Regional differences in plant levels and investigations on the phytotoxicity of lithium[☆]

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ABSTRACT

The growing use of lithium (Li) in industrial and energetic applications and the inability to completely recycle the alkali metal will most likely increase anthropogenic emissions and environmental concentrations in the future. Although non-essential to plants, Li^+ is an important ultra-trace element in the animal and human diet and is also used in the treatment of e.g. mental disorders. Most of the lithium is consumed with the drinking water and vegetables, but concentrations in foodstuffs vary with the geochemistry of the element. In order to identify potential risks and to avoid an overmedication due to consumption of Li rich or Li contaminated foods it is advisable to identify background levels and to derive recommended Daily Allowances (RDAs) for the element. Although Germany does not possess large amounts of primary or secondary resources of lithium, geochemical investigations (mineral and ground waters and soils) in this country confirm a wide variation of environmental concentrations with generally higher levels in the southwest. Despite the large number of soil and water data, only very few data exist on lithium concentrations in plants and its phytotoxicity. Within the scope of present study common grassland plant species were sampled in regions of SW-Germany with reportedly high geogenic levels of Li. The data are discussed with regard to literature surveys and existing reference values. Since lithium has phytotoxic effects a greenhouse experiment was performed with different Li salts (LiCl and Li_2CO_3) and plant species (maize, bean and buckwheat) to derive dose-response relationships for the endpoint shoot growth. While corn growth was not reduced significantly by soil concentrations of 118 ppm, EC50 values in buckwheat were 47 and 16 ppm for lithium derived from LiCl and Li_2CO_3, respectively.

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1. Introduction

Lithium is a relative abundant alkali metal, reaching 6‰ in the upper continental crust (Wietelmann and Bauer, 2000; Wietelmann and Steinbild, 2013). Primary sources stem from granitic pegmatites in the minerals spodumen and lepidolith, while secondary resources comprise various lithium salts resulting from the weathering of Li^+ rich minerals accumulating in the brines of large salt lakes (e.g. Salar de Uyuni, Bolivia). Concentrations of Li^+ in primary and secondary sources as well as in-situ resources of the largest deposits are given by Gruber et al. (2011). Global recoverable resources are estimated to range between 13 and 18 million tons, with largest secondary reserves in Chile, Argentina and Bolivia (Gruber et al., 2011; Gernuks, 2013). Currently, 500.000 tons per annum are produced worldwide.

During the last two decades, Li has gained enormous economic and geopolitical importance due to its growing use in mobile communication systems, cordless power tools and electric vehicles (Umweltbundesamt, 2011). One third each of the processed lithium are used for the production of primary and secondary batteries and as floating agents in the glass and ceramic industry (Jaskula, 2011, 2012). Other uses are the production of lubricants (12%), while only 2% of the lithium are used in the pharmaceutical sector. The projected boom of the E-mobility as well as the transition to renewable energies will increase the demand for Li based energy storage systems. Due to the rising prices, much of the material used in Li ion batteries (LIBs) will have to be re-used as a secondary raw

material in the future (Gernuks, 2013; Hanisch et al., 2015). However, this involves mainly the transition metals Co, Cu, Ni and Mn, while Li recycling is not yet economically feasible. Currently, the collection rate of Li batteries and accumulators amounts to 40% in Germany, but information on how much material is being recycled and will be recyclable is not available (Umweltbundesamt, 2012).

Although no data are at hand on industrial releases (emission inventories) and discharges of lithium from E-waste and other sources, it can be assumed that the element will become more ubiquitous and locally reach higher environmental concentrations. Another pathway by which lithium may enter the environment are pharmaceutical residues from sewage treatment facilities. According to the German Drug Report, 70.000 packages of the mood stabilizer lithium carbonate (ATC-Code: N05AN01) are sold yearly (Glaeske and Schicktanz, 2013), which equals 2.8 t of Li_2CO_3. It has been shown that large quantities of pharmaceuticals including synthetic organic anti-depressants can enter the water cycle (Umweltbundesamt, 2014; Schlüsener et al., 2015), but the environmental concentrations of inorganic lithium salts have not been addressed yet.

The mood stabilizing effect of the alkali metal e.g. in natural spring waters or as an additive to beverages had been suspected for over a century, but only after the 1950s Li therapies were introduced to treat mental disorders. Although most of the involved physiological mechanisms remain unclear, it is now generally agreed that lithium is an essential ultramicronutrient in the human and animal diet (Schrauzer, 2002). Meanwhile, Recommended Daily Allowances (RDAs) in the range of 1 mg per person with a standard body weight of 70 kg have been proposed (EPA, 2007; Gallicchio, 2011; Schäfer, 2012). Nevertheless, reference values for lithium in foods have not yet been established (Ekmekcioglu, 2006; DGE, 2013), which is partly due to the lack of information on lithium concentrations. Most of the available data refer to ground and bottled waters (Birke et al., 2010; Reimann and Birke, 2010; BGR, 2014), but analyses of Li^+ in drinking waters is not compulsory. Anke et al. (1998), however, have presented data from various foodstuffs and beverages.

Recent investigations in Austria, Japan and Texas (Kapusta et al., 2011; Helbig et al., 2012; Sugawara et al., 2013; Blüml et al., 2013) found an inverse relationship between suicide rates and the concentrations of lithium in drinking waters. Furthermore, Young (2011) suggests that lithium may prevent dementia. Although such correlative studies may not explain the cause and the effects, some doctors suggest enriching drinking waters with lithium to stimulate the mental health of the population (Spitzer and Graf, 2010). No information exists on the lithium exposure of workers and the general public that comes from air pollution and lithium deposition being caused by the ever growing industrial uses of the alkali metal. However, Anderson (1990) showed phytotoxic responses in a number of plant species that were exposed to low levels of lithium containing air pollutants near a not further specified source in North Carolina. Since environmental levels of lithium and the exposure of biota will be increasing in the future, environmental health criteria will be needed. Potentially positive effects of the increasing exposure to the element on the mental health in few people may be outweighed by negative effects of rising lithium levels e.g. kidney diseases in many people.

Despite present paper focuses on the uptake of lithium in plants, Fig. 1 introduces a summary of reported levels in different environmental media. While Markert (1992) gives an average concentration of 0.2 ppm for his "reference plant", other authors found much higher levels in plants in dry land areas (e.g. Aral and Vecchio-Sadus, 2008; Ammari et al., 2011; Figueroa et al., 2013). Li levels are lower in fungi on average (0.189 ppm) than in plants and dicots reach higher levels than monocots (Vetter, 2005).

According to Macholz and Lewerenz (1989), leafy vegetables will have much higher Li concentrations than seeds, indicating that the element is easily translocated via the xylem with the transpiration stream. It is generally agreed that lithium is non-essential to plants but can soon reach phytotoxic levels.

Main objective of the study was to determine lithium levels in plants from different regions of Southwestern Germany, where the geology and weathering processes would lead to potentially higher soil concentrations. Common grassland species were analyzed for lithium to study regional patterns and potentially different accumulation potentials in different species. Since lithium has been described as being highly phytotoxic at soil levels of above 50 ppm (Frerking, 1915; Bingham et al., 1964; Sneva, 1979; Jurkowska et al., 1997; Hawrylak-Nowak et al., 2012; Yalamanchali, 2012), we performed a growth experiment with various crop species using different Li salts and concentrations.

2. Materials and methods

2.1. Field study

Reports from European and national geochemical analyses were used to identify areas with potentially high lithium background levels. According to the Geochemical Atlas of Western Germany (Fauth et al., 1985) in which over 53.000 stream sediments had been analyzed, a clear regional pattern can be observed. Highest concentrations of over 60 ppm Li occur in the Devonian (Rhenanian) Slate Regions and the Southern Mesozoic Areas, whereas the quaternary regions e.g. the sandy soils in Northern Germany show low lithium levels of <10 ppm. A similar pattern with lower levels in the younger European sediments as compared to the older bedrocks in the Southern areas has been observed in the Geochemical Baseline Mapping Programme (Salminen et al., 2005) and the Geochemical Mapping of Agricultural and Grazing Land Soil (GEMAS) by Reimann et al. (2014). According to these data, highest lithium levels of over 80 ppm occur in the top soils of Southwest Germany, but sampling density was too low for the full spatial representativeness of soil lithium contents. However, it can be concluded that regions made up of Upper Triassic cuesta and sandstone mountains and the Devonian slates generally have elevated lithium contents, so that plants growing on these soils should contain higher levels of this element than those thriving on young diluvial sands and peatlands (Szentmihályi et al., 1983; Regius et al., 1983). At the same time, it can be hypothesized from Geochemical Mapping that there may be regions in the EU where soil lithium concentrations could naturally exceed the phytotoxic threshold of 50 ppm.

Sampling of 13 common grassland species (see Table 2) took place in June 2015. Based on the available geochemical information, plant samples were collected at random at 60 locations in four study regions with elevated lithium soil levels: the Saar-Hunsrück Mountains (73 samples from 27 sites), the Black Forest (33 samples from 15 sites), the Swabian cuesta and sandstone mountains (24 samples from 15 sites) and the Saar-Nahe region (6 samples from 1 site). The analyses served as a first orientation for lithium plant levels in SW-Germany, while a grid-based approach and a high sampling frequency would have to be used to be fully representative for the study region. Furthermore, four samples were collected at a distance of 50 m downwind from gradation works in two German spa resorts (Bad Westernkotten and Bad Münster am Stein). We hypothesized that aerosols from these installations would deposit onto nearby vegetation and lead to elevated levels of lithium.

Table 1 gives an overview of the geology of the regions and results of the lithium analyses, while Table 2 gives a summary of the
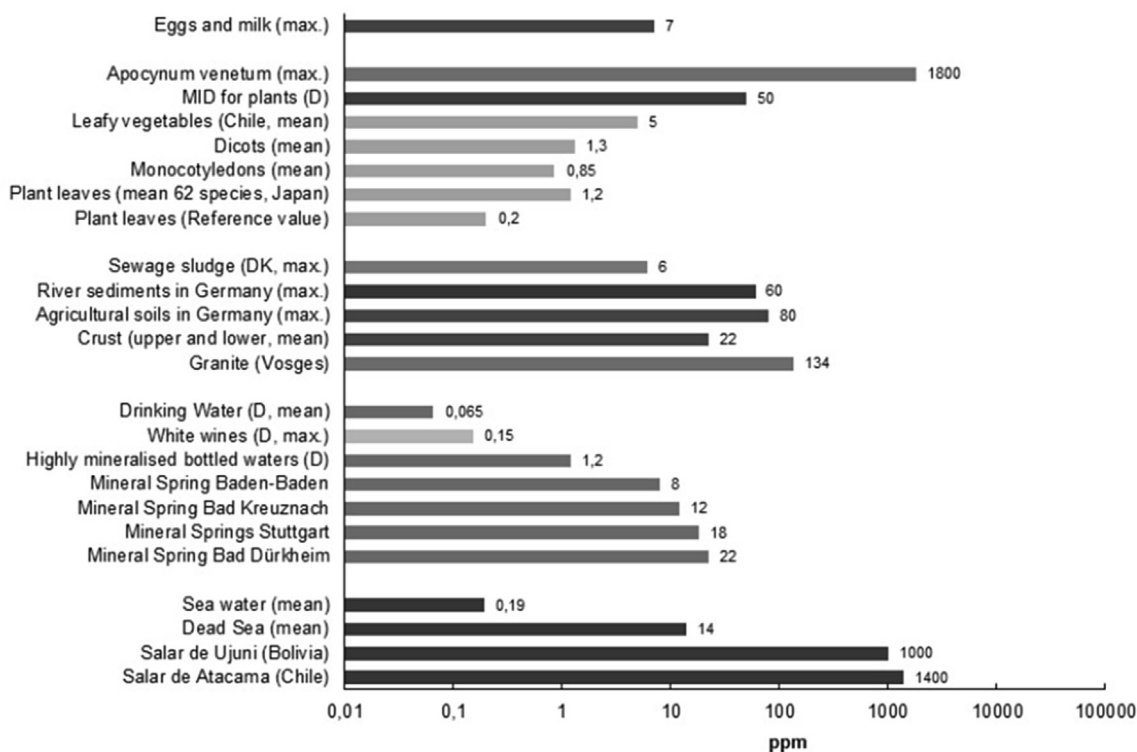
Fig. 1. Concentrations of lithium (mean or maximum) in waters, rocks, sediments, soils, plants, beverages and foods. Data were compiled from Ogawa et al. (2014), Li Jiang et al. (2014), Reimann et al. (2014), BGR (2014), Ternes (2013), Figueroa et al. (2013), Birke et al. (2010), Lemarchand et al. (2010), Aral and Vecchio-Sadus (2008), Bäderbetriebe Stuttgart (2008), VDI (2006), Castiñeira-Gomez (2004), Kjølholt et al. (2003), Jäger (2002), Anke et al. (1998), Wedepohl (1995), Markert (1992); Maarse et al. (1987), Fauth et al. (1985), Memon et al. (1983) and Cannon et al. (1975).

Table 1
Number of plant samples and lithium leaf levels determined in four study regions and at German salinas.

Study region or sites	Plant samples (n)	Li concentrations (ppm)	
		$\overline{x}$	Range
Saar-Hunsrück	73	0.34	(0.03–3.26)
Black Forest	33	4.5	(0.06–105.7)
Schwäbische Gäue	22	0.81	(0.01–5.01)
Saar-Nahe	6	0.5	(0.03–2.16)
Gradation Works	4	5.2	(0.16–10.1)

identity and number of plant species that were sampled including the lithium levels (see results). Sampling took place in June and July 2015. Coordinates, altitude above sea level and photographs of the sampling locations were recorded using a GPS-camera. Plant leaves were collected manually, stored and dried in a drying cabinet to constant weight in labeled paper bags.

2.2. Growth experiment

To address potential phytotoxic effects of lithium in different plant species, the four crop species buckwheat (*Fagopyrum esculentum* L.), corn (*Zea mays* L.), garden bean (*Phaseolus vulgaris* L.), spelt wheat (*Triticum spelta* L.) and the common wild species ribwort plantain (*Plantago media* L.) were cultivated in plastic pots (h: 6.8 cm, Ø: 9 cm, A: 63.9 cm^2, Volume: 0.344 L) in a greenhouse experiment. Three seeds were sown per pot. The soil substrate consisted of a 1:1 (vol/vol) mixture of washed river sand and a standard growth substrate (Fruhstorfer LD80, Achut GmbH). The material is a mixture of peat, volcanic clay, bark

humus and a slow release fertilizer. It has a pH of 5.9 and contains 35% organic matter. Nutrient supply amounted to 150 mg L^{-1} nitrogen and P$_2$O$_5$ each and to 250 mg L^{-1} for K$_2$O. Chemical analyses yielded a mean concentration of 2 ppm Li in the mixed substrate.

Each pot was filled with 250 g of the substrate mixture and 100 mL pot^{-1} of lithium solutions were applied to the pots containing 2000, 1000, 500, 200, 100, 20 and 0 ppm Li yielding seven lithium treatments in total, representing 800, 400, 200, 80, 40, 8 and 0 mg kg^{-1} soil. Two forms of lithium, LiCl (CAS 7447-41-8, EMSURE, Merck, Darmstadt) and Li$_2$CO$_3$ (CAS 554-13-2, SIGMA Aldrich) were used in the experiment, to see whether the higher solubility of LiCl would lead to higher uptake rates and phytotoxicity than lithium carbonate. A control group of plants was exposed to different concentrations of NaCl to study whether sodium created different effects than lithium and whether the anticipated effects of LiCl could be related to chloride. Three replicates per concentration, salt and species were used in the experiment and the resulting 285 pots were randomized on large tables once a week. Experiments were performed in a greenhouse in June 2015 without the supply of extra light. Plants were watered on demand. To avoid leakage from pots, saucers were placed underneath the pots.

Germination rates, shoot length increments and the development of leaf damage were thoroughly followed throughout the experiment. Three days after germination, the number of seedlings was reduced to one plant per pot to avoid intraspecific competition. Shoot mass of plants was harvested two weeks after germination. Fresh and dry shoot mass served as response parameters to derive dose response curves and effective concentrations that created an adverse effect of 50% (EC$_{50}$).

Table 2
Median element concentrations in thirteen plant species collected in the field study as compared to those indicated for the "reference plant" by Markert (1992). Color formatting of cells in the same column enables the reader to identify low (green) and high (red) element concentrations.

Plant species	Samples (n)	Li	Ca	K	Mg	Na	Fe	Co	Ni
Plantago lanceolata L.	42	0.42	18283	25043	3023	843	173	0.15	0.6
Rumex obtusifolius L.	17	0.16	11473	33236	7233	56	94	0.12	1.0
Urtica dioica L.	15	0.14	37134	23658	4435	47	174	0.05	0.7
Hypericum perforatum L.	12	0.05	4030	13241	2393	10	66	0.13	0.9
Vitis vinifera L.	8	0.05	10528	16691	2263	40	78	0.05	0.7
Tanacetum vulgare L.	7	1.09	24252	30656	3885	25	85	0.15	0.5
Cirsium arvense (L.) Scop.	7	0.09	7284	35400	2724	24	90	0.07	1.4
Solidago canadensis L.	6	0.24	16961	23576	3999	23	103	0.18	0.5
Centaurea jacea L.	6	0.37	9831	28120	3035	21	110	0.05	0.2
Teucrium scorodonia L.	4	0.19	38771	55675	2754	109	152	0.12	1.7
Echium vulgare L.	4	0.23	9884	13860	1790	37	154	0.14	1.9
Rumex acetosa L.	2	0.15	24425	22281	8349	1535	173	0.13	1.6
Ranunculus sardous Crantz	1	2.16	11594	17299	2090	157	140	0.14	2.1
Reference Plant (Markert, 1992)		0.2	10000	19000	2000	150	150	0.2	1.5

2.3. Chemical analyses

Dried plant material from the field and the phytotoxicity study was ground with a zirconium ball mill (MM2000, Retsch GmbH Haan, Germany) and subjected to element analyses. After microwave digestion of the samples and reference materials in nitric acid, levels of Ca, K, Mg, Na and Fe were determined by inductively coupled plasma optical emission spectrometry using an ICP-OES Vista-PRO (Varian, Germany). External calibration was made using the multi-element standard solution ESI-2 (Inorganic Ventures, USA). Since ICP-OES proved to be too insensitive for lithium in the low concentration range, inductively coupled plasma mass spectrometry (ICP-MS NexION 300×, Perkin Elmer, Germany) was used for the analyses. External calibration was made using the ICP multi-element standard VI (Merck, Germany). In the samples from the field, lithium was determined using mass 7, since on a global scale ^7Li is by far the dominant (92.4%) isotope. However, lithium analyses in corn leaves from the phytotoxicity study were based on mass 6 since ^6Li gave more stable results in the higher concentration range. A high coefficient of determination (R^2 0.99) was obtained between the results determined with the masses 6 and 7. The overall limit of detection (LOD) was 0.05 ppm and the repeated determination of blind values and reference materials served as a quality control of the analyses. The concentrations of Ni and Co were also determined by ICP-MS.

2.4. Statistics

Descriptive statistics and histograms served to derive and visualize mean, minimum and maximum concentrations determined in the different plant species, study sites and sampling regions.

Results from the phytotoxicity study were analyzed using the 'drc' package available for the statistical software R (Venables and Ripley, 2001; Ritz and Streibig, 2005). Four parameter log-logistic regressions and Cedergreen-Ritz-Streibig hormetic dose-response models were fit to the data resulting in dose-response curves, from which EC_{50} values could be derived.

3. Results and discussion

3.1. Field study

Tables 1 and 2 give the concentration ranges and means of lithium leaf levels in the different study regions and plant species, respectively. Highest lithium concentrations of 105.7 ppm were determined in thistle leaves that were collected near a granite quarry in the Black Forest. Since it is known that granite may contain high levels of lithium, we hypothesized that elevated concentrations at this site will partly result from dust deposition. In the nearby granites of the French Vosges, Lemarchand et al. (2010) found Li levels of 134 ppm, which are only slightly higher than the levels determined in thistle leaves.

In order to differentiate between external and internal lithium, we rinsed half of the leaf sample with deionised water and compared the levels of washed and unwashed samples. Washing reduced levels by 20%, indicating that deposition of minerals and soil particles may indeed elevate Li concentrations in plants. Interestingly in the Saar-Hunsrück region, Li concentrations were higher in plants of *P. lanceolata* that stemmed from open land or were collected in close vicinity to vineyards as compared to samples from dense grassland stands (data on spatial differences not shown). It is thus likely that deep ploughing (rigole soils) in vineyards and weathering will release much lithium from the Devonian slates and that dust particles blown to adjacent vegetation can raise the levels. Also the elevated Li concentrations observed in the stream sediments in the region (Fauth et al., 1985) in open landscapes as compared to the closed forests suggest the release of lithium via suspended soil particles from local agricultural and viticultural activities. In the end, the elevated concentrations of lithium in plants collected near gradation works give further support for the importance of deposition of Li containing particles and

aerosols.

The high average Li concentrations in plant leaves from German salinas are comparable to those reported for crops on saline soils in Chile by Figueroa et al. (2013), see Fig. 1. Second highest lithium levels of on average 4.5 ppm were found in the samples from the Black Forest, with higher values on granite as compared to the sandstone substrates (data not further separated after geology). Third highest plant lithium concentrations of 0.81 ppm were determined in the samples from the Swabian Keuper and Muschelkalk regions. Plant lithium concentrations (average of 0.34 ppm) were lowest in the Saar-Hunsrück region and were much lower than the values of over 60 ppm reported in stream sediments of the same region by Fauth et al. (1985). Also the values from Li leaf analyses from the Saar-Nahe site with a mean value of 0.49 ppm were much lower than the soil concentrations of 84 ppm Li determined at the same location in the GEMAS-Project (Reimann et al., 2014). It must be noted that geochemical studies are based on total amounts that do not necessarily reflect how much lithium will be available to plants via cation exchange from clay minerals. Pasture concentrations of lithium were in the range from 0.5 to 6 ppm and also much lower than soil concentrations (0.08–92 ppm) in New Zealand (Yalamanchali, 2012), but plant lithium concentrations were positively associated with the clay content of soils. In a Japanese study with 61 species, Memon et al. (1983) found a mean lithium level of 1.2 ppm (0.11–45 ppm) as compared to 1.55 ppm in present study. When omitting the extraordinary high Li value determined near the granite quarry in the Black Forest, the grand mean in this region reduces to 0.78 ppm. Overall, the mean lithium levels were still three times higher than the value of 0.2 ppm suggested for a "reference plant" by Markert (1992). However, only the above-mentioned sample from the granite quarry had an analytical value above the feed limit concentration of 50 ppm Li for the protection of farm animals established by VDI (2006).

In order to study relationships between lithium and the elements Na, K, Mg, Ca, Fe, Ni and Co, correlation matrices were derived differentiating between study regions and individual plant species. Highest positive relationships were observed between Li and Fe levels in leaf samples from the Saar Hunsrück ($r = 0.94$) and the Black Forest ($r = 0.46$) regions (see Fig. 2c), while element concentrations were only slightly and insignificantly related to lithium in other geological backgrounds and in the same plant species that were collected in different regions. Positive significant relationships were also noted between lithium and the heavy metals Ni and Co in plant leaves from the Saar-Hunsrück region, which was observed before by Lambert (1983) in grassland samples from the Belgian Ardennes, a region sharing the same Devonian geology.

Median element concentrations in leaves from different plant species are presented in Table 2. In total thirteen plant species were sampled, in which apart from lithium, concentrations of Ca, K, Mg, Na and the metals Co, Fe and Ni were determined. While concentrations among species varied by less than a factor of 10 for the heavy metals, K, Ca and Mg, lithium and sodium concentrations varied by factors of 24 and 150, respectively. The wide variation suggests that there are species-specific differences in the accumulation potentials of macro-, micro and ultra-trace elements, but side-by-side comparisons on the same sampling sites would have to be performed to identify lithium accumulators.

Out of the six species sampled at a site with high Li soil levels in the Saar-Nahe region, *Ranunculus sardous* had the highest lithium concentrations. Hairy buttercup is a potential halophyte and is recognized as a problem weed that is avoided by grazers and resistant to herbicides (Cordes and Winkelmann, 2008; Eerens and Mellsop, 2008). Further buttercup species have been described as lithium accumulators. *R. repens* accumulated over 20 ppm Li in Poland (Lambert, 1983), while 7 ppm Li had been found in *R. polyanthemos* in Hungary (Tölgyesi, 1983). In general, grasses accumulate less Li than herbs and young plants will have higher Li levels than old plants (Lambert, 1983). Further information on plant lithium levels in highly Li rich sediments is available from Cannon et al. (1975) pointing out that highest concentrations may be observed in the Chenopodiaceae family.

3.2. Greenhouse trial on the phytotoxicity of lithium salts

Since spelt and ribwort plantain did not germinate readily, only the results from buckwheat, corn and garden bean were evaluated in present study. Fig. 3a gives an impression on the response of corn to seven soil concentrations administered by the use of the three tested salts. A clear reduction in shoot length above a soil Li concentration of >80 ppm was observed in both Li salts, while NaCl did not create negative effects even at the highest sodium concentration of 800 ppm.

Shoot dry mass decreases with increasing soil Li levels are shown in Fig. 3b, while the lithium concentrations in leaves are related to soil lithium levels in Fig. 3c. Corn leaves exposed to a soil concentration of 400 ppm showed lithium accumulation by a factor of 10 in Li_2CO_3 exposed soil and an even higher enrichment if the lithium was supplied as LiCl. At the same time sodium analyses made in the corn leaves indicate that sodium transfer rates from soil to corn leaves only reached a factor of 4 (data not shown).

It therefore appears that lithium is accumulating at higher rates in plant leaves than the element sodium. A reason may be that the small ion lithium is more mobile than the essential plant nutrient sodium. Nevertheless, LiCl has a lower solubility in water than NaCl, but solubility in plant tissues depends on pH and the presence of e.g. organic acids. Due to the slightly acidic pH (5.9) of the substrate we used, a relatively high availability of lithium and thus a high transfer factor (see below) can be suggested.

Another outcome was that calcium, magnesium and potassium levels decreased sharply in corn leaves from plants that were grown on lithium treated soils, while the metal levels Fe, Ni and Co were unaffected (data not shown). In contrast to the different soil Li concentrations, NaCl treatments did not affect the leaf levels of these essential nutrients. Calcium concentrations in corn leaves decreased from 8.000 in the control to 2.000 ppm in the plants that were grown on soil with a concentration of 400 ppm Li (lithium chloride). In contrast, magnesium and potassium concentrations were only reduced by 50%. Interactions between lithium and calcium and to a lower extent the other alkali metals have been suggested before by Shkolnik (1984), which may be related to the blocking of carrier enzyme systems and a reduction of the cellular transport through membranes. Already Frerking (1915) noted an antagonism between lithium and calcium, but the effects of ion ratios on membranes and metabolism are still unclear (Anderson, 1990). While lithium prevents the uptake of calcium, high calcium soil levels will limit the toxic effects of lithium. Calcicole plant species might therefore show lower levels of the element and should be better protected against phytotoxic effects of lithium at their natural environment. On the other hand organisms preferring high calcium levels or physiological processes depending on calcium might be affected strongly if lithium levels reduce the uptake of calcium in places with a low calcium supply. The results indicate that Li-salts and NaCl will cause different responses in plants that involve changes in ionic ratios, membrane properties and osmotic adjustments via ion channels. Interestingly, plants exposed to increased soil lithium had higher Na-levels in their tissues (data not shown) indicating co-uptake of the elements.

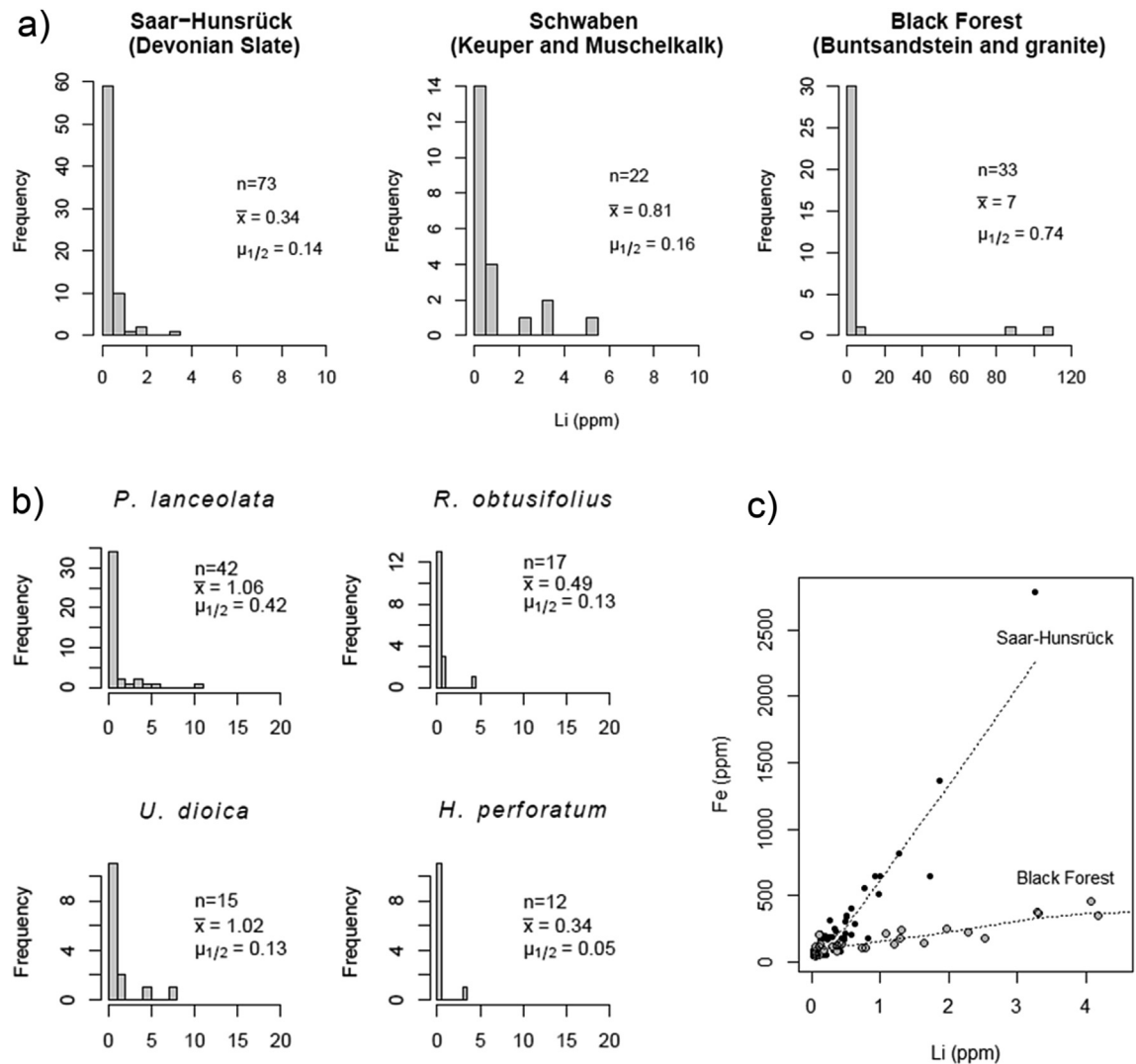Based on the response parameter shoot mass, an EC_{50} of

Fig. 2. Histograms of lithium leaf levels after three study regions (a) and four plant species (b) and relationships between Fe and Li concentrations (c).

118 ppm was derived for LiCl-Li in corn, while lower effective doses of 55 and 47 ppm were derived for garden bean and buckwheat, respectively (Fig. 4). EC_{50} values for Li_2CO_3-Li (data not shown) were higher in corn (171 ppm) and bean (71 ppm), but lower in buckwheat (16 ppm). Interestingly, toxicity was inversely related to relative growth rate (RGR) in both lithium salts, indicating that the acquisition of carbon may mitigate direct and indirect effects of lithium toxicity.

Kalinowska et al. (2013) also addressed differences in lithium toxicity resulting from different chemical forms. While in hydroponic culture LiOH reduced the yield in lettuce at a Li concentration of 20 ppm, effects of LiCl were only significant at a concentration of 50 ppm. Interestingly, LiCl created growth stimulations at Li concentrations of 8 ppm in present study. Also Anderson (1990), Jurkowska et al. (1997) and Aral and Vecchio-Sadus (2008) found that plant growth of some species may profit from soil Li concentrations of up to 5 ppm, while concentrations of over 15 and 60 ppm have been reported to reduce the growth of roots and shoots, respectively (Sneva, 1979).

At the highest concentration of LiCl, an enrichment factor ($EF_{soil\ to\ plant}$) of 12 was observed in corn. Hawrylak-Nowak et al. (2012) and Kalinowska et al. (2013) found very similar results for the same species in hydroponic cultures. In contrast, Sneva (1979) found an enrichment factor of 70 in *Poa ampla* in shoots of soil grown plants, while lower Li accumulation was observed in the plant roots. This suggests some limiting dose-dependent steps in the processes involved in Li uptake, translocation and accumulation by different plant species.

4. Conclusions

Although lithium levels of over 50 ppm have been reported in some agricultural soils in SW-Germany present investigation on lithium in common grassland species indicates that the alkali metal does not reach high concentrations in plant leaves in undisturbed conditions. An exception was the high level determined in thistles growing on granitic bedrock in the Black Forest. Besides the uptake of mobile lithium from the soil solution plant unavailable lithium is probably deposited with aerosols and dust from nearby operations (blow off from gradation works, brines, spodumene mines and quarries). Emission inventories for lithium (e.g. manufacturing of LiB's, lubricants, ceramics and glasses) are however unavailable so that potential industrial hotspots cannot be identified. Based on the results from the field study a strong positive relationship was only observed between iron and lithium levels in plants from the Devonian region, while in other regions element concentrations
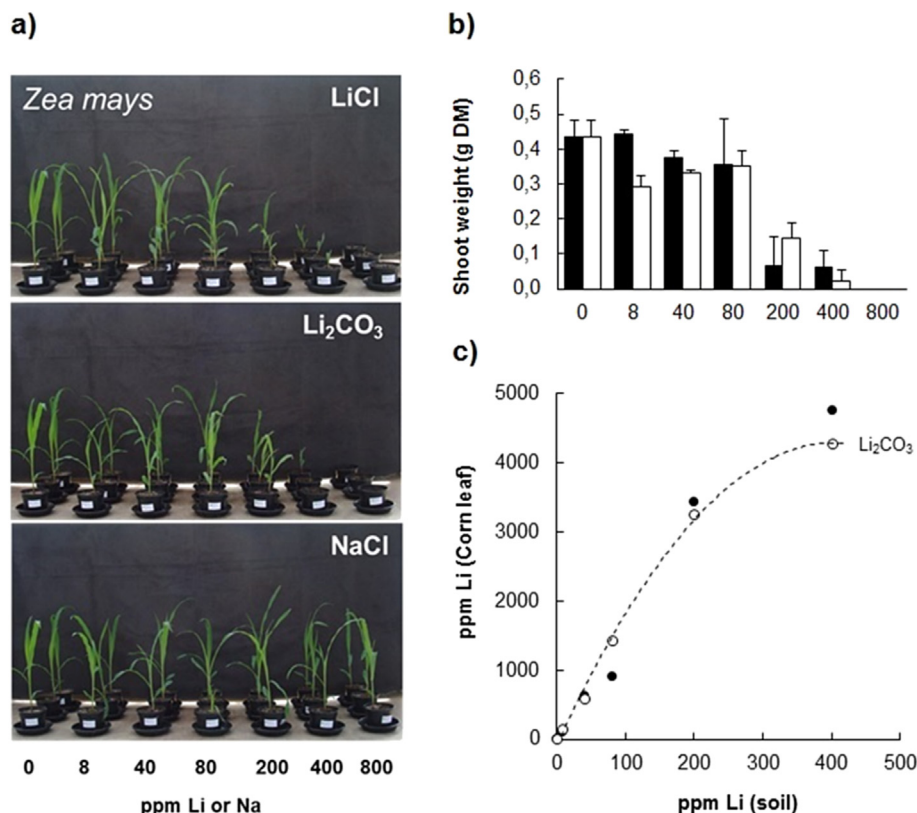
Fig. 3. a) Growth response of corn to increasing concentrations (from left to right) of lithium and sodium supplied in different chemical forms, b) mean shoot dry weights (+sd) determined in the different lithium treatments (open bars: Li_2CO_3, closed bars: LiCl) and c) relationship between Li concentrations determined in the soil and the corn shoots.
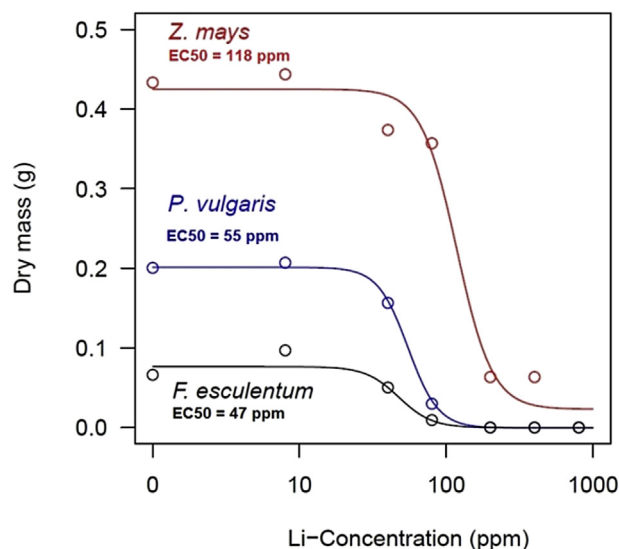

Fig. 4. Dose-response relationships between Li concentrations (as LiCl) and shoot growth in corn, garden bean and buckwheat.

proved to be largely unrelated.

The phytotoxicity study confirmed strong differences in the sensitivity of crop species to lithium with corn being the most tolerant out of the tested species. Nevertheless, a sharp decrease in the concentrations of macroelements was observed in plants without foliar symptoms confirming that plant nutrition and crop quality may be affected in lithium enriched soils. While further investigations on anthropogenic lithium emissions and their effect on nearby ecosystems should be performed to understand the environmental behaviour of the potentially emergent pollutant, phytoremediation studies at former lithium mines (Elektorowicz and Keropian, 2015) could help to mitigate environmental risks of lithium and the associated heavy metals in the future.

Acknowledgments

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