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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.

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

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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