affected plant respiration (Okhrimenko & Kuzmenko, 1975).

Based on the available results, it remains possible that oxidative stress, higher production of reactive oxygen species (ROS) and alteration in antioxidant activity are important mechanisms of the toxic effects of Li ions (Shahzad et al., 2016). Kalinowska et al. (2013) found that L-ascorbic acid non-enzymatic anti-oxidant accumulation in lettuce remained unaffected by different Li stress concentrations. Based on this, the same authors concluded that Li phytotoxicity in plants is not related to the disturbances in the accumulation of L-ascorbic acid. Makus et al. (2006) also indicated that Li application to the soil did not affect the total ascorbate in mustard and spinach leaves.

Many authors observed reduced biomass, yield and growth in cultivated species under higher Li concentrations (Tab. 2). Several studies showed that high Li concentrations affected plant metabolism and growth; however, it seems that this Li role is non-specific and based on the substitution of other monovalent cations in the cell (Kabata-Pendias & Mukherjee, 2007). Additionally, excess of Li can disturb normal pollen development (Zonia & Tupy, 1995a), block its germination (Zonia & Tupy, 1995b) and inhibits the seismonastic closure of leaflets of *Mimosa pudica* (MacStay, 1980). In many plant species seed germination rate decreased with increased Li concentration (Kavanagh et al., 2018). According to Gupta (1974), seed germination reduced at 5 ppm Li in rice and gram, while no decrease occurred in barley or wheat, even at 100 ppm. Li influences the biological clock in plants. Under persistent treatment with 0.5 and 20 mM Li^+, the period of circumnutation in sunflower was significantly prolonged by approx. 18 % (30 min.) (Stolarz et al., 2015).

Table 2. Overview of the toxic effects of Li on higher plants

Li application	Plant species	Effect	Author
650 kg LiCl/ha	Wheat, barley, peas, clover	Complete inhibition of seed germination	Voelcker (1903)
Water culture and sand culture 1 mM Li as Li_2SO_4	Rye, barley, oats	Increased fresh weight	Scharrer & Schropp (1933)
Solution 1 mM Li*	Sugar beet	Reduced biomass	Sims & Atkinson (1971)

Soil 2.5 ppm Li	Cool season grasses	Increased yield	Sneva (1979)
Substrate 500 ppm Li*	Barley	Reduced biomass	Wallace (1979)
Nutrient solution >0.1 mM Li*	Tomato, bush bean	Reduced yield	Patel et al. (1980)
0.25 mg Li /kg soil*	Oat	Decreased yield	Jurkowska et al. (1998)
40 mg Li/kg soil*	Maize, spinach		
Nutrient solution 50 mg Li /L*	Sunflower, maize	Reduced shoot biomass	Hawrylak-Nowak et al. (2012)
Hydroponic culture 20 ppm LiOH, LiCl	Lettuce	Reduced yield of edible parts	Kalinowska et al. (2013)
Hydroponic medium 0.2 and 20 mM Li*	Sunflower	Hypocotyls were shorter	Stolarz et al. (2015)
Soil >118 Li*	Maize	Reduced shoot dry weight	Franzaring et al. (2016)
30 mg Li/kg soil*	Beet root, lettuce, black mustard	Toxic effect	Robinson et al. (2018)

Legend: *In the form of LiCl

Apart from reduced growth, toxic Li concentrations cause other visual morphological symptoms. Li toxicity-induced symptoms are not distinct and are difficult to be recognized. Most often they occur on older leaves where Li chiefly accumulates. Toxic Li concentrations cause necrosis along the leaf margins, subsequent interveinal chlorosis and leaf abscission. Older leaves of lettuce showed necrotic spots at 100 mg Li/L (Kalinowska et al., 2013). When exposed to Li, Arabidopsis plants showed chlorosis mainly on older leaves and leaf curling (Duff et al., 2014). Similarly, higher Li concentrations caused necrotic lesions predominantly on older tobacco leaves (Naranjo et al., 2003).

CONCLUSION

Li has recently received increased attention due to testing results indicating potential beneficial and toxic effects of Li on higher plants and other living organisms, and its wide application in different industries and pharmacology. It is found in low concentrations in the Earth's crust, soil, surface and groundwater, air, as well as all organs and tissues of the living organisms. Intensity of Li uptake by plants depends on many internal and environmental factors, primarily its concentration in the environment. During uptake, Li ion exhibits interaction primarily with other alkali metals and with alkaline earth metals. Application of chelating agents significantly increases its uptake. Li is transported from root to shoot in ascending movement by means of the transpiration stream. Li mobility in the phloem is low, which is why it mostly accumulates in lower older leaves, and to some extent in the reproductive organs. High Li-accumulating ability is found in plants from the families *Asteraceae, Rosaceae, Solanaceae* and halophilic plants, which also have a higher tolerance to elevated Li concentrations. According to the available data, Li is a non-essential element for higher plants, which can complete their life cycle without its presence. Low Li concentrations can be stimulating to plant life processes, and consequently their chemical composition, growth and development. Li also has numerous effects on humans and animals – it is used in human medications for dementia, suicidal behaviour, aggression and violence. Li is mildly toxic for humans and animals. However, high Li concentrations are toxic for all higher plants, but its uptake, accumulation and plant sensitivity are species-dependent. Plant organs also exhibit different levels of Li tolerance. Ca can be added to soils to prevent Li toxicity. Risk from soil contamination with Li is likely to increase due to its wider dispersal in the environment, primarily due to its wide applications in the production of Li-ion based batteries in electronic goods. Phytoremediation and agromining by using Li-hyperaccumulating plants could decrease its concentration in topsoil. Agromining of Li is a potentially viable process. Since plants uptake and accumulate Li easily, they can be used as indicators of Li presence in the soil. The results showed various areas which are in need of further studies regarding Li biological activity in plants. It is still debated and insufficiently understood whether higher plants require Li.

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