

**A comparative assessment of lesser-studied trace elements in the soil-plant system:  
implications for environmental quality**

## **Notes on the thesis and contributions by others**

**This thesis has been prepared as a series of manuscripts, two of which have been published. Note that there is necessarily repetition in the introduction sections of the thesis Chapters.**

Chapter 6: Samples collected by Rene Reiser and samples analysed for Iodine by Barbara Orth.

## **Publications arising from thesis**

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## Acronyms and abbreviations

**BAC** Bioaccumulation coefficient

**dl** Detection limit

**ETEC** Emerging trace element contaminant

**GOO** Peaty orthic gley soil

**K<sub>d</sub>** Distribution coefficient

**OM** Organic matter

**REE** Rare earth element

**RFMW** Mottled-weathered fluvial recent soil

**RFT** Typic fluvial recent soil

**TE** Trace element

**TF** Translocation factor

## Abstract

The study of the chemical elements in the environment has focused on common, easily measured nutrients and contaminants that commonly affect humans and ecosystems. Technological development has resulted in the increased use of chemical elements that have received scant scientific attention as environmental contaminants. These Emerging Trace Element Contaminants (ETECs), include (in order of atomic number) beryllium (Be), gallium (Ga), indium (In), tellurium (Te), lanthanum (La), cerium (Ce), neodymium (Nd), gadolinium (Gd), and bismuth (Bi). Similarly, studies on iodine (I) have been limited due to analytical challenges.

The behaviour of ETECs and I in the soil – plant system is critical to understanding how these elements may affect humans and ecosystems. This thesis aimed to quantify the comparative behaviour of the ETECs and I in the soil-plant system, and determine the factors affecting their mobility. The ETECs were compared to cadmium (Cd), a well-studied relatively mobile contaminant. When the capacity of the ETECs and Cd to sorb to soil was measured in spiked soil, solid-solution distribution coefficients ( $K_D$ ) increased:  $I < Cd < Be < In < La < Ce < Nd < Gd < Ga$ , from  $<1$  (I) to  $>800$  (Ga). Bismuth and Te formed insoluble precipitates in solution thus had higher  $K_D$  than the other ETECs and Cd, although their values could not be quantified.  $K_D$  was highest for the trivalent cations, and within the same valency,  $K_D$  increased with ionic potential. The  $K_D$  values of Be, Cd, La, Ce, Nd, and Gd increased exponentially with increasing pH, which is typical for cations. In contrast the  $K_D$  of Ga increased from pH 4.5-6 then decreased at pH  $>6$ . The pH had little effect on the  $K_D$  of In. As the concentration of the ETECs added to soil increased, the  $K_D$  of Be, La, Ce, Nd, and Gd decreased due to saturation of sorption sites, however, the  $K_D$  of Ga and In increased due to precipitation. Langmuir and Freundlich sorption isotherms described the soil: solution partitioning of Be, Cd, La, Ce, Nd, and Gd at concentrations  $<100 \text{ mg L}^{-1}$  in ambient solution. However, the fit was poor at  $100 \text{ mg L}^{-1}$  TE added to solution, and for Ga and In.

Plant uptake was determined using experiments with perennial ryegrass (*Lolium perenne*) in pot trials using spiked soil that had been left to equilibrate. Bioaccumulation coefficients (BACs) increased in the order  $Ce < In < Nd \cong Gd < La \cong Be \cong Ga < Cd < I$ . Due to plant uptake and the phytotoxicity thresholds, Be and La are the ETECs likely to be taken up and translocated into above-ground biomass at high concentrations. Analyses of *Camellia sinensis* (common tea, an aluminium hyperaccumulator) leaves revealed concentrations of In, La, Ce, Nd, and Gd that were higher than concentrations in *Camellia sinensis* than in *L. perenne* growing in unspiked soil, but less (except for In) than *L. perenne* growing in soil spiked with 20x the background concentration.

Analysis of the concentrations of I, in New Zealand pastures revealed that distance to the coast had a stronger correlation with pasture I concentrations than soil I concentrations, due to the sea being a source of I to plants and soil. As a monovalent anion,  $K_D$  of I in soil was less than the ETECs and Cd, and bioaccumulation factors (BACs) in perennial ryegrass were higher than the ETECs and Cd.

For elements with atomic numbers 13 (Al) – 49 (In), there was a significant negative correlation between their respective  $K_D$  values and the Me-O bond length in the hydrated ions. Therefore, Me-O bond length could be used to calculate  $K_D$  and of ETECs in uncontaminated soils. A similar negative correlation existed for the Rare Earth Elements. As  $K_D$  was inversely proportional to BAC, the Me-O bond length could also indicate plant uptake.

Due to their strong sorption to soil and limited leaching and plant uptake, the most likely exposure pathway for Be, Ga, In, La, Ce, Nd, and Gd to enter humans is through the ingestion of contaminated soil, either directly (pica children, dust) or indirectly (soil particles attached to plants). Sites contaminated with ETECs should be managed to reduce soil erosion and thus reduce the fluxes of these elements. Future work should quantify interspecific differences in plant uptake of ETECs, analyse the distribution of the ETECs in plant material surrounding contaminated locations, and determine the bioaccessability of ETECs to humans and other organisms.

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Date: 10/02/2022

# 1. Introduction

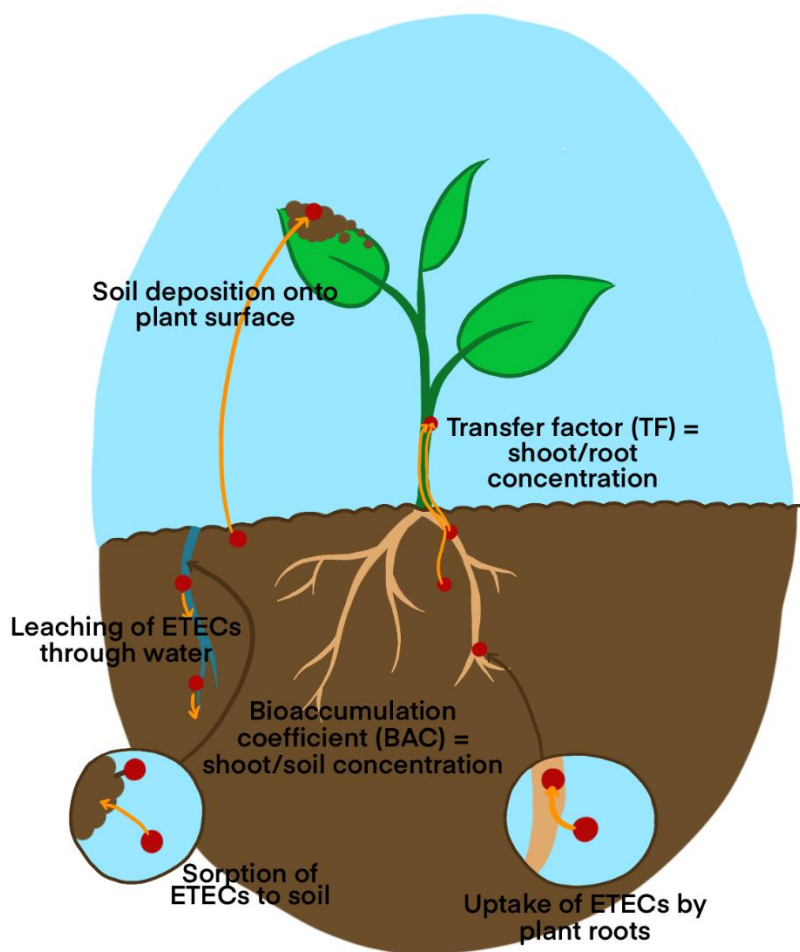
## 1.1. Emerging Trace Element Contaminants and Iodine

Trace elements occur at  $<1000 \text{ mg kg}^{-1}$  in organisms and include 82 of the 92 natural elements. Just 7-10 trace elements (depending on the organism) are essential for lifecycle completion. Some of the remaining 72 elements (such as Li, F, and lanthanides) are occasionally beneficial (Robinson et al., 2009; Schäfer, 2012; Tyler, 2004b). Soil is the largest source of trace elements to terrestrial organisms (West, 1981). Due to strong retention to the soil matrix and the inability to degrade to less harmful forms (unlike organic molecules), most trace elements accumulate in soil (Hooda, 2010; McLaren & Cameron, 1996).

Technological development has created novel uses for many trace elements that have received scant scientific attention as environmental contaminants. These include Be, Ga, In, Te, La, Ce, Nd, Gd, Bi henceforth referred to as Emerging Environmental Contaminants (ETECs), which are increasingly extracted, used, and disposed of into the biosphere thereby increasing the likelihood of soil contamination. In particular, these elements may be discharged uncontrolled into the environment from the informal reprocessing of electronic waste, end-of-life electronic products (e-waste) (Robinson, 2009). Soil contamination through e-waste has predominantly been limited to developing countries through acceptance and rudimentary recycling of electronic equipment. However, the recent reduction in these countries accepting e-waste and lack of efficient and accessible recycling centres in developed countries (Patil & Ramakrishna, 2020) means that most of the electronic equipment will be disposed of into landfills in the future (Shaikh et al., 2020). Thus, ETECs released into soil as landfill leachate, or be disposed of in inappropriate locations such as lakes, rivers, and rural areas, where exposure to water and air will release the ETECs and carry them into soil. In soil, ETECs may leach into receiving waters or be taken up by plants, further endangering humans and ecosystems.

Iodine (I) is a lesser-studied trace element that is essential for animals but not plants (Robinson et al., 2009), therefore plants have not evolved specific mechanisms for the uptake of I, and animal deficiencies can arise (Whitehead, 1984). Research into the mobility of I has also been limited, due to the lack of accuracy and sensitivity of measurement before Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) methods were developed (Fuge & Johnson, 2015; Humphrey et al., 2018).

As with other moieties in soil, the migration of ETECs and I into receiving waters or into plants is dependent on the concentration of the element present in soil solution (Hooda, 2010). The other method by which ETECs enter plant shoots is by the deposition of soil containing sorbed ETECs onto the surface of plant leaves and other shoot material (Alloway, 2013). Trace elements can enter the food chain from this system through ingestion of plant material by animals and humans, drinking contaminated groundwater, and animals eating the soil directly (Beyer et al., 1994). Movement from root to shoot is defined as translocation, and soil to shoot is bioaccumulation (Fig. 1.1).



**Fig. 1.1** The potential pathways of ETECs upon entry to soil.

## 1.2. Thesis structure

Chapter 2 reviews the literature and identifies key unknowns relating to the behaviour of ETECs in soil. It develops testable hypotheses and delineates formal aims for the experimental sections of the thesis.

Chapter 3 describes preliminary work that measured the mobility of Ga and In in the soil-plant system, and was expanded upon in the following chapters.

Chapter 4 uses batch sorption experiments and speciation modelling to determine the solubility and speciation of ETECs and a reference element, Cd, in soil as affected by physicochemical conditions.

Chapter 5 reports the results of a pot trial that determines the effect on perennial ryegrass (*Lolium perenne*) of ETECs in soil at background concentrations as well as 5x, 10x, 20x and 40x background concentrations. Commercial tea, which is a hyperaccumulator of Al, is analysed for comparison.

Chapter 6 reports batch sorption experiments with iodine as well as the results of a field survey of iodine concentrations in soils and *Lolium perenne* around New Zealand.

Chapters 7 and 8 discuss the results as a whole and conclude the thesis.

Throughout this thesis, the ETECs are listed in order of atomic number.

## 2. Literature review

### 2.1. Increasing use of lesser studied trace elements

The lesser-studied TEs Be, Ga, In, Te, La, Ce, Nd, Gd, and Bi have a variety of applications in emerging sectors, though predominantly electronic. Industries, end-products, and consumption of the elements are listed in Table 2.1. Beryllium is used in many sectors, with 75% in Cu alloys containing <2% Be due to its strengthening properties-addition of 2% Be to Cu can increase its strength by a magnitude of six (Taylor et al., 2003)-though its x-ray transparency and electrical insulation are also utilised (Trueman & Sabey, 2014). Bismuth has long been appreciated medicinally-since the middle ages-and is antagonistic against *Helicobacter pylori* (Ahmad et al., 2006), it improves the quality of metal alloys and is a less-toxic alternative to Pb (Anderson, 2018a). The most important forms of Ga are GaAs followed by GaN semiconductors. Gallium integrated circuits and optoelectronic devices account for approximately 70% and 30% of recent US consumption (Jaskula, 2018b), and have high electron speed and mobility, quietness, a large operation temperature range and semi-insulation (Butcher & Brown, 2014). Indium-tin oxide coatings are the largest consumption of In, at approximately 65%, and are useful for increasingly-utilised touchscreens due to electrical conductivity, heat reflectivity and transparency properties (Schwarz-Schampera, 2014; Shanks et al., 2017). Approximately 70% of Te is used in CdTe solar cells and for thermoelectric cooling, with good electrical conductivity, machinability and strength (Anderson, 2018b; Goldfarb, 2014).

Rare Earth Elements (REEs) differ in industrial utilisation, though often the uses involve a combination of several lanthanides. Most La is used as a fluid cracking catalyst, breaking crude oil into lighter products within the petroleum industry, with 46% of total La use in 2008 (Akah, 2017; Goonan, 2011b). Cerium is more commonly used as a protective coating in automobile catalytic converters (16%), and glass polishing and additives (44%) (Goonan, 2011b). Neodymium is paramagnetic and is predominantly used as NdFeB permanent magnets (Stegen, 2015; Wall, 2014). Magnets were responsible for 76 and 89% of global Nd consumption in 2008 and 2012 (European Commission, 2014; Goonan, 2011a). Magnets can also contain 2% of other REEs including Gd, praseodymium (Pr), terbium (Tb), and dysprosium (Dy) (Goonan, 2011b).

All of the ETECs selected for study (except Bi and Te) have extensive use in electronic equipment (Butcher & Brown, 2014; Goonan, 2011a; Robinson, 2009; Schwarz-Schampera, 2014). Electronic waste (e-waste) production is increasing, reaching 44.7 Mt in 2016 and 53.6 Mt in 2019, and predicted to further increase 3-4% annually (Balde et al., 2017; Forti et al., 2020). Global production has increased 43-421% since 2000 for Bi, Ga, Ge, In and REEs (Table 2.1). The increase in Bi utilisation is

partially due to the restrictions of Pb; in 1996 a US act required future water pipes to be Pb free, with further restrictions in electronics, shooting and fishing (Klochko, 2018; Krenev et al., 2015).

Data for the REEs is usually compiled together, but their utilisation suggests that demand will continue to increase; NdFeB magnets will be used in energy-efficient alternatives, particularly electric cars and renewable electricity. Magnets are expected to become the largest REE sector-hence supply limitations may shortly hinder Nd usage (European Commission, 2014; Gambogi, 2015; Stegen, 2015). Lanthanum and Ce can be used in electric cars, and their use in non-electric cars will continue as the transition has been relatively slow. Tellurium data is unavailable, though theoretically consumption may increase as its two largest sectors are involved in renewable power and electronics.

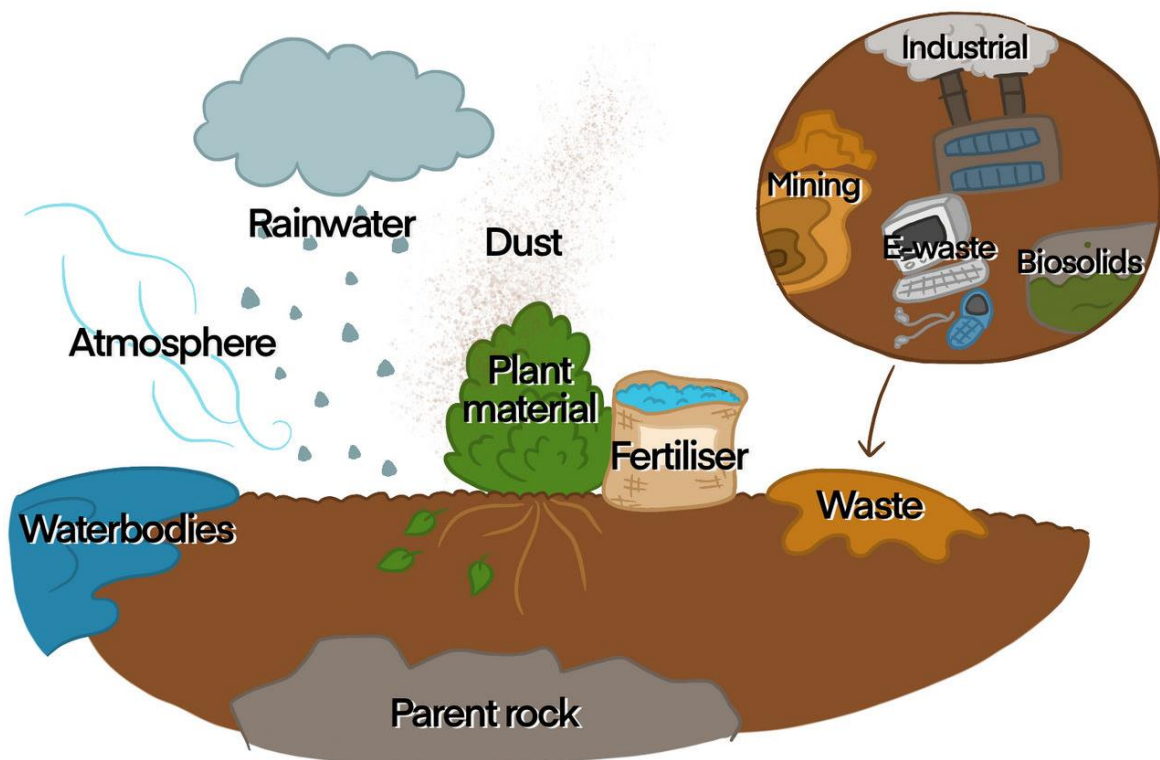
**Table 2.1 The largest sources, common applications, global production and US consumption data for Be, Ga, In, Te, La, Ce, Nd, Gd, and Bi.**

Element	Applications	End-products	Yearly global production (t) <sup>f</sup>	Yearly US consumption (t) <sup>f</sup>
	Sectors or components		(% change 2000-2020)	
Be	Consumer electronics and appliances <sup>a</sup>	Aircraft altimeters and landing gear <sup>a</sup>	2018: 243	2018: 202
	Military	Fuel containers	(+7.5%)	(-33%)
	Automotive construction and electronics	Fire sprinklers		
	Industrial equipment	Computers		
	Telecommunications infrastructure	Cars		
	Connector terminals and relays	Cars		
	Electrical insulator	Neutron probes (soil moisture measurement)		
Ga	Wireless communications <sup>b</sup>	Cell phones <sup>b</sup>	2017: 317	2017: 17.9
	Military	Global positioning systems	(+252%)	(-55%)
	Semiconductors	Night-vision devices		
	Integrated circuits	Touch-screens		
	Optoelectronic devices	Blu-ray players		
		Light emitting diodes	Solar cells	
	Laser diodes			
	Infrared emitting diodes			
In	Indium-tin oxide (ITO) coating <sup>c</sup>	Touch-screens <sup>c</sup>	2017: 714	2017: 129
	Solders and fusible alloys	Flat panel displays, e.g. liquid-crystal displays	(+113%)	(+135%)
	Semiconductors	Streetlights		
		Solar cells		
	Light emitting diodes			
	Laser emitting diodes			
Te	Metal additive <sup>e</sup>	Solar cells <sup>e</sup>	2017: 467	<sup>i</sup>
	Vulcanising agent for rubber	Glass and ceramics	(+325%)	
	Catalyst for fiber			
	Pigment			
	Integrated circuits			
La	Fluid cracking catalyst <sup>d</sup>	Petroleum <sup>d</sup>	2017: 132,000 REE oxide	2017: 9,060 REE oxide
	Metal additive	Fluorescent lighting	(+45%)	(-25%)
	Phosphors	Electric cars	2012: 26% <sup>g</sup>	2012: 28% <sup>g</sup>
	Battery alloy		2012: 38% <sup>g</sup>	2012: 40% <sup>g</sup>
Ce	Catalytic converter coating <sup>dh</sup>	Automobiles <sup>h</sup>		
	Glass polishing and additive <sup>d</sup>	Coloured glass <sup>d</sup>		
	Metal additive	Fluorescent lighting		
	Phosphors	Electric cars		
	Battery alloy			
Nd	NdFeB magnets <sup>d</sup>	Air conditioners <sup>d</sup>	2012: 17% <sup>g</sup>	2012: 18% <sup>g</sup>
		Hybrid and electric cars		
	Motors	Wind turbines, and other renewable energy production		
	Generators	Hard disk drives		
	Metal additive	Speakers		
		Thermoelectric cooling	Microphones	
		YAG lasers		
Gd	Phosphors <sup>d</sup>	Fluorescent lighting <sup>d</sup>	2012: 2% <sup>g</sup>	2012: 1% <sup>g</sup>
	NdFeB magnets			
	Motors			
	Generators			
Bi	Metal additive <sup>b</sup>	Fuel tank safety plugs <sup>b</sup>	2017: 16,900	2017: 756
		Fire sprinklers	(+349%)	(+19%)
	Fusible alloy or improved machinability	Small shot		
	Less-toxic Pb alternative	Fishing sinkers		
	Pearlescent pigment	Cosmetics and paint		
	Medicinal	Pepto-Bismol, De-Nol and Pylorid (medicine)		
	Gastrointestinal disorders (diarrhea, dyspepsia and peptic ulcers)			

<sup>a</sup>European Commission (2014); Jaskula (2018a); Li et al. (2003); Taylor et al. (2003); Trueman and Sabey (2014); <sup>b</sup>Ahmad et al. (2006); Anderson (2015); Krennev et al. (2015); <sup>c</sup>Ladenberger et al. (2015); Schwarz-Schampera (2014); Shanks et al. (2017); <sup>d</sup>Goonan (2011a); Schulze and Buchert (2016); <sup>e</sup>Anderson (2018b); Goldfarb et al. (2017); <sup>f</sup>(U.S. Geological Survey, 2021a, 2021b); <sup>g</sup>oxide production and worldwide consumption, as a percentage of total REE oxides (European Commission, 2014); <sup>h</sup>Bahaloo-Horeh and Mousavi (2020); <sup>i</sup>Data withheld.

### 2.1.1. Entry to soil

There are several sources of ETECs to soil, natural and anthropogenic (Fig. 2.1). The initial source is the parent rock that the soil is formed from. ETECs can be deposited anthropogenically through fertiliser and deposition of waste, or naturally through soil, water, plants and the atmosphere (Engel-Di Mauro, 2021; Kim et al., 2020). The natural sources can act as pathways for contamination in other areas.



**Fig. 2.1 Sources and transport of ETECs to soil.**

### 2.1.2. Comparison of ETECs to well-studied TE contaminants

The mobility of some TEs have been extensively studied in the environment, such as Cd due to its long history of contamination and high capacity to be taken up by plants and translocated into edible material (Rizwan et al., 2017), Pb due to its high risk to human health (Goyer, 1990), and I has been recently studied due to animal deficiencies arising from it not being essential for plants, but previously hindered by analytical challenges (Flachowsky, 2007; Robinson et al., 2009). As these TEs, particularly Cd and Pb have been measured in many studies, they can be used as benchmarks, e.g. Cd as a relatively mobile TE, Pb as an immobile TE (Sheppard et al., 2009), and I can be used to compare the distribution of TEs in the environment (Fuge & Johnson, 1986).



## **2.2. Natural sources of ETECs in the environment**

The largest source of the ETECs for industrial use is metalliferous rocks. Beryllium and REEs are lithophilic (Table 2.4), thus are mostly present in silica-minerals and are mined directly. Bismuth, Ga, In, and Te are extracted as byproducts from ores of geochemically similar chalcophilic (sulphur-associated) elements (Goldschmidt, 1937). The economic value and/or concentrations of the latter elements in mineral deposits are too low for direct mining to be economically feasible. The major economic sources of the elements are listed in Table 2.2. Minor sources of Bi are fluorspar, Sn and W ores (Anderson, 2015a), Ga is also extracted from sphalerite ore (Rongguo et al., 2016), In from Sn and Cu sulphide ores (Schwarz-Schampera, 2014), and Te from Bi, Cu, Pb-Zn and Au ores (Anderson, 2018b).

### **2.2.1. Contamination**

Soils can be contaminated with ETECs from the disposal of mining waste, industrial and fossil fuel waste products (Ha et al., 2011; Mandal & Sengupta, 2006; Taylor et al., 2003), rudimentary recycling and landfill leaching of discarded electronic equipment (Ha et al., 2009; Hester & Harrison, 2009; Perkins et al., 2014; Robinson, 2009), and impurities in inorganic fertiliser and biosolids (Eriksson, 2001; Zhang et al., 2002) (Table 2.2).

**Table 2.2 Sources of ETECs for extraction, crustal and natural soil concentrations, and contamination of ETECs in soils.**

Element	Extractable source	Upper continental crust concentration (mg kg <sup>-1</sup> ) (Wedepohl, 1995)	Natural soil concentration (mg kg <sup>-1</sup> ) (Kabata-Pendias & Mukherjee, 2007)	Contaminant concentration	Contaminant source	Reference
Be	Bertrandite and beryl ore (Lederer et al., 2016)	2.4	0.1-4.9	113 97.1 5.63	Copper smelter slag Copper smelter slag Coal ash	Taylor et al. (2003) Tetra Tech EM (2001) Mandal and Sengupta (2006)
Ga	Bauxite byproduct (Rongguo et al., 2016)	15	3-70	441	Zinc industrial plant	Poędniok et al. (2012)
In	Sphalerite ore byproduct (Tolcin, 2017)	0.05	0.01-0.5	100 75 4.62	Lead and zinc mine Lead and zinc smelter E-waste recycling	Ha et al. (2011) Boughriet et al. (2007) Ha et al. (2009)
Te	Cu extraction anode slime (Anderson, 2018)	0.005	0.02-4	18	Au and Ag mine tailings	Qin et al. (2017)
La	REE carbonatite ore (Wall, 2014)	30	8.4-35.2	6,905 630 94.67	Iron and steel tailings Rare-earth mine tailings Previous mining	Jinxia et al. (2010) Guo et al. (2013) Khan et al. (2017)
Ce		60	15.8-97.4	12,170 1,420 420.5	Iron and steel tailings Rare-earth mine tailings Previous mining	Jinxia et al. (2010) Guo et al. (2013) Khan et al. (2017)
Nd		27	7.6-29.5	5,727 410 112.3	Iron and steel tailings Rare-earth mine tailings Previous mining	Jinxia et al. (2010) Guo et al. (2013) Khan et al. (2017)
Gd		4.0	1.23-4.8	14 42.26	Rare-earth mine tailings Previous mining	Guo et al. (2013) Khan et al. (2017)
Bi	Pb ore (Anderson, 2015)	0.085	0.04-1.5	1,672 1,510 75.2	Sb mine tailings Cu-W mine tailings Military	Wei et al. (2011) Jung et al. (2002) Berthelot et al. (2008)

## 2.3. Soil mobility

### 2.3.1. Mobility of ETECs in soil

For ETECs to be mobile and migrate through the soil profile or be taken up by plants, they must be soluble and present in the soil solution. Solubilised ETECs may form hydrated ions or soluble complexes. When sorbed to soil, the sorption strength and lability of ETECs varies from inner-sphere adsorption (weak and labile) to specific adsorption (strong direct bonds) to absorption (incorporation in the mineral matrix, immobile until the mineral is broken down) (Bradl, 2004). When soluble,

diffusion or preferential flow can cause ETECs to migrate in soil, although insoluble ETECs can also migrate through colloidal transport, but is more likely to be restricted by pore size and adsorption of other soil constituents (Carrillo-González et al., 2006).

The size of the soluble fraction of the ETECs and I can be described using a distribution coefficient ( $K_D$ ), which is calculated through the concentration of the ETEC in the solid divided by soluble phases (Shaheen et al., 2013). Methods either employ a single extractant, such as 0.05 M  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{CaCl}_2$  or  $\text{NH}_4\text{NO}_3$ , to determine the concentration of a ETEC in the soluble phase, or multiple sequential extractants to find the proportions of ETECs present in specific phases, namely bound as hydrated complexes, carbonate bound, organically complexed, Fe and Mn oxide bound, and residual (Rao et al., 2008; Tessier et al., 1979). In single-extractant methods, the results are often reported as distribution coefficients ( $K_D$ ), which are calculated by dividing the concentration of a ETEC in the solid phase ( $\text{mg kg}^{-1}$ ) by the concentration in the soluble phase ( $\text{mg L}^{-1}$ ) (Shaheen et al., 2013). Multi-extractant methods (also referred to as sequential extraction procedures) usually display the results as the percentage of the TE in each fraction. As many different extractant solutions are used, and a plethora of soil properties affect ETEC immobilisation in soil, the solubility between ETECs should be compared in the same environment with the same method. Hence, it is not feasible to compare the solubility of the ETECs to that of Cd and Pb when data for the elements is from different studies, and that will not be done in this review.

There is a large variation in the  $K_D$  of individual ETECs, spanning from <100 to >10,000 for Be and Bi and <1,000 to >10,000 for other elements (Table A.1). These differences were present even within the same methodology and across short geographical distances, hence  $K_D$  data cannot be compared for different elements in different soil types. For example, the  $K_D$  of Nd varied from 430 to 1,100,000 in various Canadian soils in Sheppard et al. (2007), and the  $K_D$  of Ga increased from 2,600 to 14,000 in soil from two sites less than 2 km apart (Sheppard et al., 2009).

### 2.3.2. Comparison of soil solubility between the ETECs and Pb

Few studies have directly compared the soil sorption capacity of the ETECs to that of Cd and Pb. In distribution coefficients calculated from bioavailable TE fractions in Canadian shooting-range soil, the  $K_D$  of Bi was 30% higher than Cd and 86% lower than Pb (Berthelot et al., 2008). Soil from a German construction site had soluble La and Nd fractions that were one-tenth the proportion of the soluble Pb fraction (Wiche et al., 2016). Favas et al. (2011) and Pueyo et al. (2003) reported that Bi has similar

solubility to Pb. Zádřapová et al. (2019) found that the mobility of Be was intermediate between Cd and Pb.

Distribution coefficients of ETECs and Cd and Pb are compared in Table 2.3.  $K_D$  values of Ce, Cd, Ga, Gd, La, Nd and Pb were measured in seven natural Swedish soil types (Sheppard et al., 2009). Cadmium had the lowest  $K_D$  in all seven soils. Lead had the highest average  $K_D$ , followed by Ce and Nd; the ranking varied between soil types, with Pb having the second and fifth-highest immobilisation in two soil types apiece. Gallium had a higher  $K_D$  than the REEs in four soil types but lower in the other three. In two sites with available data, Be had  $K_D$  values that were 32% and 133% higher than Cd but an order of magnitude lower than the other elements. Tyler and Olsson (2002) measured partitioning in natural Swedish soil for a wide range of elements and found that the  $K_D$  ranking was  $Cd < In < Bi < Pb < Be < La < Ce < Nd < Gd < Ga$ . Like the other study, Cd was more soluble than the elements analysed in this review, but Pb was more soluble than Be, Ga and the REEs.

Beryllium is less soluble than Cd in several soil types and commonly has  $K_D$  values between 100-1000 thus it is relatively immobile in soil. For Bi, In, and Te, there is insufficient data to compare the soil solubility of them to Cd and Pb, but where available,  $K_D$  is usually larger than for Be. Gallium and the rare earth elements have a similar solubility as Pb, and  $K_D$  values are typically  $>1000$  in most soils. Therefore, upon entry to soil Bi, Ce, Ga, Gd, In, Nd, La, and Te will become immobile, making direct soil ingestion the most likely path of entry into the food chain. Beryllium has a higher potential than the other ETECs to leach through the soil profile and is more bioavailable to plants. Overall, there is a lacuna of studies comparing the solubility of the selected ETECs under identical environments. Using Cd and Pb as benchmarks of high and low solubility will enable the assessment of the relative mobility of Be, Bi, Ce, Ga, Gd, In, La, Nd and Te in soil.

**Table 2.3 Comparison of the  $K_D$  between Cd and Pb, and for Be, Ga, In, Te, La, Ce, Nd, Gd, and Bi. Columns are arranged low – high.**

Forest topsoils <sup>a</sup>	Clayey till (Site A) <sup>b</sup>	Clayey till (Site G) <sup>b</sup>	Clay gyttja (Site D) <sup>b</sup>	Clay gyttja (Site F) <sup>b</sup>	Peat (Site B) <sup>b</sup>	Peat (Site E) <sup>b</sup>	Sandy till (Site C) <sup>b</sup>
Cd 356	Cd 73	Cd 1,200	Cd 150	Cd 150	Cd 480	Cd 220	Cd 190
In 967	Ga 2,600	Ga 14,000	Gd 3,700	Be 350	Ga 1,300	Be 290	Gd 1,200
Bi 1,522	Pb 6,000	Pb 25,000	Nd 5,200	La 2,700	Gd 1,800	Gd 2,400	Nd 1,500
Pb 1785	Gd 22,000	Gd 51,000	La 5,900	Ce 4,400	Nd 2,100	Nd 3,200	Ce 1,700
Be 2,200	Ce 39,000	Nd 76,000	Ce 5,900	Gd 5,100	La 2,600	Ce 3,800	La 1,800
La 5,305	La 44,000	La 80,000	Ga 9,400	Nd 7,300	Pb 3,100	La 4,000	Pb 2,000
Ce 5,490	Nd 46,000	Ce 88,000	Pb 11,000	Ga 7,800	Ce 4,100	Ga 7,800	Ga 5,900
Nd 5,854				Pb 44,000		Pb 17,000	
Gd 6154							
Ga 14,211							

<sup>a</sup>Tyler and Olsson (2002); <sup>b</sup>Sheppard et al. (2009)

### 2.3.3. Soil properties that affect the solubility of the ETECs in soil

Soil properties significantly affect the solubility of ETECs in soil and can be naturally and anthropogenically altered (Hooda, 2010). Soil pH is dynamic and is altered by introducing acidic and basic ions into the system, such as through fertiliser, carbonic acid in rainwater and microorganism respiration, and the release of H<sup>+</sup> from plant roots. Soil organic matter contents vary with the rates of plant material addition and soil microorganism respiration. Periods of heavy rain and waterlogging can reduce the oxygen content and redox potential of soil. The chemical properties of the ETECs that are relevant for mobility in the soil - plant system are listed in Table 2.4.

**Table 2.4 Chemical properties affecting the solubility of Be, Cd, Ga, In, Te, La, Ce, Nd, Gd, and Bi.**

Element	Ionic potential <sup>a</sup> of aqueous-stable oxidation states <sup>b</sup> (coordination) <sup>x</sup>	Aqueous species <sup>c</sup>	Average aqueous charge at pH 4, 6 and 8 <sup>d</sup>	Hydroxide/oxide or carbonate precipitation		Hard/soft <sup>f</sup>	Goldschmidt classification <sup>v</sup>	
				Minimum solubility <sup>e</sup>	pH of maximum precipitation			
Be	Be <sup>2+</sup> 74 nm <sup>-1</sup> (IV)	Be <sup>2+</sup> <sup>ij</sup> Be(OH) <sup>+</sup> Be <sub>3</sub> (OH) <sub>3</sub> <sup>3+</sup> Be(OH) <sub>2</sub> <sup>0</sup> Be(OH) <sub>3</sub> <sup>-</sup>	+2.0 +1.3 0.0	Total Be <1 mg L <sup>-1m</sup>	<1	8-10 <sup>l</sup>	Hard	Lithophile
Cd	Cd <sup>2+</sup> 21 nm <sup>-1</sup> (VI)	Cd <sup>2+</sup> CdCO <sub>3</sub> <sup>0</sup> Cd(CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	+2.0 +2.0 +1.9			8-10 <sup>l</sup>	Soft	Chalcophile
Ga	Ga <sup>3+</sup> 48 nm <sup>-1</sup> (VI)	Ga <sup>3+</sup> <sup>o</sup> Ga(OH) <sup>2+</sup> Ga(OH) <sub>2</sub> <sup>+</sup> Ga(OH) <sub>3</sub> <sup>0</sup> Ga(OH) <sub>4</sub> <sup>-</sup>	+1.4 -1.0 -1.0	α-GaOOH 10 <sup>-9.3</sup> M <sup>o</sup>	10 <sup>-</sup>	4-5 <sup>o</sup>	Hard	Chalcophile
In	In <sup>3+</sup> 38 nm <sup>-1</sup> (VI)	In <sup>3+</sup> <sup>o</sup> In(OH) <sup>2+</sup> In(OH) <sub>2</sub> <sup>+</sup> In(OH) <sub>3</sub> <sup>0</sup> In(OH) <sub>4</sub> <sup>-</sup>	+1.7 0.0 0.0	In(OH) <sub>3</sub> 10 <sup>-7.3</sup> M <sup>o</sup>	10 <sup>-7.3</sup>	4.5-9 <sup>o</sup>	Hard	Chalcophile
Te	Te <sup>6+</sup> 107 nm <sup>-1</sup> (VI)  Te <sup>4+</sup> 61 nm <sup>-1</sup> (IV)	H <sub>2</sub> TeO <sub>4</sub> <sup>0s</sup> HTeO <sub>4</sub> <sup>-</sup> TeO <sub>4</sub> <sup>2-</sup> TeO-OH <sup>+</sup> TeO <sub>2</sub> <sup>0</sup> HTeO <sub>3</sub> <sup>-</sup> TeO <sub>3</sub> <sup>2-</sup>	0 0 -1 0 -1 -2	-		Varies with Eh-related to reduction to insoluble Te <sup>0st</sup>	Soft	Chalcophile
La	La <sup>3+</sup> 25 nm <sup>-1</sup> (IX)	La <sup>3+</sup> La(CO <sub>3</sub> ) <sup>+</sup> La(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup>	+3.0 +3.0 +1.6	REE hydroxides 10 <sup>-6</sup> M <sup>r</sup>	10 <sup>-</sup>	>8 <sup>l</sup>	Hard	Lithophile
Ce	Ce <sup>3+</sup> 25 nm <sup>-1</sup> (IX)	Ce <sup>3+</sup> Ce(CO <sub>3</sub> ) <sup>+</sup> Ce(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup>	+3.0 +3.0 +1.3	1.6 <sup>-20</sup> g 100gH <sub>2</sub> O <sup>-1w</sup>	10 <sup>-</sup>	>7.5 <sup>l</sup>	Hard	Lithophile
Nd	Nd <sup>3+</sup> 26 nm <sup>-1</sup> (IX)	Nd <sup>3+</sup> <sup>i</sup> Nd(CO <sub>3</sub> ) <sup>+</sup> Nd(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup>	+3.0 +3.0 +1.5	REE hydroxides 10 <sup>-6</sup> M <sup>r</sup>	10 <sup>-</sup>	>7.5 <sup>l</sup>	Hard <sup>h</sup>	Lithophile
Gd	Gd <sup>3+</sup> 25 nm <sup>-1</sup> (IX)	Gd <sup>3+</sup> Gd(CO <sub>3</sub> ) <sup>+</sup> Gd(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup>	+3.0 +3.0 +0.8	REE hydroxides 10 <sup>-6</sup> M <sup>r</sup>	10 <sup>-</sup>	>7.5 <sup>l</sup>	Hard	Lithophile
Pb	Pb <sup>2+</sup> 26 nm <sup>-1</sup> (VI)	Pb <sup>2+</sup> Pb(OH) <sup>+</sup> PbCO <sub>3</sub> <sup>0</sup> Pb(CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	+2.0 +2.0 +0.4			7-9 <sup>l</sup>	Borderline	Chalcophile
Bi	Bi <sup>3+</sup> 26 nm <sup>-1</sup> (VIII)	Bi <sup>3+</sup> <sup>i</sup> Bi(OH) <sup>2+</sup> Bi(OH) <sub>2</sub> <sup>+</sup> Bi(OH) <sub>3</sub> <sup>0</sup> Bi(OH) <sub>4</sub> <sup>-</sup>	+1.0 +0.2 0.0	α-Bi <sub>2</sub> O <sub>3</sub> 3.63-4.52 x10 <sup>-6</sup> M <sup>m</sup>	3.63-4.52 x10 <sup>-6</sup>	5-13 <sup>n</sup>	Borderline	Chalcophile

<sup>a</sup>Charge/ionic radius (nm) (Tyler, 2004a) of aqueous coordination (referenced), ionic radii from Shannon (1976) (VI coordination); <sup>b</sup>Kabata-Pendias and Mukherjee (2007); <sup>c</sup>Predicted for low temperature (25°C) systems with H<sub>2</sub>O and CO<sub>2</sub> in order of increasing pH, some minor species not included, grey species are <10% of the total aqueous forms at pH 4-8 (Gustafsson, 2013); <sup>d</sup>Net charge on Fig. S1. Unless specified; <sup>e</sup>At 25°C where applicable; <sup>f</sup>Pearson (1968); Wood and Samson (2006); <sup>g</sup>Nieboer and Richardson (1980); <sup>h</sup>Assumed as smaller and larger REEs La<sup>3+</sup>, Ce<sup>3+</sup>, Gd<sup>3+</sup> and Lu<sup>3+</sup> were classified as hard, and La<sup>3+</sup> and Gd<sup>3+</sup> are class A; <sup>i</sup>Gustafsson (2013) with same parameters as Fig. S1.; <sup>j</sup>Brown et al. (1992); <sup>k</sup>Foley et al. (2017); <sup>l</sup>EPRI (2006); <sup>m</sup>Tooth et al. (2013); <sup>n</sup>Murata (2010); <sup>o</sup>Wood and Samson (2006); <sup>p</sup>Pokrovski et al. (2000); <sup>q</sup>Pokrovski and Schott (1998), GeO<sub>2</sub>(hexagonal) is more soluble Wood and Samson (2006); <sup>r</sup>Hu et al. (2006); <sup>s</sup>Qin et al. (2017), within the Eh range of -0.4 – 0.6V McLaren and Cameron (1996); <sup>t</sup>Ba et al. (2010); <sup>u</sup>Trueman and Sabey (2014); <sup>v</sup>White (2013). <sup>w</sup>(Dahle & Arai, 2015); <sup>x</sup>Be (Grzybkowski, 2006), Bi (Sadler et al., 1999) IX coordination but radii value not available, REEs (Cotton, 2005), Cd (Andersen, 1984), Ga and In (Wood & Samson, 2006), Pb usually crystallises without full hydration, thus VI coordination assumed for comparison (Persson et al., 2011), Te (Christy et al., 2016).

The ETECs hydrolyse in solution, forming hydroxyl or carbonyl compounds when the concentrations of other common ligands (e.g. chloride, sulphate, etc.) are low. In pH ranges listed in Table 2.4, the hydrolysis products are neutral compounds, which usually have low solubility thus precipitate. Grzybkowski (2006) stated that divalent metals hydrolyse from pH 6-12, and trivalent metals hydrolyse in the natural water pH range-the values of this range were not specified by Grzybkowski (2006) but is considered to be 6.0-8.5 by Oram (2021). The common soil pH range is 4-8 (Smith & Doran, 1997), thus trivalent Bi, Ga, In, and the REEs are expected to hydrolyse, and Be, Cd and Pb will not hydrolyse in acidic soils with a pH <6. Elements with an ionic potential of 30-100 nm<sup>-1</sup> will hydrolyse and precipitate in soil, with those below 30 remaining as free ions, and those above 100 nm<sup>-1</sup> hydrolysing to soluble oxyanions (Sposito, 2008). By these criteria, Be will hydrolyse due to its small ionic radii, and so will Ga, In, and Te<sup>4+</sup>, but the radii of the REEs from Shannon (1976) suggests that they are too large to undergo hydrolysis in soil. Tellurium as Te<sup>6+</sup> will exist as an oxyanion. The ionic potential of Be<sup>3+</sup> is probably higher, as the radii of Be in IX coordination was unavailable.

Equilibrium speciation modelling, using Visual MINTEQ (version 3.1) (Gustafsson, 2013), was used to calculate the transitions of the aqueous species of the ETECs from pH 4 to pH 8 (Fig. A.1), and the average charge was calculated. MINTEQ indicates that Bi, Ga, In, and Te hydrolyse below pH 4 and the REEs between pH 6 and pH8. Of the divalent elements, hydrolysis of Be occurs between pH 4 and pH 6, Pb hydrolyses above pH 6, and only some Cd<sup>2+</sup> ( $\approx 5\%$ ) will have hydrolysed at pH <8. The pH of peak precipitation is linked to when >80% of the ions hydrolyse to neutral forms. In fly ash across the pH range of 2-13, Ga and In reached almost minimum solubility by pH 3.84, the REEs at 5.21-5.47, Be at pH 5.47-6.7, and Cd slowly decreased to hit minimum solubility at pH 6.97 (Zhang et al., 2019). For Be, precipitation of its neutral hydrolysed form, Be(OH)<sub>2</sub>, largely controls sorption above pH 6 (Islam et al., 2021).

Changes in pH can alter many factors which contribute to the partitioning of ETECs in soil. As the pH increases, Fe and Al precipitate, creating binding sites for ETECs, less H<sup>+</sup> is available to compete for sorption sites, and variable-charge sorption sites loose protons thus become more negatively charged (Hooda, 2010). Soil pH responses are complex, thus the effect and extent of pH affecting partitioning can vary between soils. Increasing the soil solution pH usually decreased solubility of the ETECs in studies, with the increase in negatively charged sorption sites favourable for the cations. As the pH of a moraine Cambisol increased from 5.2-7.8, the solubility of Bi, Ce, Ga, Gd, La and Nd decreased, Be and Cd decreased then increased, with significant relationship observed for Pb (G. Tyler & T. Olsson, 2001). In Swedish soils, the K<sub>D</sub> of Bi, Ga, Pb, Te and the REEs increased with increasing pH (Sohlenius

et al., 2013), and in forest topsoils, pH was significantly negatively correlated to solution concentrations of Be, Gd, In and Pb (Tyler & Olsson, 2002). Adsorption of La, Ce, Pr and Nd increased as the pH increased from 3-8 in the presence of organic acids in Chinese topsoils (Shan et al., 2002), and the extractability of these elements was negatively correlated with pH in Chinese wheat-growing topsoil (Fang et al., 2007).

Iron and manganese oxides and clay-sized particles are known to retain large quantities of ETECs (Shaheen et al., 2013). Sohlenius et al. (2013) demonstrated that this is also true for the ETECs reviewed herein. The net effect of this group on the solubility of ETECs may vary with the soil composition. Fang et al. (2007) found that amorphous Fe was highly significantly correlated with the extraction of La, Ce, Pr and Nd, but crystalline Fe was not. Qin et al. (2017) demonstrated differences in the capacity of ferrihydrite, goethite and illite with pH.

The Hard-Soft Acid-Base theory (HSAB) shows that the ETECs are 'hard' Lewis acids, i.e. they bind preferentially to 'hard' Lewis bases such as carboxyl and hydroxyl functional groups (Alloway, 2013; Kinraide & Yermiyahu, 2007; Stumm & Morgan, 2009), which bind well to the reviewed elements, especially hard Be, Ce, Ga, Gd, In, La and Nd. Organic matter can be present in solid and aqueous states, and binding by aqueous OM can limit precipitation and increase solubility, thus the net effect of OM is dependent on the composition. There are examples of the solubility of Be, Bi, Ce, Ga, Gd, In, La and Nd being increased by soluble OM (Boschi & Willenbring, 2016a; Murata, 2010; Ringering et al., 2019; Shan et al., 2002; Tyler & Olsson, 2002; Wen et al., 2013). Soluble organic acids are present in root exudates and are sometimes released in response to metal stress and may additionally increase mobility of ETECs via soil acidification (Chang et al., 2017; Vranova et al., 2013).

Soil redox potential indirectly modifies the solubility of the ETECs, through the dissolution of Mn and Fe precipitates below 0.4-0.2 V and 0.3-0.1 V, respectively, and formation of sulphide precipitates below -0.1 V, particularly for the chalcophiles Bi, Ga and In (Table 2.4) (Alloway, 2013; Hooda, 2010; McLaren & Cameron, 1996). The aforementioned elements are stable in their di- and trivalent states. Cao et al. (2001) found that when Eh decreased from 0.4 to -0.1 V, the REEs La, Ce, Gd and Y were released from the exchangeable and Fe/Mn oxide fractions into solution, with behaviour not believed to be influenced by sulphides.

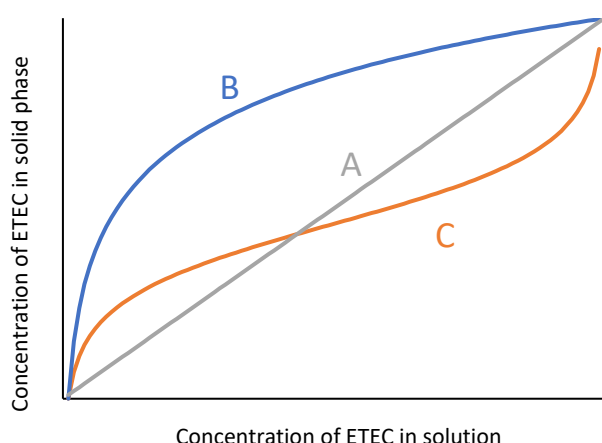
Tellurium is redox-active in soil, which complicates its behaviour. Within the typical soil Eh range of 0.6 - -0.4 V, Te can transition between the +6, +4, 0 and -2 oxidation states (Figure S4 in Qin et al.



(2017) demonstrates these). The former two are soluble, but limited evidence suggests that sorption characteristics may differ-Te(IV) has a greater tendency to form neutral and cationic forms, which have larger attractions for negative soil colloids-though data has shown that Te in both +6 and +4 oxidation states form similar inner-sphere complexes with Fe oxides (Harada & Takahashi, 2008; Qin et al., 2017). As with Be, Bi, Ga, Ge and In, as Eh decreases, Te may be indirectly mobilised by Fe/Mn oxide dissolution (Harada & Takahashi, 2008) and potentially immobilised by sulphides, but  $\text{Te}^0$  is insoluble (Qin et al., 2017) thus reduction to this oxidation state is expected to reduce solubility. Furthermore, some evidence suggests that among the suite of microbial processes, some microorganisms are capable of reducing Te to  $\text{Te}^0$ , a form that is less biologically active and thus less (Qin et al., 2017). Like Te, Ce is a redox-active element (Dahle & Arai, 2015) but reduces from  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  at 1.44 V, which is above the soil range (Soudek et al., 2014).

#### 2.3.4. Other factors that affect the solubility of the ETECs in soil

The total ETEC concentration affects the speciation and partitioning between the solid and aqueous phases. Fig. 2.2 A shows that at low concentrations the contaminant will partition between the solid and aqueous phases at a consistent rate. At higher concentrations soil sorption sites become saturated (Shaheen et al., 2013), and ions remain in solution, causing the  $K_D$  to decrease (Fig. 2.2 B). These curves are often fitted to Langmuir and Freundlich equations (Mesquita & e Silva, 2002). Some of the ETECs selected have the capacity to precipitate under normal soil solutions, which may produce the logit curve shown in Fig. 2.2 C when the excess in solution precipitates to the solid phase. Contamination from mining, industrial processes, and e-waste brings many different trace elements to the system, thus increasing the likelihood of the scenarios in graphs B and C.



**Fig. 2.2 Models of the partitioning of ETECs between the solid and aqueous phases.**

A represents a linear response of sorption to increasing the concentration of ETEC in the system, B an exponential/logarithmic response, and C a logit response.

Trace element solubility and mobility decreases with time as elements age and transition to less labile soil fractions and structural forms. For example, residual In at 0-4 cm depth increased from ~30 to >60% eight years after contamination (Murata et al., 2018), and leachable Nd decreased from >1.5 to <0.1 mg L<sup>-1</sup> within eight days (Liang et al., 2010). Amorphous Ga(OH)<sub>3</sub> can transition to higher crystallinity α-GaOOH with time (Bernstein, 1998; Pokrovski et al., 1997).

## 2.4. Plant uptake

### 2.4.1. Plant uptake and translocation of ETECs

The available data for the concentrations, soil-plant transfer, and root-shoot transfer of the ETECs in terrestrial plant species was compiled and is presented in Table A.2. In uncontaminated soils, plant Be concentrations are usually <0.2 mg kg<sup>-1</sup>, but higher uptake of ≥0.6 mg kg<sup>-1</sup> occurred in the shoots of barley (*Hordeum vulgare*), cabbage (*Brassica oleracea*), collards (*Brassica oleracea*), oats (*Avena sativa*) and potato (*Solanum tuberosum*) plants which had been supplied with additional Be (Bohn & Seekamp, 1979; Davis et al., 1978; Hara et al., 1977; Kaplan et al., 1990; Sajwan et al., 1996). The concentrations in Table A.2 are for plant material unaffected by ETEC toxicity. Table A.2 shows that crop species can, potentially sustainably, take up higher concentrations of Be than those measured in unspiked soils. Plants vary in their physiological responses to Be, as shown by the variation in root-shoot translocation factors, from 0.0022 in cabbage (Hara et al., 1977) to 6.8 in Mexican turnip (*Pachyrhizus erosus*) shoots (Wang et al., 2021). Although Be has the lowest K<sub>D</sub> of the ETECs studied, it still has a high retention to soil compared to Cd (Sheppard et al., 2009), limiting plant uptake.

The patterns identified here for Be are applicable to the other ETECs, where data is available. Higher concentrations of ETECs measured in plant material when supplied to the system have been shown for Ga in rice (*Oryza sativa*) and wheat (*Triticum aestivum*) seedlings (Su et al., 2018; Syu et al., 2021; Syu et al., 2020; Syu et al., 2017; Yu et al., 2015), Te in garlic and Indian mustard leaves (Ogra et al., 2015; Ogra et al., 2010), and the REEs in barley (Kotelnikova et al., 2020). Despite being added to the system at high concentrations (up to 574 mg kg<sup>-1</sup>), one study found that In was immobilised in soil, limiting uptake by wheat and rice (Chang et al., 2020), which is consistent with its large flat period of peak precipitation in the common soil pH range (Table 2.4), whereas the other ETECs have sharp points of peak precipitation (Fig. A.1).

Variation in uptake between plant species occurs for Te in edible species, with BACs of 0.015-0.11 (Yang et al., 2013, 2014). As it is in the same group, Te may be taken up by the same pathways as S, an essential element.

Some mushrooms accumulate high concentrations of ETECs. Up to 8,894 mg kg<sup>-1</sup> Bi was found in mushrooms (Elekes & Gabriela, 2010). High concentrations of Ga, In, and Nd were also found, at 1.4, 7.5 and 7.1 mg kg<sup>-1</sup> respectively (Dursun et al., 2006; Muñoz et al., 2005; Niedzielski et al., 2017). Elekes and Gabriela (2010), reported that some species of mushroom (*Marasmius oreades* and *Cortinarius largus*) accumulated Bi to concentrations higher than the underlying soil. As some species of mushroom are ingested by humans and animals, the bioaccumulation of ETECs in mushrooms in uncontaminated soils should be investigated.

Wild species naturally growing in contaminated areas often have the capacity to take up and detoxify high concentrations of ETECs. Hence, these species have high bioaccumulation coefficients (BACs) and translocation factors (TFs) for the elements. For example, maximum concentrations of Ga and In in plants in Vietnam were 6.75 mg kg<sup>-1</sup> Ga and 5.14 mg kg<sup>-1</sup> In (Ha et al., 2011), and in Malaysia plants reached up to 2,290 mg kg<sup>-1</sup> Ce (Khan et al., 2017). Finding species such as those in the aforementioned studies, which grow in contaminated areas, can be useful for identifying plants most at risk of transporting ETECs to the food chain. Therefore, grazing stock should be kept away from contaminated locations until the uptake capacity of the plants growing in these locations is assessed.

High concentrations of REEs occur in plants that have been treated with REE fertiliser (Pang et al., 2002), which has been a common practise in China. However, that is not further covered in this review as the fertiliser is not applied to soil for plants to take up, but rather it is applied through foliar application or soaking of seeds

Most crops grown in uncontaminated environments usually contain <0.2 mg kg<sup>-1</sup> of the ETECs, with ts <0.5 and BACs <0.1. Lanthanum, Ce and Nd may naturally be present in soils at concentrations up to 2-3 mg kg<sup>-1</sup>, consistent with their higher abundance in the upper continental crust and thus soil (Kabata-Pendias & Mukherjee, 2007; Wedepohl, 1995). Gallium may naturally be present at closer to 1 mg kg<sup>-1</sup> in crops, but there is currently insufficient data. Therefore, there is a low risk of crops directly being transport vectors of ETECs, but in or near contaminated there is a high risk there is a high risk of ingestion of ETECs through soil retained on plant material.

It is currently not possible to compare the capacity of different types of vegetables (e.g. leafy, root) to take up ETECs from soil and into the food chain, due to a lack of data, and variation in the environments and methodologies. For example, garlic (*Allium sativum*) may take up more La if grown

in a soil naturally rich in the element. Brown rice and leafy crops had the highest uptake and bioaccumulation of Te, followed by root vegetables, then wheat and barley (Yang et al., 2013, 2014). In contrast, potatoes contained more Te than leafy vegetables (Filippini et al., 2019), demonstrating the need for more data. Grains and vegetables grown in uncontaminated soil contain low concentrations of a range of ETECs, thus at this stage pose a low risk for ETECs entering the food chain. Further study should elucidate plant uptake and bioaccumulation in a range of environments (Eriksson, 2001; Omberg et al., 2011), and plant species (Yang et al., 2014).

#### 2.4.2. Comparison of plant uptake and translocation of the ETECs to Cd and Pb

BACs and TFs of the ETECs in terrestrial plants are compared with Cd and Pb in Table 2.5 and Table 2.6. These values were used, rather than total concentrations, to account for variation in environmental abundance and thus size of the bioavailable pools of the elements in soil. From the limited data set, the movement of the ETECs was often higher than Cd and Pb in wild plants growing in contaminated locations. Indium had higher TFs than Cd and Pb in 90% of the Vietnamese wild species in Ha et al. (2011), but lower BACs than Cd in ryegrass (*Lolium*) and lettuce (*Lactuca sativa*), which was directly planted into contaminated soil (Waterlot et al., 2013). The same Vietnamese wild species had high translocation of Ga, but the TFs were usually less than that of In; Ga had higher movement than Cd and Pb in just five of the ten species. Bismuth had more bioaccumulation than Pb but less than Cd in wild species (Pueyo et al., 2003). Beryllium had less plant uptake and mobility than Cd and Pb in 20 of the 36 vegetable measurements calculated from data in Wang et al. (2021). These data show that the ETECs are less mobile than Cd, and have greater similarity in plant mobility to Pb, except for wild species in contaminated locations.

**Table 2.5 Comparison of mean soil-plant BACs and root-shoot TFs between Cd and Pb, and Be, Cd, Ga, In, Te, La, Ce, Nd, Gd, and Bi.**

ETEC	Species	BAC or TF	ETEC	Cd	Pb	Reference
Be	<i>Pachyrhizus erosus</i> (Linn.) Urb	BAC	0.07	1.31	0.25	Wang et al. (2021)
		TF	6.8	4.89	4.7	
	<i>Ipomoea aquatica</i> Forsk	BAC	0.04	2.42	0.17	
		TF	0.32	2.14	0.99	
	Lettuce	BAC	0.03	1.68	0.37	
		TF	0.93	2.92	0.46	
		BAC	0.02	3.31	0.44	
		TF	1.96	3.9	5.27	
	Amaranth ( <i>Amaranthus</i> )	BAC	0.06	0.94	0.21	
		TF	1.96	1.4	0.15	
	<i>Beta vulgaris</i> L	BAC	0.06	1.4	0.15	
		TF	1.96	1.36	0.79	
		BAC	0.02	0.39	0.05	
		TF	0.37	2.81	1.61	
	<i>Brassica oleracea</i> L	BAC	0.01	2.09	0.06	
		TF	2.67	2.74	0.67	
		BAC	0.27	1.68	0.32	
		TF	1.03	3.15	0.84	
	<i>Allium fistulosum</i> L	BAC	0.26	1.06	0.35	
		TF	0.05	0.79	0.32	
		BAC	0.05	1.57	0.1	
		TF	0.12	3.11	0.62	
	<i>Capsicum annuum</i> L	BAC	0.06	2.7	0.2	
		TF	2.86	2.7	0.2	
<i>Sonchus oleraceus</i>	BAC	0.21	4.78	0.38		
	TF	0.36	2.23	0.3		
	BAC	0.08	3.33	0.33		
	TF	0.47	0.81	0.44		
<i>Cichorium endivia</i> L	BAC	0.04	10.3	0.15		
	TF	1.15	2.42	0.9		
	BAC	0.05	1.7	0.004		
Ga	<i>Ageratum houstonianum</i> Mill.	TF	1.7	1.5	1.0	Ha et al. (2011)
	<i>Commelina communis</i> L.		0.57	0.11	0.83	
	<i>Diplazium esculenta</i> (Retz.) Sw.		0.22	0.065	0.11	
	<i>Equisetum diffusum</i> D. Don		0.13	0.10	0.15	
	<i>Houttuynia cordata</i> Thunb.		0.87	0.29	0.45	
	<i>Kyllingia nemoralis</i>		0.48	0.52	0.69	
	<i>Leersia hexandra</i> Sw.		0.058	0.042	0.039	
	<i>Potamogeton oxyphyllus</i> Miq.		0.86	1.5	0.76	
	<i>Pteris vittata</i> L.		0.17	0.14	0.099	
	<i>Selaginella delicatula</i> (Desv.) Alst		0.43	0.85	0.58	
In	<i>Ageratum houstonianum</i> Mill.	TF	0.82	1.5	1.0	Ha et al. (2011)
	<i>Commelina communis</i> L.		1.1	0.11	0.83	
	<i>Diplazium esculenta</i> (Retz.) Sw.		2.6	0.065	0.11	
	<i>Equisetum diffusum</i> D. Don		0.25	0.10	0.15	
	<i>Houttuynia cordata</i> Thunb.		3.7	0.29	0.45	
	<i>Kyllingia nemoralis</i>		1.7	0.52	0.69	
	<i>Leersia hexandra</i> Sw.		0.17	0.042	0.039	
	<i>Potamogeton oxyphyllus</i> Miq.		1.8	1.5	0.76	
	<i>Pteris vittata</i> L.		0.62	0.14	0.099	
	<i>Selaginella delicatula</i> (Desv.) Alst		9.7	0.85	0.58	
	Ryegrass	BAC	0.081	0.28	0.0037	
Lettuce leaves		0.062	1.5	0.011		
Bi	Umbelliferae family	BAC	0.07	1.2	0.004	Pueyo et al. (2003)
			0.009	0.96	0.0002	

**Table 2.6 Comparison of BACs between Cd and Pb, and Be, Cd, Ga, In, Te, La, Ce, Nd, Gd, and Bi in barley/wheat, in vertical order from low to high bioaccumulation (Omberg et al., 2011).**

	Be	Ga	Cd	Te	La	Ce	Nd	Pb	Bi
Stem	0.0029	0.0024	0.00087	0.022	0.0024	0.0048	0.0022	0.0046	0.0036
Grain	0.0016	0.0016	0.00025	0.013	0.00061	0.14	0.00053	0.002	0.0014

### 2.4.3. Toxicity of ETECs to plants

The concentrations of ETECs which caused significant toxicity to plants, either added directly to soil, added via solution which was exposed to plants or added to soil, or the concentrations in plant material when toxicity was found are present on Table 2.7. Beryllium can induce toxicity at <math>0.5-5 \text{ mg L}^{-1}</math> in solution and  $14-150 \text{ mg kg}^{-1}$  added to soil (Table 2.7), with symptoms such as chlorosis, leaf curl, purplish spots, and stubby roots. This is consistent with the previously established toxicity threshold ranges of  $10-50 \text{ mg kg}^{-1}$  soil and  $2-16 \text{ mg L}^{-1}$  (Kabata-Pendias & Mukherjee, 2007). REEs reduce photosynthesis in plants at high concentrations (Hu et al., 2016).

For the other ETECs, phytotoxic soil concentrations are usually  $>100 \text{ mg kg}^{-1}$  ETEC in soil due to strong sorption to and hence reduced bioavailability in soil. Su et al. (2018) and Sajwan et al. (1996) showed that reducing the pH and thus increasing bioavailability decreased the toxicity thresholds of Ga in rice seedlings and Be. Likewise, precipitation in solution, particularly for Be, Ga and In, could be partially responsible for the variation in aqueous concentrations required to achieve toxicity. These values were usually less than  $5 \text{ mg L}^{-1}$  and often below the lowest concentration tested.

There are insufficient data to identify any visible symptoms consistently related to the toxicity of these ETECs. Gallium, Gd, In, and La caused rupturing in the roots of cowpea (*Vigna unguiculata*), which is directly related to the trivalent cations binding strongly to the cell walls, albeit this occurred in solution (instead of soil) where availability is higher (Kopittke et al., 2008; Kopittke et al., 2009). Browning of roots was observed for bok choy (*Brassica rapa* subsp. *chinensis*) and sunflower (*Helianthus*) plants contaminated with La and Nd (Rezaee et al., 2018), and Te caused various symptoms in wheat, barley and garlic.

**Table 2.7 Toxicity thresholds and symptoms of Be, Cd, Ga, In, Te, La, Ce, Nd, Gd, and Bi in terrestrial species.**

Element	Species	Growth stage <sup>a</sup>	Toxicity threshold <sup>b</sup>			Visible symptoms <sup>c</sup>	Reference
			Soil (mg kg <sup>-1</sup> )	Solution (mg L <sup>-1</sup> )	Plant material (mg kg <sup>-1</sup> DM)		
Be	Oat	Pre-germination	<30		8		Bohn and Seekamp (1979)
	Barley	Seedling		0.6 <sup>d</sup>		Yellow leaves Stunted stems	Davis et al. (1978)
	Cabbage	Mature		5	15	Interveinal necrosis Death and abscission of outer leaves	Hara et al. (1977)
	Collards	Pre-germination	150	4	31.9		Kaplan et al. (1990)
	Kale	Seedling		2	0.4	Small, dark, pitted, necrotic spots Purplish speckling Curled leaves	Williams and Le Riche (1968)
	Oilseed rape ( <i>Brassica napus</i> )	Seedling		<0.9		Reduced chlorophyll content Oxidative damage	Ali et al. (2018)
	Mustard ( <i>Brassica</i> )	Seedling		2		Reduced radicle length	Williams and Le Riche (1968)
	Bush bean ( <i>Phaseolus vulgaris</i> )	Seedling		<0.5	4-8	Browning of roots Stubby roots Less fruit pods with earlier maturation	Romney et al. (1962)
	Soybean ( <i>Glycine max</i> )	Pre-germination	<25		1.25-31.33	Dark-green leaves Purple stems	Sajwan et al. (1996)
	Potato	Pre-germination	100				Bohn and Seekamp (1979)
		14			Reduced leaf area index	Juzl and Stefl (2002)	
Ga	Wheat	Seedling	<0.17				Snowden et al. (1995)
			120 (plant biomass)				Wheeler and Power (1995)
			400	15.8			Syu et al. (2021)
	Rice	Seedling	<50		5		Su et al. (2018)
				2.14	14.5	Reduced transpiration rate Reduced water use efficiency	Yu et al. (2015)
				>15		-	Syu et al. (2017)
	Cucumber ( <i>Cucumis sativus</i> )	Seedling		<5.6			Johnson and Barton (2007)
	Cowpea	Seedling		0.047		Ruptures in roots	Kopittke et al. (2009)
	Onion	Post-germination		<16.6			Clarkson (1965)
	<i>Arabidopsis thaliana</i>	Seedling		<0.42		Oxidative damage	Chang et al. (2017)
In	Wheat	Seedling	<0.29				Snowden et al. (1995)
			400		2.53		Syu et al. (2021)
	Rice	Seedling	100		6.6		Su et al. (2018)
				<0.04		Reduced chlorophyll content	Syu et al. (2017)
	Cowpea	Seedling		0.041		Ruptures in roots	Kopittke et al. (2009)
	Onion	Post-germination		<23.8			Clarkson (1965)

Te	Wheat	Seedling		<2		Failure of normal secondary root development Yellow-white mottling Drying near edges of leaves	Martin (1937)
	Barley	Seedling	-			Red stems Premature leaf senescence	Davis et al. (1978)
	Indian mustard ( <i>Brassica juncea</i> )	Seedling		>51.04			Ogra et al. (2010)
	Garlic	Seedling		<69		Blackening of roots Withering of leaves	Tanaka et al. (2020)
La	Maize ( <i>Zea mays</i> )	Seedling	100		0.95		Hao et al. (2021)
	Wheat	Seedling	50 (plant biomass)				Wheeler and Power (1995)
		Seedling		1.0			X Hu et al. (2002)
		Seedling		<0.5		15.3	Xin Hu et al. (2002)
	Bok choy		96.9			Browning of roots	Rezaee et al. (2018)
	Onion	Pre-germination	200		<10		Kotelnikova et al. (2019)
	Sunflower		111		120	Browning of roots	Rezaee et al. (2018)
Ce	Onion ( <i>Allium cepa</i> )	Pre-germination	200		<2		Kotelnikova et al. (2019)
	Wheat	Seedling		1.0			X Hu et al. (2002)
		Seedling		<0.5		16	Xin Hu et al. (2002)
Nd	Switchgrass ( <i>Panicum virgatum</i> )	Pre-germination	260		6.69		Carpenter et al. (2015)
	Tomato ( <i>Solanum lycopersicum</i> )	Pre-germination	1025				Carpenter et al. (2015)
	Radish ( <i>Raphanus sativus</i> )	Pre-germination	542		25.5		Carpenter et al. (2015)
	Bok choy		151			Browning of roots	Rezaee et al. (2018)
	Sunflower		193		221	Browning of roots Purpling of shoot	Rezaee et al. (2018)
	Common milkweed ( <i>Asclepias syriaca</i> )	Pre-germination	216		7.18		Carpenter et al. (2015)
	Showy ticktrefoil ( <i>Desmodium canadense</i> )	Pre-germination	232		8.45		Carpenter et al. (2015)
	Gd						
Bi	<i>Arabidopsis thaliana</i>	Pre-germination		0.21			Nagata (2015)

<sup>a</sup>Growth stage when exposed to the contaminant ; <sup>b</sup>mg L<sup>-1</sup> in nutrient solution, mg kg<sup>-1</sup> in soil, or mg kg<sup>-1</sup> dry matter (DM) in plants; <sup>c</sup>Other than reductions in germination and biomass production, which are present in most examples of toxicity; <sup>d</sup>Nutrient solution added to soil.



Two studies have directly compared the toxicity of the ETECs to that of Cd and Pb in identical environments. Beryllium was less toxic than Cd but more toxic than Pb to barley seedlings (Davis et al., 1978). In a comparison of the toxicity of Be and Cd to potato leaf area index, the concentration of Be added to soil which caused toxicity was higher than the maximum concentration of Cd added to soil, which did not cause toxicity (Juzl & Stefl, 2002).

Most ETECs are toxic to plants at less than five mg L<sup>-1</sup> in solution if bioavailability is high. Sorption to soil greatly reduces bioavailability and the reductions to plant yields. More examples are needed to establish thresholds for phytotoxicity in soil and solution. Due to variation in toxicity in the environment, it is important to compare the toxicity thresholds of the ETECs to Cd, Pb and other common contaminants in the same study.

#### 2.4.4. ETEC uptake via the pathways of essential elements

The ETECs Be, Ga, In, La, Ce, Nd, and Gd are not essential for plants or animals (Robinson et al., 2009), thus mechanisms have not been evolved for their uptake and translocation in plants, and absorption into the digestive tract in animals. However, ETECs can substitute for essential ions similar in size and partially follow some of their metabolic pathways, which is often reported in literature through correlations and interactions. The substitution of some elements is due to their position in the same group of the periodic table thus similar electronic configurations, e.g. Be, Ca, and Mg, and others have ions of a similar size to essential elements, e.g. Ga and Fe, and the REEs and Ca (Table 2.8).

**Table 2.8 Comparison of the ionic radii between the ETECs and essential elements they can substitute for in biological molecules**

ETEC		Essential element		Reference
Ion	Ionic radii (Å)	Ion	Ionic radii (Å)	
<sup>a</sup> Be <sup>2+</sup>	0.27	<sup>b</sup> Ca <sup>2+</sup>	1.00	Shah et al. (2016)
		<sup>b</sup> Mg <sup>2+</sup>	0.720	
<sup>b</sup> Ga <sup>3+</sup>	0.620	<sup>be</sup> Fe <sup>3+</sup>	0.645	Bernstein (2005)
<sup>d</sup> La <sup>3+</sup>	1.216	<sup>b</sup> Ca <sup>2+</sup>	1.00	Tyler (2004b)
<sup>d</sup> Ce <sup>3+</sup>	1.196			
<sup>d</sup> Nd <sup>3+</sup>	1.163			
<sup>c</sup> Gd <sup>3+</sup>	1.193			
<sup>d</sup> Gd <sup>3+</sup>	1.247			

<sup>a</sup>IV coordination; <sup>b</sup>VI coordination; <sup>c</sup>VII coordination; <sup>d</sup>IX coordination; <sup>e</sup>high spin. Ionic radii from Shannon (1976); coordination (of hydrated ions) from Persson (2010).

## 2.5. Food safety and animal toxicity

To date, there are no food safety standards for the majority of the ETECs. The World Health Organisation has established a tolerable daily intake of  $2 \mu\text{g Be kg bodyweight}^{-1} \text{ day}^{-1}$  (Pearson & Ashmore, 2020). In China, there are limits for the concentration of REE oxide which is allowed in various foods (Table 2.9).

**Table 2.9 Maximum concentrations of REE oxides allowed in foods in China (Butterworth & Bugang, 2006).**

Food	Maximum level ( $\text{mg kg}^{-1}$ of total REE oxide)
Grains (paddy, maize, wheat)	2.0
Vegetables (excluding spinach)	0.7
Fruit	0.7
Peanut kernels	0.5
Potatoes	0.5
Green beans	1.0
Tea	2.0

Despite the lack of food safety standards, the ETECs are toxic to animals and humans at high concentrations, as has been demonstrated in rodents. The  $\text{LD}_{50}$  values (oral lethal dose for 50% of the population) for these elements, for rats and mice, are presented in Table 2.10. Cadmium is moderately toxic with an  $\text{LD}_{50}$  of  $100\text{-}300 \text{ mg kg}^{-1}$ , whereas the  $\text{LD}_{50}$  for Pb is  $1.2 - 105 \text{ mg kg}^{-1}$ , depending on the speciation (Rahde, 1994). The  $\text{LD}_{50}$  values for Be ranged from  $18\text{-}200$ , and ATSDR (2002) reported that the variation is due to differences in solubility and capacity to form insoluble Be compounds. The other elements usually had  $\text{LD}_{50}$  values of  $>1,000$ , although Bi and Te did not have definite values.

**Table 2.10 LD<sub>50</sub> values in mice and rats for oral ingestion of Be, Bi, Ce, Ga, Gd, In, La, Nd and Te.**

Element	Compound	Concentration		Species	Reference
		mg ETEC kg <sup>-1</sup> bodyweight	mmol ETEC kg <sup>-1</sup> bodyweight		
Be	Be(SO <sub>4</sub> )	120	13	Rat	ATSDR (2002)
		140	16	Mouse	
	BeCl <sub>2</sub>	200	22	Rat	
	BeF <sub>2</sub>	18-20	2.0-2.2	Mouse	
	Be <sub>2</sub> O <sub>3</sub>	18.3	2.0	Rat	
Cd	-	100-300	0.89-2.67	Mouse and rat	ATSDR (2012)
Ga	Ga(NO <sub>3</sub> ) <sub>3</sub>	4,360	63	Mouse	Santa Cruz Biotechnology Inc (2010)
In	-	>2,000	>17	Rat	Asakura et al. (2008)
	In(NO <sub>3</sub> ) <sub>3</sub>	3,350	29	Mouse	U.S. Department of Health and Human Services (2001)
	InCl <sub>3</sub>	4,200	37	Rat	
Te	-	>5,000	>39	Mouse and rat	MAK-Commission (2006)
La	La(NO <sub>3</sub> ) <sub>3</sub>	1,450	10	Rat	U.S. EPA (2018)
	LaCl <sub>3</sub>	2,370	17	Rat	
	La(NO <sub>3</sub> ) <sub>4</sub> NH <sub>4</sub>	830	6.0	Rat	
Ce	Ce(NO <sub>3</sub> ) <sub>3</sub>	4,200	30	Rat	USEPA (2009)
	Ce(NO <sub>3</sub> ) <sub>3</sub>	1,178	8.4	Mouse	
	CeO <sub>2</sub>	622	4.4	Mouse	
Nd	Nd(NO <sub>3</sub> ) <sub>3</sub>	2,750	19	Rat	ECHA
	NdCl <sub>3</sub>	3,024	21	Mouse	U.S. EPA (2009)
Gd	Gd(NO <sub>3</sub> ) <sub>3</sub>	1,743	11	Rat	Dean (2018)
Pb	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>4</sub> Pb	1.2	0.0058	Rat	Rahde (1994)
	(CH <sub>3</sub> ) <sub>4</sub> Pb	105	0.51	Rat	
Bi	-	>2,000	>9.6	Rat	Sano et al. (2005)

## 2.6. Hypotheses and aims

At present, there is a lack of knowledge of the mobility of the ETECs Be, Ga, In, La, Ce, Nd, and Gd in comparison to each other and to a common contaminant such as Cd in the soil-plant system.

It was hypothesised that the ETECs will sorb strongly to soil, with  $K_D$  values of 100-1000 for Be and >1000 for Ga, In, Te, La, Ce, Nd, Gd, and Bi, and all of the ETECs will have higher  $K_D$  values than Cd.  $K_D$  values will decrease as the concentrations of the ETECs added to soil increases.  $K_D$  values will increase as the soil solution pH increases. Due to the strong sorption to soil, bioaccumulation of the ETECs in perennial ryegrass will be low. Bioaccumulation coefficients of the ETECs in perennial ryegrass will be inversely proportional to  $K_D$ . There is likely a low risk of the ETECs entering the food chain via plant material, but a high risk of ETECs entering via contaminated soil.

The aim of this thesis is to identify the critical factors affecting the mobility of the ETECs Be, Ga, In, Te, La, Ce, Nd, Gd, and Bi in the soil-plant system-in particular, how contaminant concentration, soil solution pH and soil type affect sorption of the ETECs to soil, and how the mobility of these elements in soil and grass compares to each other and to Cd. Soil mobility will be assessed by comparing the  $K_D$  values of ETECs added to natural soil with the common contaminant Cd, and the effect of changing the soil solution pH and concentration added on  $K_D$  will be determined. Bioaccumulation and phytotoxicity of the ETECs in perennial ryegrass (a common agricultural crop) grown in soil spiked with the elements will be found and compared to Cd, to assess their relative plant mobility. A case study will identify the critical factors affecting the bioavailability of the essential micronutrient I, which can then suggest information on the risks of the other ETECs in the environment. From the aforementioned findings, the risk of these elements entering the food chain can be identified.

### 3. The mobility and plant uptake of the gallium and indium, two emerging contaminants associated with electronic waste.

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#### Abstract

The trace elements gallium (Ga) and indium (In) are increasingly susceptible to soil contamination via disposal of electronic equipment. Chemically similar to Al, these elements may be mobile and bioavailable under acidic conditions. We sought to determine extent and nature of Ga and In mobility in the soil – plant system and thus their potential to enter the food chain. Batch sorption experiments on a high fertility silt loam (pH 5.95, CEC 22 meq 100 g<sup>-1</sup>) showed strong retention of both elements to the soil matrix, with mean distribution coefficient ( $K_D$ ) values of 408 and 2021 L kg<sup>-1</sup> for Ga and In respectively. Unexpectedly,  $K_D$  increased with concentration, which we attributed to precipitation of excess ions as insoluble hydroxides.  $K_D$  decreased with increased pH as Ga/In(OH)<sup>2+</sup> and Ga/In(OH)<sub>2</sub><sup>+</sup> transitioned to Ga/In(OH)<sub>4</sub><sup>-</sup>. Movement into the aboveground portions of perennial ryegrass (*Lolium perenne* L.) was low, with bioaccumulation factors (BAF) of 0.0037 for Ga and 0.0002 for In; foliar concentrations peaked at 11.6 mg kg<sup>-1</sup> and 0.015 mg kg<sup>-1</sup> respectively. The mobility of Ga and In in the soil plant system is low compared to other trace element contaminants such as cadmium, copper and zinc, indicating that negligible amounts of Ga and In will leach or be taken up by plants. Therefore, these elements are likely to accumulate in soils and soil ingestion will be the largest pathway into the food chain. Future work should focus on the effect of redox conditions on Ga and In, as well as uptake into acidophilic plants such as *Camellia* spp., which accumulate Al.

#### 3.1. Introduction

Gallium (Ga) and indium (In) are chalcophilic metallic trace elements that are non-essential for life. (Ladenberger et al., 2015; Połedniok et al., 2012). Crustal concentrations of Ga and In average 15-19 mg kg<sup>-1</sup> and 0.05-0.07 mg kg<sup>-1</sup> respectively and their respective soil concentrations range between 3-300 mg kg<sup>-1</sup>, and 0.01-0.5 mg kg<sup>-1</sup> (Kabata-Pendias & Mukherjee, 2007; Lokanc et al., 2015; Połedniok et al., 2012).

Both elements are used extensively in electronic equipment. Gallium arsenide (GaAs) and gallium nitride (GaN) semiconductors are used in wireless and optoelectronic applications (Butcher & Brown, 2014). Indium-tin oxide (ITO) is used as a coating on liquid crystal displays, plasma displays and touch screens (Schwarz-Schampera, 2014). Western societies are becoming increasingly dependent on these

devices. From 1995 – 2015, Ga production increased from 62 to 469 tonnes and In 239 to 769 tonnes (U.S. Geological Survey, 2017a, 2017b). Both elements could enter the environment through the manufacture or disposal of electronic equipment (Maneesuwannarat et al., 2016; Robinson, 2009). Chen et al. (2015) reported that industrial sludge associated with electronic manufacturing contained 40-42 mg kg<sup>-1</sup> In. Up to 4.6 mg kg<sup>-1</sup> In was present in soil surrounding recycling sites in Indian slums (Ha et al., 2009), and up to 2.8 mg kg<sup>-1</sup> In near a site in Ghana (Tokumaru et al., 2017).

Neither Ga nor In are mined in isolation, but are produced as a by-product during the processing of other metals (Lu et al., 2017; Schwarz-Schampera, 2014). Ha et al. (2011) and Boughriet et al. (2007) measured up to 97 and 75 mg kg<sup>-1</sup> In respectively in soil surrounding a Pb-Zn mine and a smelter. Others reported lower concentrations of 1.6 mg kg<sup>-1</sup> (Waterlot et al., 2013), 1.4 mg kg<sup>-1</sup> (Li et al., 2016), 0.55 mg kg<sup>-1</sup> (Sterckeman et al., 2002) and 0.37 mg kg<sup>-1</sup> (Aide, 2009). Poedniok et al. (2012) reported soil Ga concentrations at five sites near mines or metal processing plants ranging 93-441 mg kg<sup>-1</sup> Ga and nearby agricultural soils contained 39-219 mg kg<sup>-1</sup> Ga. Coal is a major source of Ga, which is further concentrated in fly ash (Lu et al., 2017). Qin et al. (2015) found 100-263 mg kg<sup>-1</sup> Ga in coal from China and the Former Soviet Union, while Font et al. (2007) and Fang and Gesser (1996) reported fly ash concentrations of 37.5-320 mg kg<sup>-1</sup> at power plants in Spain, Canada, China and Israel. Biosolids may become a significant source if they are contaminated with industrial waste (Sharma et al., 2017). Zhang et al. (2002) reported Japanese biosolids contained 91-339 mg kg<sup>-1</sup> Ga, and studies in Sweden reported biosolids concentrations of 1-41 mg kg<sup>-1</sup> (Ahlberg et al., 2006; Eriksson, 2001).

Gallium and In have the potential to adversely affect animal health if they enter the food chain, though little is currently known of their toxicity thresholds and effects. Large increases of any element from background concentrations may negatively affect animal health (White & Hemond, 2012). While there are data for acute and chronic human and animal exposure to In and Ga (Ayadi et al., 2014; Homma et al., 2003; Ivanoff et al., 2012; Kjølholt et al., 2003), current data is too sparse to form food and drinking water safety limits. Given the likely increases in soil Ga and In concentrations, human exposure may arise from direct soil consumption, plant uptake or leaching to groundwater.

As group 13 metals, the behaviour of Ga and In in soil is likely dominated by the stability of their respective aqueous trivalent species, ion hydrolysis and hydroxide precipitation. The octahedral hydrated cations Ga<sup>3+</sup> and In<sup>3+</sup> are acidic, and upon hydrolysis form the aqueous species Ga/In(OH)<sup>2+</sup>, Ga/In(OH)<sub>2</sub><sup>+</sup>, Ga/In(OH)<sub>3</sub><sup>0</sup> and Ga/In(OH)<sub>4</sub><sup>-</sup>, depending on the pH of the surrounding solution (Bernstein, 1998). However, their ionic potentials drive key differences between the three, such as the

pH range at which hydrolysis occurs (Kabata-Pendias & Mukherjee, 2007). The hydroxide forms  $\text{Ga}(\text{OH})_4^-$  and  $\text{In}(\text{OH})_3$  are the dominant species in most agricultural soils, with pHs of 5.5-7.0 (Desutter & Godsey, 2010; McLaren & Cameron, 1996; Wood & Samson, 2006). Neutral forms of Ga and In are poorly soluble and rapidly precipitate, with this process peaking when these species' concentrations are the highest (Ga at pH 4.3-5.2, In at pH 6.0-8.0), and dissociation to ionic forms outside of that range causing dramatic variation. Solubility of  $\alpha\text{-GaOOH}$  (a crystalline compound) was modelled to range from  $10^{-9.3}$ - $10^{-4}$  M at pH 3-10 in pure water at 25°C, and an equally large range of  $10^{-7.3}$ - $10^{-4}$  M has been reported for amorphous  $\text{In}(\text{OH})_3$  (Wood & Samson, 2006). Transformation of  $\text{Ga}/\text{In}(\text{OH})_3$  to  $\alpha\text{-GaOOH}$ ,  $\beta\text{-Ga}_2\text{O}_3$ , In analogues and other mineral forms occurs from aging, heat and/or pressure (Bernstein, 1998; Pokrovski et al., 1997). Due to their high ionic potentials of 48  $\text{nm}^{-1}$  for  $\text{Ga}^{3+}$  and 38  $\text{nm}^{-1}$  for  $\text{In}^{3+}$  (Shannon, 1976), both elements likely bond with hard inorganic ligands such as  $\text{F}^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$ ; softer In also bonds strongly with  $\text{Cl}^-$  (Wood & Samson, 2006). Both elements are frequently complexed by organic acids, such as citric, malic and acetic, released in soil by root exudation (Boros et al., 2014; Chang et al., 2017; Jaitz et al., 2011). Although their aqueous oxidation state is always +3 (Wood & Samson, 2006), movement may be influenced by reduction and oxidation of Mn, Fe and S, whose redox-active solid phases can serve as sites at which sorption and mineral formation occurs (Kabata-Pendias & Mukherjee, 2007; Połedniok et al., 2012).

As precipitation and adsorption cause solubility to be low, soil contaminants are likely readily immobilised and rendered unavailable to organisms, although there are reports that as little as 67% of In was sorbed in many soils (Boughriet et al., 2007; H. Hou et al., 2005; Waterlot et al., 2013) and just 55-85% of Ga was sorbed in (Połedniok et al., 2012). (Sheppard et al., 2007) reported that  $K_D$  values (solid / solution concentration coefficients) of Ga and In in Canadian soils were 11,000 and 2,800 respectively.

There is limited information on plant uptake of Ga and In. Gallium concentrations of  $<0.001 \text{ mg kg}^{-1}$  were reported in wheat and barley grains (Eriksson, 2001). Edible mushrooms contained  $1.4\text{-}6.6 \text{ mg kg}^{-1}$  Ga (Dursun et al., 2006) and agricultural species in Vietnam contained  $0.36\text{-}2.57 \text{ mg kg}^{-1}$  Ga (Ha et al., 2011). Higher concentrations have been obtained under hydroponic conditions with  $2 \text{ mg kg}^{-1}$  and  $74 \text{ mg kg}^{-1}$  found in wheat and rice (Syu et al., 2017; Wheeler & Power, 1995). Indium concentrations were  $<0.005 \text{ mg kg}^{-1}$  in wheat and barley (Eriksson, 2001), and  $<0.05$  in perennial ryegrass (Waterlot et al., 2013). Cabbage, garlic and water spinach contained  $0.001\text{-}0.005 \text{ mg kg}^{-1}$  In (Li et al., 2016), while Vietnamese vegetables contained  $0.14\text{-}3.89 \text{ mg kg}^{-1}$  (Ha et al., 2011), with up to  $151 \text{ mg kg}^{-1}$  in rice. Most Ga and In accumulate in the roots with shoot: root ratios of 0.028 and 0.11 Ga in barley and

wheat (Omberg et al., 2011; Wheeler & Power, 1995), 0.082-0.22 Ga in *Arabidopsis Thaliana* (Chang et al., 2017), and <0.32 of both elements in rice (Syu et al., 2017; Yu et al., 2015). Gallium and In may behave similarly to Al, which is retained in epidermis and outer cortex of the roots (Eticha et al., 2005; Horst et al., 2010; Mauseth, 2014). Kopittke et al. (2009) reported that Ga reduced elongation in cowpea roots through strong cellular binding. Therefore, we would hypothesise that only limited amounts of Ga and In are likely to be transported from soil to shoot biomass.

The aim of this study was to determine the mobility of Ga and In in the soil – plant system, and evaluate their potential to enter into the food chain. Batch sorption experiments were used to measure the partitioning of the metals between the soil solid and solution phases; pot trials were employed to estimate capacity for uptake and translocation by perennial ryegrass (*Lolium perenne* L., a common agricultural species); and aqueous speciation modelling was completed with Visual MINTEQ 3.1.

## **3.2. Materials and methods**

### **3.2.1. Soil properties**

A high fertility vegetable-growing mottled/typic orthic granular silt loam (Landcare Research, 2018) was collected near Pukekohe, New Zealand (37°13'18.92''S 174°52'5.94''E), during summer 2012/13. The physical and chemical properties of the soil were measured in two previous studies (Al Mamun et al., 2016; Valentinuzzi et al., 2015) and are presented in Table 3.1. The pH of the soil was adjusted approximately 4 years before this work by mixing the soil thoroughly with laboratory grade lime (CaCO<sub>3</sub>) in the following proportions: 0.3, 0.6, 1.3 or 10 wt%, resulting in soil pH (1:2.5 mass soil: vol. H<sub>2</sub>O) values of 5.5, 6.0, 6.8, 7.0 and 7.1 respectively (Valentinuzzi et al., 2015)



**Table 3.1 Physical and chemical properties of Pukekohe soil, from <sup>a</sup>Landcare Research (2018) and Valentinuzzi et al. (2015). Values in brackets represent the standard error of the mean (n=3).**

<sup>a</sup> Texture profile	Loam/silty loam over clay
<sup>a</sup> Topsoil clay	22-34%
<sup>a</sup> Drainage class	Imperfectly/moderately well drained
<sup>a</sup> Profile available water (0-30 cm)	High (51-66 mm)
pH (H <sub>2</sub> O)	5.95 (0.04)
CEC (cmol(+) kg <sup>-1</sup> )	22
Base saturation (%)	70
C (%)	2.1
N (%)	0.23
Olsen P (cmol kg <sup>-1</sup> )	290
N available (kg ha <sup>-1</sup> )	50
Total P (mg kg <sup>-1</sup> )	3414 (26)
Total S (mg kg <sup>-1</sup> )	491 (6)
Total Ca (mg kg <sup>-1</sup> )	4147 (117)
Total Mg (mg kg <sup>-1</sup> )	2400 (95)
Total K (mg kg <sup>-1</sup> )	1951 (59)
Total Cd (mg kg <sup>-1</sup> )	1.5 (0.0)
Total Cu (mg kg <sup>-1</sup> )	65 (0)
Total Mn (mg kg <sup>-1</sup> )	1266 (12)
Total Zn (mg kg <sup>-1</sup> )	173 (1)
Total Fe (mg kg <sup>-1</sup> )	44606 (96)
Total Pb (mg kg <sup>-1</sup> )	61 (1)
Cd Ca(NO <sub>3</sub> ) <sub>2</sub> -extractable (mg kg <sup>-1</sup> )	0.015 (0.002)
Cu Ca(NO <sub>3</sub> ) <sub>2</sub> -extractable (mg kg <sup>-1</sup> )	0.13 (0.02)
Mn Ca(NO <sub>3</sub> ) <sub>2</sub> -extractable (mg kg <sup>-1</sup> )	40 (4)
Zn Ca(NO <sub>3</sub> ) <sub>2</sub> -extractable (mg kg <sup>-1</sup> )	0.37 (0.06)
Fe Ca(NO <sub>3</sub> ) <sub>2</sub> -extractable (mg kg <sup>-1</sup> )	0.65 (0.20)

### 3.2.2. Batch sorption experiments

The partitioning of Ga and In between the soil solid and solution phases was determined using the approach described by Al Mamun et al. (2016). Briefly, 5 g ( $\pm$  0.1) of soil was equilibrated with a 0.05 M Ca(NO<sub>3</sub>)<sub>2</sub> solution that had been spiked with a known amount of Ga or In by mixing the soil and solution in a lidded centrifuge tube in an end-over-end shaker. Preliminary experiments showed that after 120 minutes of shaking relatively little further sorption occurred (Fig. B.1), thus subsequent experiments used this equilibration time to analyse sorption isotherms. The extraction mixture was centrifuged at 1880 g force for 10 minutes, after which the extractant was filtered through a Whatman 51 filter. The filtrate was stored at 4°C prior to analysis. All extractions were carried out in triplicate.

We measured the effect of concentration on the amount removed from the solution phase, using soil-affected change in solubility from 0.05 M Ca(NO<sub>3</sub>)<sub>2</sub> solutions spiked with 1, 3, 10, 30, 100 or 1000 mg L<sup>-1</sup> Ga or In. The effect of pH was determined by equilibrating with the series of limed soils, using 10 mg L<sup>-1</sup> Ga/In spiked 0.05 M Ca(NO<sub>3</sub>)<sub>2</sub>. The extractant pH in un-spiked extracts of the entire lime series was measured after 120 minutes agitation, using a Mettler Toledo pH meter.

### 3.2.3. Plant uptake trial

Perennial ryegrass (*Lolium perenne* L.) was grown in 250 g pots filled with the Pukekohe granular soil spiked with 0, 15, 31, 63, 125, 250, 500, 1000 or 2000 mg kg<sup>-1</sup> Ga, or 0, 1.5, 3, 6, 13, 25, 50, 100 or 200 mg kg<sup>-1</sup> In. Concentrations were based on literature contamination reports (Boughriet et al., 2007; Ha et al., 2011; Połedniok et al., 2012). Both elements were added as nitrate salts dissolved in deionized water. There were four replicates of each treatment. Before planting (50 seeds per pot), the spiked soils were put through a wet-dry cycle and placed in a growth chamber (settings on Table B.1). Saucers were filled with water daily. Four weeks after germination, 40 mL of 10,000 mg L<sup>-1</sup> urea (CO(NH<sub>2</sub>)<sub>2</sub>) was applied to each pot. After six weeks of growth, ryegrass was harvested 1.5 cm above the soil surface, rinsed with deionised water, placed in a drying oven at 60°C until a constant weight was obtained, and ground using a Cyclotech type 1093 cyclone grinder.

### 3.2.4. Sample preparation and analysis

Plant samples underwent microwave digestion (CEM MARS Xpress, CEM Corporation, NC, USA), where ca. 0.2 g of plant material was accurately weighed into a 50 mL Teflon reaction vessel with 2 mL 69% HNO<sub>3</sub>, 2 mL 30% H<sub>2</sub>O<sub>2</sub>. Following digestion, samples were diluted to 10 mL using distilled water. Batch sorption extracts were diluted fivefold. Gallium and In concentrations were measured in the extracts and digests using inductively-coupled plasma mass spectrometry (ICP-MS, Agilent 7500). None of the Certified Reference Materials tested (Wageningen ISE 921 & IPE 100 and NIST 1573a) contained values for Ga or In. Therefore, standard additions of 0.002 and 0.02 mg L<sup>-1</sup> were used for quality assurance, giving recoveries of 90 - 95%.

The distribution coefficients ( $K_D$ ) (indicative of the degree of partitioning of an element between solid and solution phases) were calculated in L kg<sup>-1</sup> (Sheppard et al., 2009) using Equation 1 and Equation 2.  $C_s$  was the concentration of Ga/In retained by the soil matrix (mg kg<sup>-1</sup>),  $C_i$  was the initial concentration in the extractant solution (mg L<sup>-1</sup>),  $C_f$  was the concentration in the filtered solution (mg L<sup>-1</sup>),  $V$  was the volume of the filtered solution (L), and  $m$  was the mass of soil used (kg). Correction factors were applied to  $C_f$  (Fig. B.2).

[Equation 1]  $C_s = (C_i - C_f)V/m$

[Equation 2]  $K_D = C_s/C_f$

Summary statistics were calculated in excel; post hoc one-way ANOVA (analysis of variance) LSD (least significance differences) tests were calculated in RStudio, significance at  $p \leq 0.05$ .

### 3.2.5. Speciation modelling

The distribution between the different species of Ga and In in the extractant solutions were modelled using Visual MINTEQ (vMINTEQ, v 3.1). This is a numerical equilibrium speciation model, which utilizes equilibrium and solubility constants, to estimate aqueous and precipitated species in an aqueous system (Gustafsson, 2013).

Parameters inputted to the software are in Table B.2. The extractant solution was simulated with the initial screen parameters. Differences in aqueous hydroxide speciation and precipitation across the pH gradient were estimated, using the multi-problem/sweep tab with each of the concentrations of Ga and In used in batch sorption experiments, with their equivalent nitrate concentrations. 'Selected sweep results' exported data. pH and partitioning across the concentration gradient, and pH of the unspiked  $\text{Ca}(\text{NO}_3)_2$  solution were estimated.

## 3.3. Results

### 3.3.1. Sorption of Ga and In by soil

Gallium and In were strongly retained by the soil matrix. Average  $K_D$  values, produced from trendlines of soil plotted against solution concentrations, were 408 (21)  $\text{L kg}^{-1}$  and 2021 (64)  $\text{L kg}^{-1}$  for Ga and In respectively (with standard errors) (Fig. B.3). The degree of sorption (adsorption and precipitation) significantly increased ( $p < 0.05$ ) when  $K_D$  was plotted against the concentration added to soil (Table 3.2). The  $K_D$  of Ga rose logarithmically from 88 to 392  $\text{L kg}^{-1}$  with 1 to 100  $\text{mg L}^{-1}$  in the extracting solution. In jumped sharply from 458 to 1812  $\text{L kg}^{-1}$  between 10 – 30  $\text{mg L}^{-1}$ .

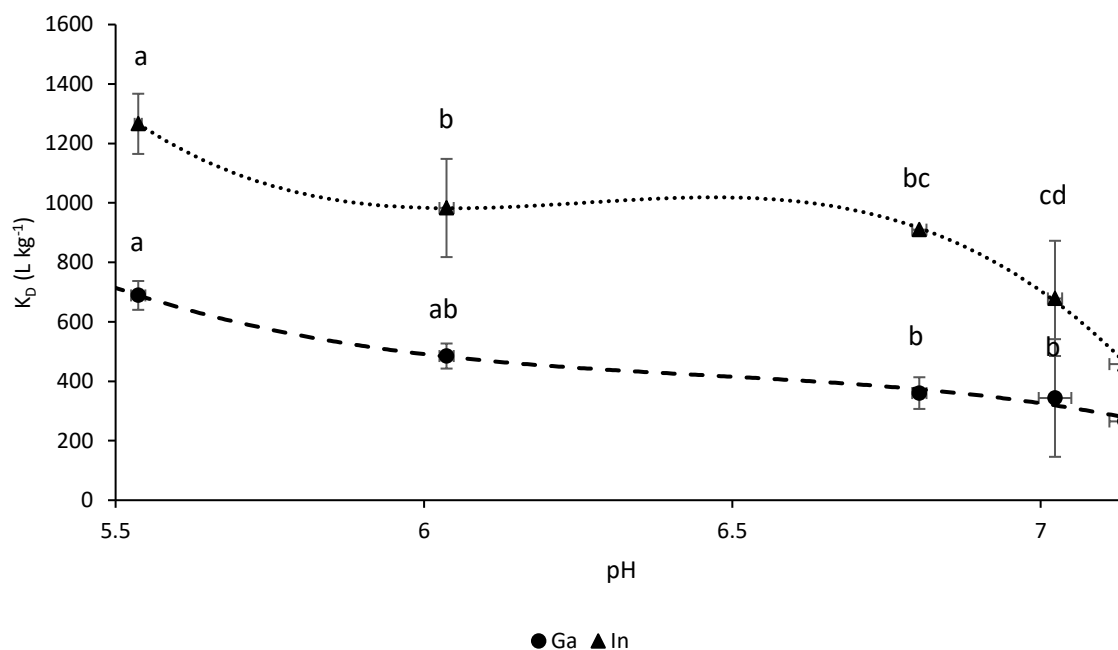
**Table 3.2 Effect of the concentration of Ga and In added to soil on  $K_D$ .**

Solution concentration ( $\text{mg L}^{-1}$ )	Soil concentration ( $\text{mg kg}^{-1}$ )	$K_D$ Ga ( $\text{L kg}^{-1}$ )	$K_D$ In ( $\text{L kg}^{-1}$ )
1	6	88 (36) a	163 (102) a
3	18	120 (73) a	339 (147) a
10	60	265 (97) b	458 (23) a
30	180	280 (33) bc	1812 (149) ab
100	600	392 (42) c	1803 (2408) b

Brackets donate standard deviation of mean values; different letters denote significance;  $n = 3$ . Soil concentration calculated from mass added to sample.

Retention of Ga and In by the soil matrix decreased as the pH of the soil solution increased, across the range tested (Fig. 3.1). The  $K_D$  of Ga significantly decreased from 689  $\text{L kg}^{-1}$  at pH 5.5, to 265  $\text{L kg}^{-1}$  at 7.1. Indium decreased from 1266 to 458  $\text{L kg}^{-1}$  respectively, with particularly significant drops in the

lowest 0.5 and highest 0.3 in the range tested. Although both trendlines were similar in shape, the  $K_D$  of In was consistently 73-153% higher than Ga.



**Fig. 3.1 Effect of extractant solution pH on  $K_D$  of Ga and In.**

Error bars denote standard deviation of mean values; different letters denote significance;  $n = 3$  except Ga pH 6.04  $n = 2$ , In pH 7.02  $n = 5$ , In pH 6.80  $n = 1$ .

### 3.3.1.1. Species present in the system

Visual MINTEQ 3.1 predicted that  $\text{Ga}(\text{OH})_4^-$  and  $\text{In}(\text{OH})_3$  were the dominant species across the pH gradient, accounting for >89.9% of all aqueous Ga and In (Table 3.3). As the pH rose from 5.5 to 7.1, anionic forms of both elements were expected to increase in dominance –  $\text{Ga}(\text{OH})_4^-$  92.4 to 99.9%, and  $\text{In}(\text{OH})_4^-$  0.008 to 0.338%. Indium was predicted to slightly complex with nitrate in acidic solutions (>1% at <pH 4.8). Sufficient precipitation data proportional to aqueous species was unable to be extracted, however Ga peaked at pH 5, thus decreased in the range tested (Fig. B.4), and In increased to peak at 6.8 – 7.3 (Fig. B.5). Saturation indexes increased with concentration. Partitioning between species with changes in acidity was polynomial (Fig. B.6 and Fig. B.7).

**Table 3.3** Minteq predictions of relative concentrations of aqueous mononuclear Ga and In hydroxyl species, and saturation indexes of Ga and In precipitates, in extractant solution across the pH range tested.

Lime applied (wt%)	pH	Aqueous species (%) <sup>a</sup>						Saturation index <sup>b</sup>	
		Ga/In <sup>3+</sup>	Ga/In(OH) <sup>2+</sup>	Ga/In(OH) <sub>2</sub> <sup>+</sup>	In(OH) <sub>3</sub> (aq)	Ga/In(OH) <sub>4</sub> <sup>-</sup>	In(NO <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	Ga/In(OH) <sub>3</sub> (am/s)	GaOOH(s)
<b>Ga</b>									
0	5.5	0.003	0.279	7.31	-	92.4	-	2.11	4.21
0.31	6.0	<0.001	0.009	0.785	-	99.2	-	1.64	3.74
0.61	6.8	<0.001	<0.001	0.020	-	99.9	-	0.84	2.94
1.25	7.0	<0.001	<0.001	0.008	-	99.9	-	0.64	2.74
10.00	7.1	<0.001	<0.001	0.005	-	99.9	-	0.54	2.64
<b>In</b>									
0	5.5	0.082	0.682	10.2	89.0	0.008	0.012	3.09	-
0.31	6.0	0.003	0.074	3.48	96.4	0.026	<0.001	3.24	-
0.61	6.8	<0.001	0.002	0.568	99.3	0.169	<0.001	3.25	-
1.25	7.0	<0.001	0.001	0.359	99.4	0.269	<0.001	3.25	-
10.00	7.1	<0.001	<0.001	0.285	99.4	0.338	<0.001	3.25	-

<sup>a</sup>Percentage of the total concentration of aqueous Ga/In. <sup>b</sup>Saturation index (SI) >0 denotes oversaturation and further precipitation; SI <0 dissolution.

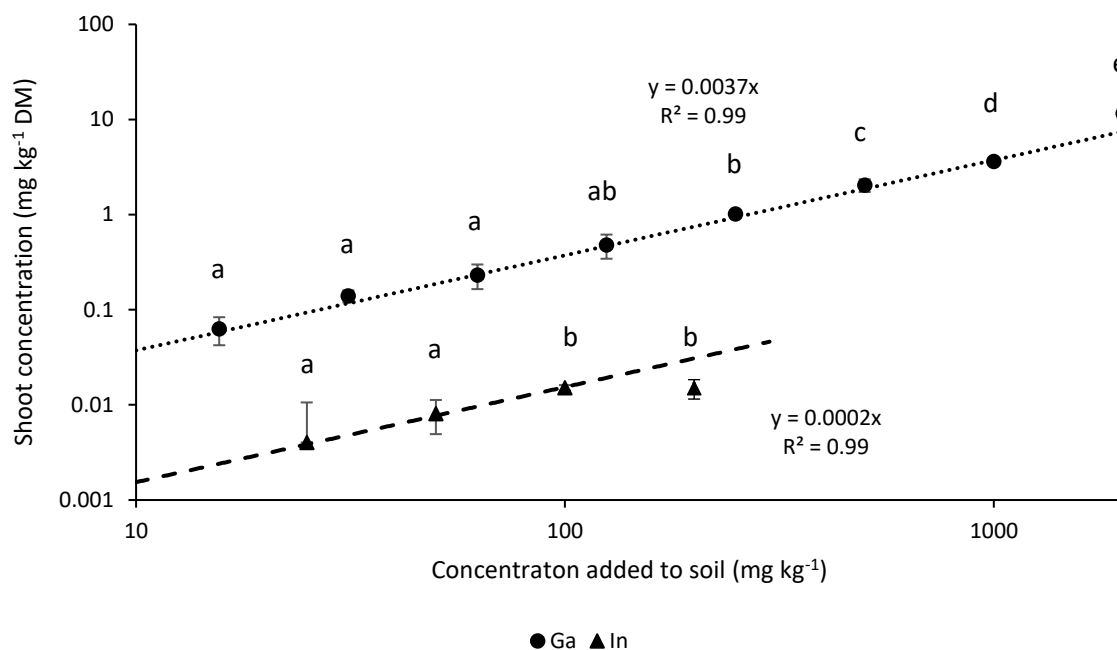
Concentration-dependent hydrolysis was modelled to alter the solution pH, hence pH was not controlled during experimentation, though due to soil buffering the extent cannot be accurately predicted. pH decreased from 5.6 with no spiking, to 3.8 with 100 mg L<sup>-1</sup> In and 3.3 with 100 mg L<sup>-1</sup> Ga; the degree increased with concentration and total hydrolysis in the system (Table 3.4). Thus, along the concentration gradient, acidity increased, and pH was lower for Ga than In. Data showed that resultant cation dominance increased with concentration, with 60.4% Ga<sup>3+</sup> and 71.9% In<sup>3+</sup> at predicted peak acidity, versus <0.1%. Above 3 mg L<sup>-1</sup> Ga and 30 mg L<sup>-1</sup> In saturation indexes decreased due to pH having a larger effect than concentration on the net values; Ga(OH)<sub>3</sub> (am) decreased from 1.27 to 0.78, despite a rise of 1.58 to 3.11 from 3 to 100 mg L<sup>-1</sup> with no pH change. In batch sorption extractions pH differences were lower than predicted, due to the soil's buffering capacity (McLaren & Cameron, 1996).

**Table 3.4** Minteq predictions of relative concentrations of aqueous mononuclear Ga and In hydroxyl species, and saturation indexes of Ga and In precipitates, in extractant solution across the concentration gradient tested.

Concentration in solution (mg L <sup>-1</sup> )	pH	Aqueous species (%)						Saturation index (at pH 5.5)	
		Ga/In <sup>3+</sup>	Ga/In(OH) <sup>2+</sup>	Ga/In(OH) <sub>2</sub> <sup>+</sup>	In(OH) <sub>3</sub> (aq)	Ga/In(OH) <sub>4</sub> <sup>-</sup>	In(NO <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	Ga/In(OH) <sub>3</sub> (am)	GaOOH(s)
<b>Ga</b>									
No soil pH change	5.5	0.003	0.279	7.31	-	92.4	-	-	-
1	4.6	1.50	18.2	65.0	-	15.3	-	1.16 (1.11)	3.26 (3.21)
3	4.3	6.44	35.0	56.0	-	2.64	-	1.27 (1.58)	3.38 (3.69)
10	3.9	20.6	47.2	31.9	-	0.268	-	1.14 (2.11)	3.24 (4.21)
30	3.6	39.8	45.1	15.1	-	0.031	-	0.99 (2.58)	3.09 (4.69)
100	3.3	60.4	33.9	5.66	-	0.003	-	0.78 (3.11)	2.89 (5.21)
<b>In</b>									
No soil pH change	5.5	0.082	0.012	10.170	89.046	0.008	0.012	-	-
1	4.8	5.95	10.0	30.1	53.1	0.001	0.896	1.98 (2.21)	-
3	4.5	22.5	19.1	29.1	25.9	<0.001	3.40	2.13 (2.68)	-
10	4.3	45.0	21.3	18.0	8.90	<0.001	6.79	2.30 (3.21)	-
30	4.1	60.8	17.8	9.34	2.87	<0.001	9.18	2.33 (3.68)	-
100	3.8	71.9	12.6	3.93	0.72	<0.001	10.9	2.05 (4.21)	-
<b>Unspiked 0.05 M Ca(NO<sub>3</sub>)<sub>2</sub> solution</b>									
0	5.6	-	-	-	-	-	-	-	-

### 3.3.2. Uptake of Ga and In by ryegrass

There was limited but significant transfer of both elements from soil to the leaves of perennial ryegrass (Fig. 3.2). Uptake of Ga peaked at 11.6 mg kg<sup>-1</sup> with 2000 mg kg<sup>-1</sup> added to soil, with the trend indicating further uptake is possible, while In plateaued at 0.02 with 100 mg kg<sup>-1</sup> in soil, significantly higher than at 25 and 50 mg<sup>-1</sup>. Bioaccumulation factors (shoot concentration/soil concentration) were low, at 0.0037 Ga and 0.0002 In, and were essentially linear for all but the highest soil concentrations (R<sup>2</sup> = 99).



**Fig. 3.2** Effect of the concentration of Ga and In added to soil on ryegrass shoot concentrations. Error bars denote standard deviation of mean values; different letters denote significance;  $n = 4$ .

### 3.4. Discussion

#### 3.4.1. Mobility of Ga and In in the soil system

Both Ga and In were bound strongly by the Pukekohe granular soil. Minimum  $K_D$  values across all independent variables (pH, concentration, time) were 82 Ga and 163 In. Solubility is prerequisite for mobility, and the capacity to move through the soil – plant system. Hence, as  $K_D$  measures the fraction left in solution, it is sufficient for evaluation of potential mobility, though is a static measure and other non-investigated factors, such as colloidal transport, also affect movement (McLaren & Cameron, 1996).

The  $K_D$  values in this study for Ga, with a mean  $K_D$  of 408 L kg<sup>-1</sup>, were significantly lower than the values of 11,000 and 13,000 L kg<sup>-1</sup> reported for Canadian soils (Sheppard et al., 2007; Sheppard et al., 2009). These differences are likely due to analytical methods since there was no aging of the Ga and In in our batch experiments, thus much of total Ga and In was still in the labile pool. Precipitated Ga(OH)<sub>3</sub> ages to less soluble  $\alpha$ -GaOOH, with geomorphological transformation to  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> and other minerals possible (Bernstein, 1998; Pokrovski et al., 1997). Adsorbed Ga and In are assumed susceptible to occlusion by Mn and Fe (hydr)oxides and diffusion into mineral structures. Aqueous forms are lost through soil profile leaching or plant uptake (Alloway, 2013).

**Table 3.5 Comparison of Ga and In  $K_D$  values in literature.**

Element	$K_D$ (L kg <sup>-1</sup> )	Statistical and experimental parameter	Soil properties	Reference	
Ga	408	Mean	Single site, loam/silty loam, vegetable growing, 0-25 cm, New Zealand, experimentally contaminated	Current study	
	82	Minimum, 3 mg L <sup>-1</sup> Ga			
	689	Maximum, pH 5.5			
	219,779	Minimum, pH 5.4	Single site, 0-10 cm, grass/deciduous trees, Sweden, uncontaminated	G. Tyler and T. Olsson (2001) <sup>a</sup>	
	1,999,999	Maximum, pH 7.1 – 7.8			
	14,211	Mean	Many sites, pH 4.29, sandy-silty, beech deciduous forest, 0-7.5 cm, Sweden, uncontaminated	Tyler and Olsson (2002) <sup>b</sup>	
	11,000	Mean			
	210	Minimum			
	200,000	Maximum	Many similar sites, sandy to sandy-loam, mature forest, 0-5 cm, Canada, uncontaminated	Watmough (2008) <sup>c</sup>	
	2000	pH 3.8			
	100,000	pH 7			
	1300	Peat ( <i>Spagnum</i> ), fen, <i>Pinus</i> forest	Individual sites, 0-30 cm, Sweden, uncontaminated	Sheppard et al. (2009)	
	2600	Clayey silty till, fen, mixed forest			
	5,900	Sandy till, oak forest			
	7,800	Peat, former fen, spruce forest			
	7,800	Clay gyttja, open fen			
	9,400	Clay gyttja, fen, alder forest			
	14,000	Clayey silty till, arable			
	5,500	Mean			
	13,000	Mean			Many sites, Canada, uncontaminated/not recently
880	5th percentile				
110,000	95th percentile				
In	2,021	Mean	Single site, loam/silty loam, vegetable growing, 0-25 cm, New Zealand, experimentally contaminated	Current study	
	163	Minimum, 1 mg L <sup>-1</sup> In			
	3,187	Maximum, 30 mg L <sup>-1</sup> In			
	967	Mean	Many sites, pH 4.29, sandy-silty, beech deciduous forest, 0-7.5 cm, Sweden, uncontaminated	Tyler and Olsson (2002) <sup>b</sup>	
	2,800	Mean			
	180	Minimum			
11,000	Maximum	Many sites, Canada, uncontaminated/not recently	Sheppard et al. (2007)		

<sup>a</sup>Calculated from graphical solution data and the total solution concentration; <sup>b</sup>calculated from table data; <sup>c</sup>collected from graph.

Gallium and In are relatively immobile compared to other common trace element contaminants in soil. Table 3.6 shows data collected from similar environments for comparison including the critical factors that affect  $K_D$ , namely pH, concentration, organic carbon, clay abundance and clay composition contribute to  $K_D$  (Sohlenius et al., 2013). Sheppard et al. (2007) ranked Ga and In as the 3<sup>rd</sup> and 7<sup>th</sup> least mobile when compared with 14 common trace element contaminants, across a range of Canadian soil types without recent contamination. Gallium was shown to be comparatively immobile across several Swedish soils (Sheppard et al., 2009), and the most immobile of the examined contaminants averaged across 30 deciduous topsoils, with In placing 9/15 (Tyler & Olsson, 2002).



**Table 3.6 Comparison of mean  $K_D$  ( $L\ kg^{-1}$ ) for Ga, In, and common TE contaminants (Robinson et al., 2009).**

Element	$K_D$ Canadian soils <sup>a</sup>	$K_D$ Swedish sites <sup>b</sup>	$K_D$ deciduous forested soil <sup>c</sup>
Zn	270	16	449
Se	290	35	378
Sb	730	520	432
As	750	140	2,000
U	960	4,000	4,000
Cu	1,200	780	746
Cd	1,300	230	356
Sn	1,500	-	-
Ni	1,600	980	1,155
<b>In</b>	<b>2,800</b>	-	<b>967</b>
W	5,900	-	500
Cr	8,100	350	3,176
Tl	8,700	2,100	1,273
<b>Ga</b>	<b>11,000</b>	<b>5,500</b>	<b>14,211</b>
Pb	18,000	9,600	1,785
Cs	43,000	38,000	6,533

<sup>a</sup>Sheppard et al. (2007), <sup>b</sup>Sheppard et al. (2009), and <sup>c</sup>Tyler and Olsson (2002).

#### 3.4.1.1. Effect of speciation on soil mobility

Adsorption and precipitation could not be separated, limiting our understanding of the behaviour of Ga and In in the system. The solubility of  $Ga(OH)_{3(aq)}$  and  $In(OH)_{3(aq)}$  are low ( $<10^{-7}$  M pH 5-7; (Wood & Samson, 2006)) and thus readily precipitate. The ionic forms are capable of labile and non-labile sorption to the soil matrix, analogous to other trace elements. As both processes can be expected to reduce the dissolved concentrations of Ga and In in the soil system, extractions do not clarify which has occurred. Data from Minteq predicted precipitation trends (Ga decreasing  $>pH$  5; In peaking 6.8-7.3; Fig. B.6 and Fig. B.7), but was unable to quantify in relation to adsorption. Kopittke et al. (2009) recorded immediate 87 and 27% decreases in aqueous Ga and In, attributed solely to precipitation (no soil or plant material)-the pH range of 3.7-5.3 was closer to Ga's peak. Sequential extraction procedures (originating from the methodology of Tessier et al. (1979), such as Połedniok (2008) Ga, and Waterlot et al. (2013), Boughriet et al. (2007) and (Hou et al., 2005) In) have the capacity to quantify the fraction sorbed to/in organic material, sulphides and residual minerals, but are unable to separate precipitated Ga and In from Mn and Fe (hydr)oxide adsorbed, in the oxide/reducible fraction.

The decrease in  $K_D$  with pH may be attributed to lesser-adsorbing anions, as suggested by modelling. Most soils have a net negative charge, with higher cation than anion adsorption capacity that increases as pH increases. Pukekohe soil had a CEC of  $22\ cmol(+) kg^{-1}$ , considered medium within New Zealand (Blakemore et al., 1981). When the distribution coefficient of In dropped from 910 to  $458\ L\ kg^{-1}$  at pH 6.80 to 7.1,  $In(OH)_2^+$  was predicted to decrease from 0.568 to 0.285%, and  $In(OH)_4^-$  increased from 0.169 to 0.338% (Table 3.3). In the first significant drop ( $1266$  to  $983\ L\ kg^{-1}$ , at pH 5.5-6.0), total cationic In decreased from 11% to 4%. Lower precipitation cannot be attributed to either scenario; the relative

saturation index remained at a maximum between 6.8 – 7.3. In the significant decrease in Ga  $K_D$  of 689-360 L kg<sup>-1</sup> at pH 5.5-6.8, cationic Ga decreased from 7.6% to 0.02%, however precipitation also decreased (14%) thus both processes are likely to contribute. Due to the acidifying hydrolysis demonstrated in Table 3.4, cationic dominance was greater than predicted, but the degree is consistent across the range and the examples are still valid. As hydroxide partitioning is not linear (Fig. B.4, Fig. B.5, Wood and Samson (2006)) and believed to be a determinant factor, a linear trendline was not forced through the data (Fig. 3.1). Data from Bi and Westerhoff (2016) supports this theory. Sorption of Ga to SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> was much lower at pH 9.5 than 4.5 and 7; Al<sub>2</sub>O<sub>3</sub> had a greater affinity for the cations, and the strongly negative SiO<sub>2</sub> (point of zero charge ~2) repelled Ga(OH)<sub>4</sub><sup>-</sup>. Precipitation of In meant the methodology was not feasible at the higher two pH parameters, thus unable to be determined if trends were similar.

Prior studies are not in agreement with the trends observed, with further work required to reach a consensus. Aqueous Ga decreased from 0.06 µg L<sup>-1</sup> to 0.015 µg L<sup>-1</sup> as the pH rose from 5.37 to 7.25 in work by G. Tyler and T. Olsson (2001). Similarly, in Su et al. (2018) pore water concentrations were approximately 514 µg L<sup>-1</sup> Ga and 474 µg L<sup>-1</sup> In in the pH 4.1 soil, versus 230 µg L<sup>-1</sup> Ga and 0.38 µg L<sup>-1</sup> In at pH 7.4, in 400 mg kg<sup>-1</sup> spiked soil zero days after planting. Lesser solubility of Al in the neutral soil was shown to be partially responsible, though differences in properties (CEC, organic matter, oxalate and dithionate extractable Fe and Al) likely also contributed. Cation exchange capacities of both their soils were lower than Pukekohe, at 7.8 and 9.3 versus 22 cmol(+) kg<sup>-1</sup> respectively, and pH values were beyond the range tested (the polynomial trendline in Fig. 3.1 cannot be accurately extrapolated). Logarithmic increases in  $K_D$  by Watmough (2008), from 10,000 L kg<sup>-1</sup> at pH 4 to almost 100,000 L kg<sup>-1</sup> at pH 7 in similar forested soils, may be attributed to acidifying weathering also increasing the rate at that Ga is released from the mineral matrix and into the exchangeable fraction (Sohlenius et al., 2013).

Hydroxide precipitation was hypothesised responsible for the increase in  $K_D$  with addition to the system. This trend observed in Table 3.2 was unexpected, as the distribution coefficient of many trace elements, such as Cd, Cu and Pb, decreases with concentration; adsorption sites become saturated, thus a larger mass must remain in solution (Shaheen et al., 2013). Aqueous Ga and In increased 2068% and 666% respectively as spiking increased from 1 to 100 mg L<sup>-1</sup>, however the larger increase in the solid fraction (11% and 102%) caused  $K_D$  to rise. Modelling by Minteq and Staff et al. (2010) predicted that hydroxide partitioning was not affected by concentration within the same pH range. Thus, production of Ga/In(OH)<sub>3</sub> increased, rising further above the low solubility threshold. Saturation indexes greater than zero (Fig. B.6 and Fig. B.7) indicated oversaturation thus precipitation

proportional to the mass entering the system. Two previous studies observed similar patterns; aqueous In was 0.02-0.04  $\mu\text{g L}^{-1}$  in contaminated Vietnamese soils, with total soil In concentration around 100  $\text{mg kg}^{-1}$  (Ha et al., 2011). Połedniok (2008) measured a 0.5  $\text{mg kg}^{-1}$  difference in extractable Ga despite the industrial soil containing 93  $\text{mg kg}^{-1}$  versus 38  $\text{mg kg}^{-1}$  total, likely attributed to precipitation in the 175% larger oxide fraction.

The pH was not controlled in the concentration gradient batch sorption experiments, thus acidity exacerbated adsorption is also likely to have contributed to the increase in matrix retention. Only soil without lime was used with pH assumed consistent at 5.5. Later modelling demonstrated that  $\text{Ga}(\text{NO}_3)_3$  and  $\text{In}(\text{NO}_3)_3$  undergo extensive hydrolysis that can greatly reduce the pH (Table 3.4). In extractant solutions, reductions of 1.8 and 2.3 were predicted with 100  $\text{mg L}^{-1}$  In and Ga respectively. Actual reductions are unknown (unspiked soil was pH tested), but were much smaller than modelled values; Minteq simulated an aqueous system, while in reality the buffering capacity of soil resisted change, and was expected to be medium-high for the Pukekohe soil (medium CEC and high base saturation (Blakemore et al., 1981)). Table 3.4 showed that acidification and resultant lesser partitioning to  $\text{Ga/In}(\text{OH})_3$  is capable of reducing the saturation index, thus increased cationic dominance and adsorption is also likely responsible for the observed  $K_D$  increase. Contributions cannot be separated, but further suggests Ga and In cations were able to quickly and strongly adsorb to the soil used. Competing process may be explanatory of the sharp increase in In  $K_D$  between 10-30  $\text{mg L}^{-1}$ ; hydroxide partitioning is not linear.

The increase in distribution coefficient with concentration trend may be explanatory of why In had a lower  $K_D$  than Ga in literature, despite the opposite in this study. Across all treatments, In retention was consistently higher than Ga (Fig. 3.1, Table 3.2, Fig. B.3). In Tyler and Olsson (2002)  $K_D$  values were 14,211 and 967  $\text{L kg}^{-1}$  for Ga and In respectively, but concentrations in the uncontaminated soils were much higher for Ga, at 5.4  $\text{mg kg}^{-1}$  Ga and 0.029  $\text{mg kg}^{-1}$  In. Data assumed close to background levels (3-70  $\text{mg kg}^{-1}$  Ga, 0.01-0.5  $\text{mg kg}^{-1}$  In (Kabata-Pendias & Mukherjee, 2007)) were used in Sheppard et al. (2007), with distribution coefficients of 11,000  $\text{L kg}^{-1}$  Ga and 2,800  $\text{L kg}^{-1}$  In.

Indium was predicted to complex with nitrate, though unlikely to be significant in the soil system nor alter behaviour. Minteq predicted formation of  $\text{In}(\text{NO}_3)_2^+$  at >1% below pH 4.8. This was likely due to the abundance nitrate in the system from the  $\text{Ca}(\text{NO}_3)_2$  extractant solution (Ashworth & Frisch, 2017), and  $\text{NO}_3^-$  is softer than  $\text{OH}^-$ , hence is outcompeted when  $\text{OH}^-$  availability is greater (Stumm & Morgan, 2009). While also considered a hard acid, In is softer so the same complex was not predicted for Ga

(Wood & Samson, 2006). In soil, nitrate is readily leached or taken up by plants, and the range of significant abundance is below ideal for most agricultural species (McLaren & Cameron, 1996). It is predicted to behave similarly to  $\text{In}(\text{OH})^{2+}$ .

Minteq modelling was used as a guide to estimate processes and identify trends within the system; few parameters and absence of soil limited its accuracy. Discussed earlier, hydroxide partitioning was believed to deviate to an unknown degree from the unspiked soil pH values inputted. The exact composition of the extractant solutions was unknown-soil colloids contain organic material and inorganic species, that had the capacity to be released during agitation. Our soil had a CEC of 22  $\text{cmol}(+) \text{kg}^{-1}$ , of which 70% was occupied by the basic cations  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$ . Lime ( $\text{CaCO}_3$ ) added to some samples was not inputted. Temperature was not consistent at 20°C, as experimentation was completed over several days. Minteq was sufficient at increasing our understanding of results produced.

#### 3.4.2. Mobility of Ga and In in the plant system

Perennial ryegrass was capable of absorbing and translocating significant quantities of Ga and In to shoot biomass, though concentrations were low compared to soil additions. Data showed just 0.37% and 0.02% of spiked Ga and In respectively entered leaves (Fig. 3.2), but statistically significantly increased with contamination. Concentrations applied (15-2000  $\text{mg kg}^{-1}$  Ga, 1.5-200  $\text{mg kg}^{-1}$  In) were above natural soil levels (particularly In), but were within the range of many earlier contamination reports (Boughriet et al., 2007; Ha et al., 2011; Połedniok et al., 2012). Higher In uptake in perennial ryegrass was recorded by Waterlot et al. (2013), peaking at 0.0509  $\text{mg kg}^{-1}$  with bioaccumulation factors of 0.04-0.22. Little physiological difference was expected as the same species were used, thus this data demonstrates the importance of soil mobility on the capacity for uptake. Contamination occurred recently (Table 3.7) so the pool of In should have been relatively labile. Although not provided, the slightly lower CEC (16.2 and 18.0 versus 22  $\text{cmol}(+) \text{kg}^{-1}$ ) and higher pH (7.3-7.5 versus 5.5) in their contaminated soils may have contributed to lower distribution coefficients and higher bioavailability. Extremely high concentrations in hydroponic rice, up to 74  $\text{mg kg}^{-1}$  Ga and 151  $\text{mg kg}^{-1}$  In may have been possible due to the absence of soil (Syu et al., 2017); soil experimentation only yielded 10  $\text{mg kg}^{-1}$  Ga and 8.3  $\text{mg kg}^{-1}$  In (Su et al., 2018). The plateau of 0.015  $\text{mg kg}^{-1}$  In observed in this study may be due to rhizotoxicity, but could not be verified with data collected. Syu et al. (2017) found that just 0.08  $\text{mg L}^{-1}$  solution In caused significant reductions in root and shoot biomass for rice seedlings, though both increased with 15  $\text{mg L}^{-1}$  Ga.

Root cell retention likely further restricted movement of these elements into ryegrass leaves. Concentrations of Ga and In below ground were not measured, but prior literature has proven this process happens in a range of species. Other members of the Poaceae family reported shoot: root ratio of <1, with 0.0279 Ga in barley/wheat stem (Omberg et al., 2011), 0.11 in wheat (Wheeler & Power, 1995), 0.082-0.223 Ga in *Arabidopsis thaliana* (Chang et al., 2017), and <0.01-0.47 Ga with <0.01-0.44 In in rice seedlings (Syu et al., 2017). Leaf: soil ratios were just 0.077 and 0.029 for Ga and In, compared to root: soil ratios of 0.15 and 0.11 in acidic beech forest, showing limited quantities had translocated (Tyler, 2004a, 2005).

Root cell retention is a likely contributing factor to the low concentrations of Ga and In present in ryegrass leaves. This factor was not measured thus cannot be verified. Shoot: root ratios of <1 have been consistently reported for other members of the Poaceae family (Omberg et al., 2011; Su et al., 2018; Syu et al., 2017; Wheeler & Power, 1995; Yu et al., 2015); the only current measurements of shoot: root >1 were collected for a variety of species by Ha et al. (2011), wherein the only Poaceae specie, *Leersia hexandra* Sw., produced values of 0.058 and 0.17 for Ga and In respectively.

Hydrolysis attributed pH inconsistencies may have arisen, but nitrogen caused the greatest variation in growth. A wide range of salt concentrations were used-0 mg kg<sup>-1</sup> to 200 mg kg<sup>-1</sup> In and 2000 mg kg<sup>-1</sup> Ga-thus acidification of soil was also possible in this stage of experimentation. With a natural soil pH of 5.5, any decrease would have deviated from the optimal growth range of 5.5-6.5 (McLaren & Cameron, 1996). However, any possible effects were overshadowed by nitrogen availability; plant available nitrogen levels were quickly insufficient for growth, pots containing 1000 and 2000 mg kg<sup>-1</sup> Ga(NO<sub>3</sub>)<sub>3</sub> had notably more biomass with greener leaves, and this issue was not ameliorated until 3 weeks after germination. Resultantly, shoot weight data was not considered sufficient for analysis.

A comparison of the bioaccumulation factors of Ga and In with other trace elements indicates that Ga and In are relatively immobile in the soil-plant system in its entirety, however data is sparse (Table 3.7). Gallium had the second and fourth lowest BAFs in barley and wheat grains, from Swedish studies by Eriksson (2001) and Oguchi et al. (2011) respectively. Waterlot et al. (2013) measured that In was the second least mobile, behind Pb, in ryegrass and lettuce leaves. Indium was less mobile than 7 other contaminants in a variety of vegetables (Li et al., 2016). Indium and Ga had the third and ninth least movement to beech leaves (Tyler, 2005), with third and fourth from soil to roots (Tyler, 2004a) in the acidic organic horizon in both studies. In Su et al. (2018) rice plant BAFs averaged 0.072 Ga 0.071 In, and 0.014 Ga 0.013 In in acidic and neutral soils respectively, attributed to pH determinant

bioavailability. As BAF values are heavily influenced by  $K_D$  and plant species, Table 3.7 is most suitable for comparing elements within a single environment. Omberg et al. (2011) found a correlation of  $r = -0.45$  between  $K_D$  and BAFs across many elements and plant organs, and the BAF of grains were lower than stems and roots on the same plants, due to the requirement for physiological transport and lack of dust particles. Of the studies in which contamination occurred, severity and time varied, altering the size of the labile pool. This was demonstrated earlier to drastically affect  $K_D$ , through comparison of our data and literature (Table 3.5). In addition, BAFs from this study and Su et al. (2018) were calculated relative to the concentration applied shortly before experimentation, versus the total concentration in the soil. Throughout various environments and methodologies, mean shoot uptake never exceeded 7.7% applied or total Ga, and 8.1% In.

**Table 3.7 Comparison of mean bioaccumulation factors for Ga, In, and common TE contaminants (mg kg<sup>-1</sup> plant biomass (Robinson et al., 2009).**

Reference	Omberg et al. (2011)	Eriksson (2001)	Tyler (2005)	Tyler (2004a)	Waterlot et al. (2013)	Li et al. (2016)	
Species	Barley/wheat grain	Wheat/barley grain <sup>a</sup>	Beech leaves	Beech roots	Ryegrass shoots	Lettuce leaves Cabbage, garlic, onion, lettuce, spinach	
Contamination	Uncontaminated	Possibly agricultural	Uncontaminated	Uncontaminated	Natural, and Pb-Zn smelter	Rare metal recycling smelter	
Time between contamination and sampling.	-	-	-	-	0-3 years for one plant (20-27 sites); 28-31 years since emissions significantly reduced for the other (7-27) <sup>b</sup>	0 years	
Cd	0.00025	0.16	0.30	0.79	0.28	1.5	0.51
U	0.00056	0.000027	0.035	0.10	-	-	-
Cr	0.0012	0.0005	0.16	0.29	-	-	-
Ga	<b>0.0016</b>	<b>0.00011</b>	<b>0.077</b>	<b>0.15</b>	-	-	-
Pb	0.0020	0.00045	0.0083	0.20	0.0037	0.011	1.1
Tl	0.0023	0.0017	0.051	5.0	-	-	0.042
Cs	0.0029	0.0016	0.65	5.0	-	-	-
As	0.0031	0.0074	0.029	-	-	-	0.61
Ni	0.0037	0.012	0.18	0.32	-	-	-
Sb	0.0039	0.0024	0.048	-	-	-	0.11
Sn	0.0096	0.054	0.022	0.11	-	-	-
W	0.012	0.0045	0.058	-	-	-	-
Se	0.031	0.052	-	-	-	-	-
Cu	0.20	0.27	0.81	1.00	0.10	0.11	0.91
Zn	0.50	0.40	0.60	0.80	0.22	0.093	6.8
In	-	-	<b>0.029</b>	<b>0.11</b>	<b>0.081</b>	<b>0.062</b>	<b>0.0021</b>

<sup>a</sup>0.8 wheat + 0.2 barley data, though only Ga barley value used; <sup>b</sup>Douay et al. (2008).

### 3.4.3. Potential for movement into the food chain

The impact of Ga and In on animal health at the concentrations taken up by perennial ryegrass are not known. Data and findings from Waterlot et al. (2013) showed that  $\leq 0.37\%$  of added Ga and  $\leq 0.05$  mg kg<sup>-1</sup> In was likely to be taken up by ryegrass, as the soil matrix and outer root cells provide effective barriers. A 500 kg Friesian cow, fed 17.3 kg of 11.0 MJ ME kg<sup>-1</sup> DM ryegrass and producing 1.6 kg milk

solids, could ingest up to 200 mg Ga or 0.88 mg In daily (Dairy NZ; Waterlot et al., 2013); A 50 kg sheep foraging 1.4 kg ryegrass could ingest 16 mg Ga or 0.071 mg In (Freer et al., 2012). However, neither the acute nor chronic consequences to animal health are known; toxicity has not been fully investigated nor is there a concentration threshold.

The risk of entry via drinking water is low, due to filtration of precipitates. The recommended pH of tap water, 7.0-8.5 (Ministry of Health, 2008), falls within the peak precipitation range of In (~4.5-9) with high precipitation of Ga (1  $\mu\text{M}$  solubility) (Bernstein, 1998; Wood & Samson, 2006). Across a range of natural waterbodies, just  $\leq 0.03 \mu\text{g L}^{-1}$  Ga and  $0.1 \text{ ng kg}^{-1}$  In has been reported (Kabata-Pendias & Mukherjee, 2007). Soil retention is effective at restricting movement into waterbodies;  $\leq 40\%$  In leached 35 cm in 18 months, with only 5-38% moving below the top 2 cm in several soil types (H. Hou et al., 2005). Stream water contained  $1\text{-}79 \text{ pmol L}^{-1}$  Ga versus  $4.6\text{-}33 \text{ mg kg}^{-1}$  in associated Californian topsoil (Shiller & Frilot, 1996).

Gallium and In have a high risk of entering the food chain through direct ingestion of soil particles on contaminated soils by animals. Gallium and In are strongly retained by the soil matrix, thus most of the contaminant mass travels with dust. Soil is frequently ingested via retention to food, inhalation of airborne matter, and directly by animals and children. This quantity is dependent on several factors including the rate of soil erosion and steps involved in food processing. Ingestion of soil containing  $200 \text{ mg kg}^{-1}$  Ga or  $20 \text{ mg kg}^{-1}$  In could cause daily consumption of 0.04-0.13 mg Ga or 0.004-0.013 mg In in humans (207-625 mg soil daily (Davis & Mirick, 2006)), 29 mg Ga or 2.9 mg In sheep (9.5% of diet DM (Ford & Beyer, 2014; Freer et al., 2012)), and 340 mg Ga or 34 mg In for dairy cattle (9% of diet (Dairy NZ; Ford & Beyer, 2014)).

### 3.5. Conclusions

Gallium and In have low mobility in the soil – plant system. As hypothesised, both elements are quickly immobilised in soil; the size of the retained fraction increases with concentration and acidity, likely due to hydroxide precipitation and transition of aqueous species to cations. Perennial ryegrass is capable of uptake and translocation of small yet significant quantities of Ga and In, thus is a small pathway for these elements to enter the food chain. Direct ingestion of soil, particularly sorbed to food, is a much larger pathway and risk. Further work should investigate their behaviour of Ga and In under contrasting redox environments and with a range of plant species, particularly those that take up large concentrations of Al, such as *Camellia* spp.

## 4. Solubility of the ETECs Be, Ga, In, La, Ce, Nd, and Gd in sandy soils

### Abstract

Technological development has resulted in increased use of Be, Ga, In, La, Ce, Nd, and Gd. There is scant information on how these Emerging Trace Element Contaminants (ETECs) behave in soil. This study aimed to evaluate the immobilisation of these ETECs upon entry to soil, as affected by pH and concentration perturbations, in comparison with the common and well-characterised soil contaminant Cd. Batch sorption experiments were used to determine distribution coefficients ( $K_D$ ) of the different ETECs as effected by concentration, pH, and organic matter (OM). Overall, sorption to soil increased in the order Cd<Be<In<La<Ce<Nd<Gd<Ga. The  $K_D$  values of Be, Cd, La, Ce, Nd and Gd exponentially increased as the pH of the soil solution increased, the  $K_D$  of Ga peaked at pH 5-6, and the  $K_D$  of In did not change with increasing soil solution pH. As the concentration of the solubilised ETECs and Cd added to soil increased, the  $K_D$  of Be, Cd, La, Ce, Nd and Gd decreased, and Ga and In increased. Isotherms describing sorption as a function of concentration could be fitted for Be, La, Ce, Nd and Gd (Langmuir), Cd and Ga (Freundlich), and In (logarithmic). pH and concentration had different effects on the  $K_D$  of Ga and In compared to the other ETECs, which may be due to those metals forming precipitates under specific conditions.  $K_D$  was positively correlated with ionic potential. Future work should determine the relationship between the solubility of ETECs in soil and their uptake by plants.

### 4.1. Introduction

Electronic waste (e-waste) contains high concentrations of metals, up to 60% (Dave et al., 2016). More than 80% of e-waste is disposed of into landfill (Liu et al., 2015), and a significant proportion of the remainder is exported (illegally) to poor countries for recycling, whereupon many of the chemical elements in e-waste enter the environment (Abalansa et al., 2021). Areas associated with e-waste recycling or disposal usually contain elevated concentrations of heavy metal(oids) (Tokumaru et al., 2017). In addition to the common environmental contaminants Pb, Cd, Cu, and Ni, sites contaminated with e-waste residues contain elevated concentrations of Emerging Trace Element Contaminants (ETECs), including beryllium (Be), gallium (Ga), indium (In), lanthanum (La), cerium (Ce), neodymium (Nd), and gadolinium (Gd) (Fujimori et al., 2012; Ha et al., 2009; Tokumaru et al., 2017). Beryllium is extracted for electronic equipment as a strengthening compound in copper alloys (Taylor et al., 2003), and Ga and In are used in GaAs semiconductors and Indium-tin oxide electronic coatings (Butcher & Brown, 2014; Schwarz-Schampera, 2014). The rare earth elements (REEs) La, Ce, Nd, and Gd are used



in fluid catalytic cracking, glass additives and polishing, magnets and phosphors, respectively (Goonan, 2011b), and have been used as plant growth promoters in China (Hu et al., 2006). Upon entry to soil or wind transport to other soils, these elements can potentially be ingested by humans and animals via soil ingestion (directly or on the surface of plant material), or through ingestion of plants that have the potential to take up ETECs if they are in a soluble form. Understanding how ETECs interact with soil is critical for assessing the risks for these elements leaching or being taken up by plants.

The partitioning of ETECs between the solid phase and liquid phase (i.e. sorption) determines the likelihood that the ETECs will leach, be taken up by plants or accumulate in soil (Hooda, 2010). Solubility is a prerequisite for bioavailability (Kumpiene et al., 2017). In soil, ETECs may sorb via outer-sphere adsorption (ion exchange), inner-sphere (specific) adsorption, surface precipitation and absorption into soil colloids. The surfaces of soil colloids-OM and Fe, Al and Mn oxides-bear functional groups capable of binding ETECs (Bradl, 2004). These are often oxygen-based, such as hydroxyl and carbonyl groups, and some are permanently negatively charged while others can accept protons at low pHs and donate at high (Bradl, 2004). Soils rich in variable-charge constituents, which have binding sites that can sorb anions at low pHs and cations at high pHs as they lose protons and transition from positive to negatively charged, are common in the tropics and less common elsewhere (Sollins et al., 1988).

The most important factors affecting the sorption of ETECs are soil pH, soil organic matter (OM) content, soil iron (Fe), aluminium (Al) and manganese (Mn) hydroxide content and redox potential (Alloway, 2013). Increasing the soil solution pH causes elements to hydrolyse through the donation of protons, and some of these hydrolysed species are neutral and precipitate, rendering them a part of the solid phase, while other species are more likely to be sorbed to soil than their predecessors (Alloway, 2013). Above a pH threshold (usually pH >5.5) the sorption of ETECs to minerals rapidly increases (Benjamin & Leckie, 1981) due to precipitation of Fe and Al creating more sorption sites and less competition from H<sup>+</sup> ions, and sorption to OM increases but is more gradual (Boschi & Willenbring, 2016b). Variable charge sorption sites cause the surface charge on soil colloids to become more negative as the pH increases, thus cation sorption becomes more likely. Waterlogging reduces Fe<sup>3+</sup> to Fe<sup>2+</sup> and Mn<sup>4+</sup> to Mn<sup>2+</sup>, which can solubilise ETECs that are specifically adsorbed to Fe and Mn oxyhydroxides (Hooda, 2010), and precipitate ETECs as the sulphide following the reduction of SO<sub>4</sub><sup>2-</sup>.

The Ionic Potential (IP) (charge/ionic radius) of the ETECs affects their solubility in soil solutions: ions with an IP <30 nm<sup>-1</sup> exist as free cations, ions with an IP of 30-100 nm<sup>-1</sup> are hydrolysed, and ions with

IP  $>100 \text{ nm}^{-1}$  are present as oxyanions (Sposito, 2008). Free cations and oxyanions are less likely to precipitate but may be sorbed to soil whereas hydrolysed ions often precipitate, depending on the pH range (Wood & Samson, 2006). Beryllium, Ga and In have IPs of 74, 48 and  $38 \text{ nm}^{-1}$  respectively, and have been modelled to hydrolyse and precipitate in soil, with precipitation of Be responsible for the sharp increase in pH (Aldahan et al., 1999; Islam et al., 2021; Wood & Samson, 2006). The REEs have IPs of  $25\text{-}28 \text{ nm}^{-1}$  thus are not expected to hydrolyse and precipitate in soil. Although Be is a divalent cation and the others are trivalent, Be has a small atomic mass hence has a high IP. The selected ETECs are all 'hard' Lewis acids (Stumm & Morgan, 2009; Wood & Samson, 2006), thus sorb preferentially and well to the hard oxygen-based functional groups, and sorb less-well to those without oxygen, such as  $\text{S}^{2-}$  and  $\text{I}^-$  (Kinraide, 2009). The trivalent charges of Ga, In, La, Ce, Nd, and Gd will allow them to outcompete lesser-charged cations such as  $\text{Be}^{2+}$  and  $\text{Cd}^{2+}$  for sorption sites, but the higher IP of  $\text{Be}^{2+}$  will cause it to outcompete other divalent cations for sorption sites, as happened in Sheppard et al. (2009) when the ranking of the  $K_D$  of the ETECs in natural soils was  $\text{Cd} < \text{Be} < \text{Gd} < \text{Ga} < \text{La} < \text{Nd} < \text{Ce}$ . A similar pattern occurred in Tyler and Olsson (2002), however, Be had a higher  $K_D$  than In, and Ga had a higher  $K_D$  than the REEs.

As the ETEC concentration increases, sorption sites become saturated, and thus the proportion of the ETEC sorbed decreases (Shaheen et al., 2013). Increasing the pH of the soil solution has been shown to increase sorption of the ETECs in soil (Boschi & Willenbring, 2016b; Dinali et al., 2019; Sohlenius et al., 2013; G. Tyler & T. Olsson, 2001), but it is unknown how the sorption responses of the ETECs to pH perturbations compare.

Distribution coefficients ( $K_D$ ), the sorbed / soluble concentration quotients (Shaheen et al., 2013), indicate the solubility of an element at set concentrations. When aqueous concentrations are plotted against total sorption for an ETEC, the trendlines are usually curved at high concentrations, thus models such as Langmuir and Freundlich are fitted to predict further sorption within a soil type (Selim & Zhang, 2013). Langmuir curves assume the sorption capacity is finite, then further ETECs remain in solution, while the Freundlich curve assumes indefinite sorption but at a reduced capacity at high concentrations.  $K_D$  values are useful to compare the sorption and thus potential mobility of ETECs, e.g. in the peat fen in Sheppard et al. (2009) Ga and Nd had  $K_D$  values of 1,300 and 2,100 respectively, thus a smaller percentage of Nd was present in the soluble fraction, and capable of being taken up by plants or leaching down the soil profile. The ETECs usually have  $K_D$  values between 100-44,000 (Sheppard et al., 2007).

Soil contaminants become less soluble and mobile with time, as they become incorporated into less-labile fractions of the solid phase of soil (Alloway, 2013; Hu et al., 2006); hence data comparing the solubility of ETECs in natural soils will differ from contaminated soil. Studies that have spiked soil with ETECs to analyse the solubility measure few elements and fail to compare the solubility to common contaminants, such as Cd. There is a lacuna of information on the relative solubility and mobility of the ETECs Be, Ga, In, La, Ce, Nd and Gd upon entry to soil in comparison to Cd, and how the elements compare in the change in solubility to relation to solution pH and the concentration added to soil.

It is hypothesised that sorption of trivalent Ga, In, La, Ce, Nd and Gd contaminants to soil will be higher than divalent Be and Cd, and Be will have higher  $K_D$  than Cd. Sorption will increase with pH for all of the ETECs, however, for Be, Ga, and In the increases in  $K_D$  with pH will be due to hydroxide precipitation. As the concentration of the ETECs or Cd added to the system increases,  $K_D$  will decrease for Cd, La, Ce, Nd and Gd, and increase for Be, Ga and In due to precipitation.

This study aimed to determine the relative solubility of Be, Ga, In, La, Ce, Nd and Gd in soil and determine the importance of soil pH and ETEC concentration, and compare how the solubility of these elements compare with the common contaminant Cd, through batch sorption experiments with a  $\text{Ca}(\text{NO}_3)_2$  extractant. Freundlich and Langmuir sorption models will be compared to see which one is most suitable for predicting the sorption of these elements and compare the results with those obtained using speciation modelling.

## **4.2. Materials and methods**

### **4.2.1. Soil collection and properties**

Three uncontaminated soils were collected from Canterbury, New Zealand for use in this study. The typic fluvial recent soil (RFT) was collected near Lake Lyndon (43.3409691 S, 171.6370203 E). The soil properties are described in Gutiérrez-Ginés et al. (2019). The peaty orthic gley soil (GOO) was collected near Leeston (-43.70709 S, 172.25244 E), and the mottled-weathered fluvial recent soil (RFMW) was collected from Christchurch (-43.5229981 S, 172.5873929 E). The three soils differed in CEC, OM, Olsen P, base saturation and chemical composition (Table 4.1 & 4.2), but had similar textures and pH, as it is well understood that soils with finer textures often have more sorption than sandier soils, and pH is one of the factors that was modified in the experiments.

**Table 4.1 Properties of the soils used in these experiments**

Property	Soil type		
	RFT	RFMW	GOO
pH <sup>ac</sup>	5.3	5.3	5.8
Olsen P (mg L <sup>-1</sup> ) <sup>a</sup>	4	27	53
CEC (cmol(+) kg <sup>-1</sup> ) <sup>ad</sup>	17	13	50
Base saturation (%) <sup>a</sup>	16	61	64
Total C (%) <sup>a</sup>	3.8	1.9	10.7
Texture <sup>b</sup>	Loamy sand	Loamy sand	Sand
Sand (%) <sup>e</sup>	83.8	80.4	88.4
Silt (%) <sup>e</sup>	13.4	16.2	10.2
Clay (%) <sup>e</sup>	2.4	3.1	1.4

<sup>a</sup>Analysis from Hill's Laboratories; <sup>b</sup>Details in the appendix; <sup>c</sup>Determined in H<sub>2</sub>O, 1:2 v/v soil:water; <sup>d</sup>Sum of extractable cations and extractable acidity; <sup>e</sup>Particle size distribution measured in a Saturn DigiSizer II 5205 V1.03, soil textures classified by the texture diagram in McLaren and Cameron (1996).

**Table 4.2 Pseudo-total and Ca(NO<sub>3</sub>)<sub>2</sub> extractable concentrations of elements used in these experiments (mg kg<sup>-1</sup>) (standard error)**

Element	Soil type					
	RFT		RFMW		GOO	
	Total	Extractable	Total	Extractable	Total	Extractable
Na	185 (11)	-	383 (21)	-	235 (31)	-
Mg	5,254 (29)	-	4,708 (21)	-	2,333 (55)	-
Al	42,396 (93)	7.6 (0.037)	23,673 (195)	2.3 (0.11)	22,962 (497)	3.8 (0.096)
P	528 (3.5)	0.19 (0.063)	599 (7.9)	0.91 (0.11)	1,310 (31)	1.9 (0.35)
K	3,763 (54)	-	6,615 (50)	-	4,860 (187)	-
Ca	564 (12)	-	885 (11)	-	2,168 (24)	-
Cr	33 (0.098)	0.064 (0.0014)	24 (0.14)	0.075 (0.00090)	25 (0.21)	0.067 (0.00057)
Mn	327 (2.8)	0.51 (0.023)	337 (5.6)	3.2 (0.044)	222 (4.6)	4.5 (0.054)
Fe	25,417 (30)	0.91 (0.034)	17,183 (116)	1.4 (0.17)	9,139 (137)	3.0 (0.054)
Co	9.4 (0.16)	0.030 (0.00094)	6.2 (0.031)	0.039 (0.00078)	5.1 (0.076)	0.049 (0.0012)
Ni	15 (0.24)	0.069 (0.00087)	12 (0.060)	0.080 (0.0020)	9.2 (0.0078)	0.079 (0.0012)
Cu	13 (0.22)	0.0050 (0.00027)	8.0 (0.057)	0.014 (0.00075)	26 (0.089)	0.026 (0.0056)
Zn	76 (0.59)	0.091 (0.012)	57 (0.32)	0.22 (0.011)	48 (0.92)	0.28 (0.018)
Be	15 (0.55)	<dl	13 (0.55)	<dl	14 (0.69)	0.017 (0.00057)
Cd	0.063 (0.0022)	<dl	0.064 (0.0018)	<dl	0.29 (0.0058)	0.0023 (0.00037)
Ga	132 (1.5)	<dl	89 (1.1)	<dl	88 (2.6)	0.0036 (0.00099)
In	0.47 (0.011)	<dl	0.31 (0.0081)	<dl	0.3 (0.0018)	<dl
La	216 (2.7)	0.069 (0.0053)	308 (1.5)	<dl	288 (3.5)	<dl
Ce	59 (0.66)	<dl	60 (0.53)	<dl	55 (0.57)	<dl
Nd	179 (0.92)	0.052 (0.0041)	256 (4.0)	0.026 (0.0014)	261 (2.8)	0.021 (0.0017)
Gd	28 (0.21)	0.0024 (0.00022)	39 (0.56)	<dl	42 (0.52)	0.0026 (0.00099)

Stones were removed, and soil was oven dried at 105°C until a consistent weight was reached, and soil was sieved to <2 mm. The RFW was chosen to be the base soil in that the ETECs were tested, because it had a lower OM content than the GOO thus had representative sorption to minerals and OM, and contained plenty of other ions, as shown by the high Olsen P and base saturation, which allowed potential sorption to, competition with, and formation of complexes with various elements, showing if the ETECs can outcompete other elements for sorption sites. Beryllium, Cd, Ga, and In were tested on the other two soil types to find if they had different effects on the solubility of the ETECs and Cd. In the RFT and GOO soils. Lanthanum, Ce, Nd, and Gd were not tested in the latter two soil types as they are chemically similar to each other, Ga and In (as trivalent cations), and Cd (relatively large ionic radii and unlikely to precipitate in soil).

#### 4.2.2. Batch sorption experiments

Adapting the methods of Al Mamun et al. (2016), 0.05 M of  $\text{Ca}(\text{NO}_3)_2$  was spiked with 1, 3, 10, 30 or 100  $\text{mg L}^{-1}$  of the ETEC or Cd as the soluble salts  $\text{BeSO}_4$ ,  $\text{Cd}(\text{NO}_3)_2$ , or  $\text{Ga/In/La/Ce/Nd/Gd}(\text{NO}_3)_3$  (Table C.1). The concentration gradient was used to test the effect of varying the concentration added on the  $K_D$  of the ETECs and Cd, and was produced by adding 0.1308-1.966 g of ETEC or Cd salt and 11.80 g of  $\text{Ca}(\text{NO}_3)_2$  to 1 L of water and diluting with unspiked 0.05 M of  $\text{Ca}(\text{NO}_3)_2$ . In centrifuge tubes, 30 mL of the solution was added to 5.0 g soil, and 30 mL of the same solution was placed in a tube without soil to measure possible sorption to the tubes. More of the 10  $\text{mg L}^{-1}$  ETEC or Cd solutions were prepared and added to tubes with soil, followed by 68-1,300  $\mu\text{L}$  of 1 M KOH (Table C.2) to produce a pH gradient. Three replicates were completed for each sample type, and controls. The tops were screwed onto the tubes, the tubes were placed into an over-end shaker for 120 minutes, centrifuged at 2012 g, and the upper 15 mL were pipetted into pottles with 1 mL of concentrated  $\text{HNO}_3$ . Samples were then diluted 100-fold using ultra-pure 2%  $\text{HNO}_3$  and measured using ICP-MS.

Concentration and pH were the two factors that were modified because the contaminant concentration will increase if contamination happens more than once in a soil, and the soil solution pH is dynamic and will change with natural processes such as plant root respiration and rainfall, and anthropogenic processes such as fertiliser addition. The other soil properties which affect sorption are unlikely to change as much within a particular soil type.

#### 4.2.3. Bismuth and tellurium

Bismuth (Bi) and tellurium (Te) were found to be insoluble in the experimental conditions and no further testing of these elements occurred.

#### 4.2.4. Calculations

$$K_D = ((C_{S\text{-soil}} - C_s)30/5)/C_s \quad (\text{Eq. 1})$$

The  $K_D$  was calculated using Eq. 1, where  $C_s$  is the concentration of the ETEC or Cd in solution ( $\text{mg L}^{-1}$ ),  $C_{S\text{-soil}}$  is the concentration of the ETEC or Cd in the solution of a batch-sorption experiment spiked with the same concentration of the ETEC or Cd as  $C_s$  but not containing soil ( $\text{mg L}^{-1}$ ), and 30/5 is used to convert  $C_{S\text{-soil}} - C_s$  to  $\text{mg kg}^{-1}$  to calculate soil sorption.

Langmuir (Eq. 2), Freundlich (Eq. 3), logarithmic (Eq. 4) and linear (Eq. 5) equations were fitted to predict soil sorption ( $Q_e$ ,  $\text{mmol g}^{-1}$ ) using soil solution concentration data ( $C_e$   $\text{mmol L}^{-1}$ ).

$$Q_{e,\text{lan}} = (C_e k_a q_m) / (1 + C_e k_a) \quad (\text{Eq. 2})$$

$$Q_{e,\text{fre}} = k_f \cdot C_e^{1/n} \quad (\text{Eq. 3})$$

In Eq. 1,  $k_a$  is a measure of sorption at the equilibrium ( $\text{dm}^3 \text{mmol}^{-1}$ ), and  $q_m$  is sorption for a complete monolayer ( $\text{mmol g}^{-1}$ ) (Wang & Qin, 2005). In Eq. 2,  $k_f$  is a measure of adsorption capacity ( $\text{L mmol}^{-1}$ ) and  $1/n$  a measure of adsorption intensity (Ayawei et al., 2017; Wang et al., 2017).

$$Q_{e,\text{log}} = a \cdot \ln C_e + c \quad (\text{Eq. 4})$$

$$Q_{e,\text{lin}} = m \cdot C_e + c \quad (\text{Eq. 5})$$

To estimate the constants in the Langmuir and Freundlich equations for more accurate fitting using solver, data were plotted using Eq. 6 (Langmuir) and Eq. 7 (Freundlich). Then, solver was used on Excel to increase the fit of the parameters for all the isotherms by altering them to minimise the normalised error (SNE) (Eq. 8). The isotherm with the lowest SNE for each element-soil combination was deemed the best fit, and then  $R^2$  values were calculated using Eq. 8, 9, and 10.

$$(C_e/Q_{e,\text{lan}}) = (1/k_a q_m) + (1/q_m)C_e \quad (\text{Eq. 6})$$

$$\text{Log}(Q_{e,\text{fre}}) = \text{Log}(k_f) + (1/n) \cdot \text{Log}(C_e) \quad (\text{Eq. 7})$$

$$SNE = \Sigma ((Q_{es}-Q_e)/Q_e)^2 \quad (\text{Eq. 8})$$

In Eq. 7,  $Q_{es}$  is the  $Q_e$  calculated via the Langmuir or Freundlich equation.

$$R^2 = (TSS-RSS)/TSS \quad (\text{Eq. 9})$$

$$TSS = RSS + \Sigma(Q_{es} - Q_{et})^2 \quad (\text{Eq. 10})$$

$$RSS = \Sigma(Q_{et} - Q_e)^2 \quad (\text{Eq. 11})$$

In Eq. 9, 10, and 11,  $TSS$  is the total sum of squares,  $RSS$  is the residual sum of squares,  $Q_{et}$  is the  $Q_e$  calculated by from the equation, and  $Q_{es}$  is the unaveraged  $Q_e$ .

#### 4.2.5. Data processing

Data were processed and displayed through Excel. Data were tested for normality, and log-normally distributed data were log-transformed before analyses. Standard errors were calculated through Descriptive statistics data analysis, Pearson correlations were calculated through Correlation data analysis and processed (Eq. 12 and 13) to find significance, and a Single-factor ANOVA data analysis was performed and least significant differences (LSD) were calculated (Eq. 14).

$$Cor2 = ABS (Cor \cdot \sqrt{(n_d-2)/\sqrt{1-Cor^2}}) \quad (\text{Eq. 12})$$

$$p = T.DIST.2T (Cor2, (n_d-2)) \quad (\text{Eq. 13})$$

$$LSD = \sqrt{(MSWG \cdot 2/n_r)} \cdot t \quad (\text{Eq. 14})$$

In Eq. 12,  $Cor$  is the Pearson correlation value gained from Excel data analysis, and  $n_d$  is the data count. In Eq. 14,  $MSWG$  is the mean squares within groups,  $n_r$  is the number of replicates in a sample (3), and  $t$  is the t value.

Detection limits (dl) for data were the concentrations present in the method blanks of the samples (Table C.8).

#### 4.2.6. Aqueous speciation modelling

The visual speciation modelling program Visual MINTEQ 3.1 (Gustafsson, 2013) was used to model the change in speciation with increasing pH in aqueous solutions. The components added to the system and system settings are in Table 4.3, and after that, the program was set to run, selected sweep results were exported to excel, and the concentration of each species was divided by the sum of soluble species at each pH unit and graphed.

**Table 4.3 Settings and components used in Minteq**

Components added to system	Concentration
CO <sub>2</sub>	Atmospheric (0.00038 atm)
Ca <sup>2+</sup>	0.05 M
NO <sub>3</sub> <sup>-</sup>	0.1 M
ETEC or Cd ion (Be <sup>2+</sup> , Cd <sup>2+</sup> , Ga <sup>3+</sup> , In <sup>3+</sup> , La <sup>3+</sup> , Ce <sup>3+</sup> , Nd <sup>3+</sup> or Gd <sup>3+</sup> )	10 mg L <sup>-1</sup>
ETEC or Cd salt anion (NO <sub>3</sub> <sup>-</sup> , or SO <sub>4</sub> <sup>2-</sup> for Be)	10 mg L <sup>-1</sup>
System settings	
Multi-problem/sweep	One parameter varied Sweep component: pH Start value: 1.0 Increment between values: 0.1 Number of problems: 91
Add comp/species	All species that the selected ETEC or Cd was in, which had the concentration option
Temperature	20 °C
pH	Varied in sweep, as above.
Ionic strength	Calculated by model

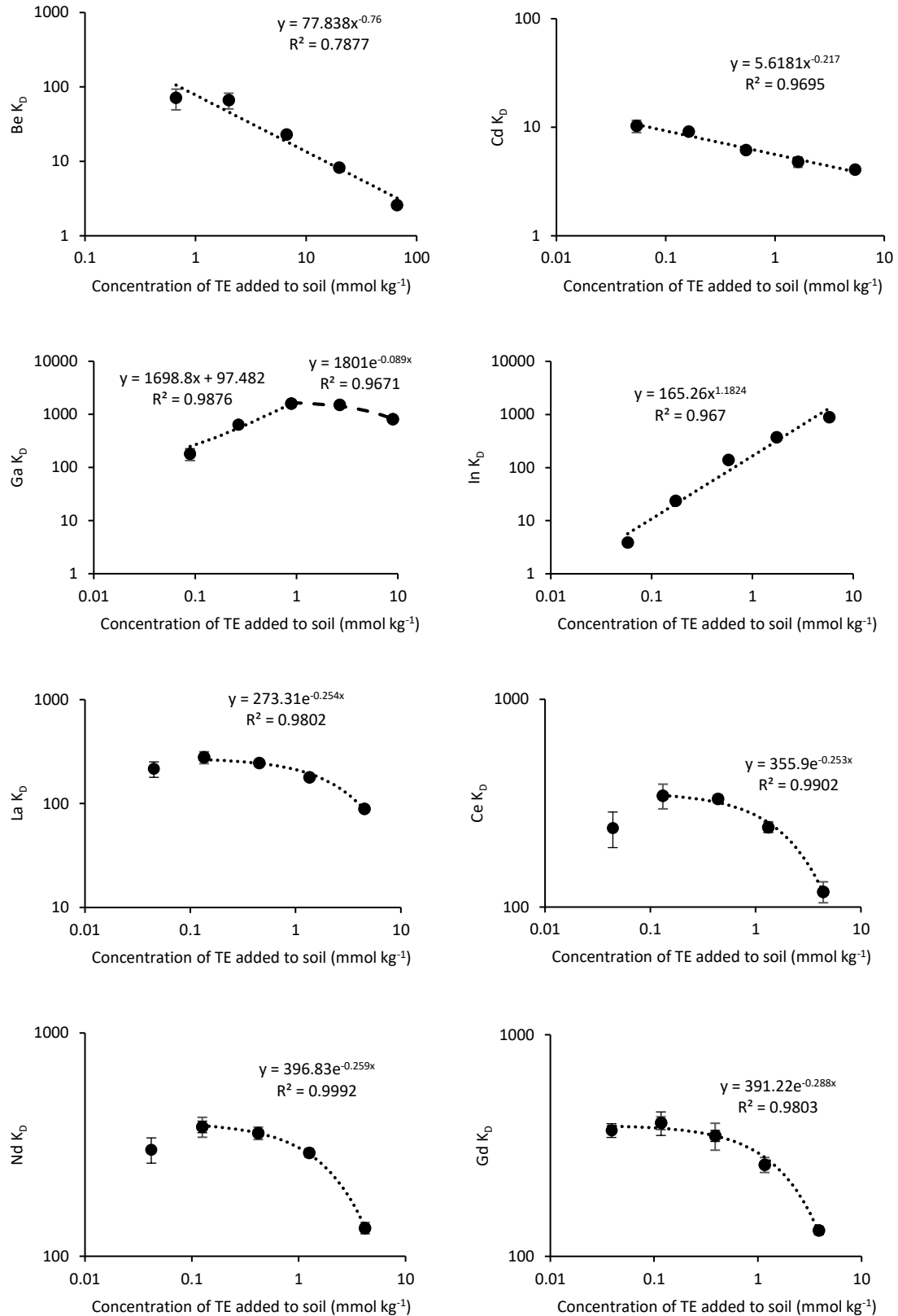
### 4.3. Results

#### 4.3.1. Effect of ETEC concentration on K<sub>D</sub> of the ETECs and Cd

##### 4.3.1.1. RFMW

As the concentration of the ETECs or Cd added to the soil increased, the K<sub>D</sub> of Be, Cd, La, Ce, Nd, and Gd decreased (Fig. 4.1). Beryllium had a higher K<sub>D</sub> than Cd at 1 mg L<sup>-1</sup> added to soil, but the K<sub>D</sub> of these elements decreased to similar values by the highest concentration tested, 100 mg L<sup>-1</sup> Be or Cd added. The K<sub>D</sub> of the REEs were highest when 3 mg L<sup>-1</sup> of the REEs were added to solution, then decreased, but the percentage decrease in the K<sub>D</sub> values were smaller for the REEs than Be and Cd. Of the REEs, Gd and Nd had the highest K<sub>D</sub> values, followed by Ce then La. The K<sub>D</sub> of In consistently increased as the concentration added increased, whereas the K<sub>D</sub> of Ga was at a maximum at 10 mg L<sup>-1</sup> added to solution, then decreased.





**Fig. 4.1 Effect of concentration on the  $K_D$  of Be, Cd, Ga, In, La, Ce, Nd and Gd in the RFMW.**

Error bars show standard error of  $K_D$ , and the trendlines show the equations of best fit for concentration versus  $K_D$ . Two different trendlines are present for Ga, calculating the increase and decrease in  $K_D$  either side of the peak.

#### 4.3.1.2. *RFT and GOO soils*

In the RFT (Fig. C.1), the  $K_D$  of Be and Cd also exponentially decreased as the concentration added to soil increased, decreasing from 66 to 4.5 and 5.2 to 2.7, respectively. In the GOO (Fig. C.2), however, the  $K_D$  of Cd increased with the concentration of Cd added to soil, reaching a maximum at 10 mg L<sup>-1</sup> added to soil. The  $K_D$  of Be was the highest at 3 mg L<sup>-1</sup> added to soil but decreased at higher concentrations.

$K_D$  consistently increased with concentration of Ga and In added to solution in the RFT and GOO soils. Gallium had higher  $K_D$  than In in the RFMW soil (except for at 100 mg L<sup>-1</sup>) and the RFT, but at 3-10 mg L<sup>-1</sup> in the GOO they crossed over, as the  $K_D$  of In had a steeper gradient.

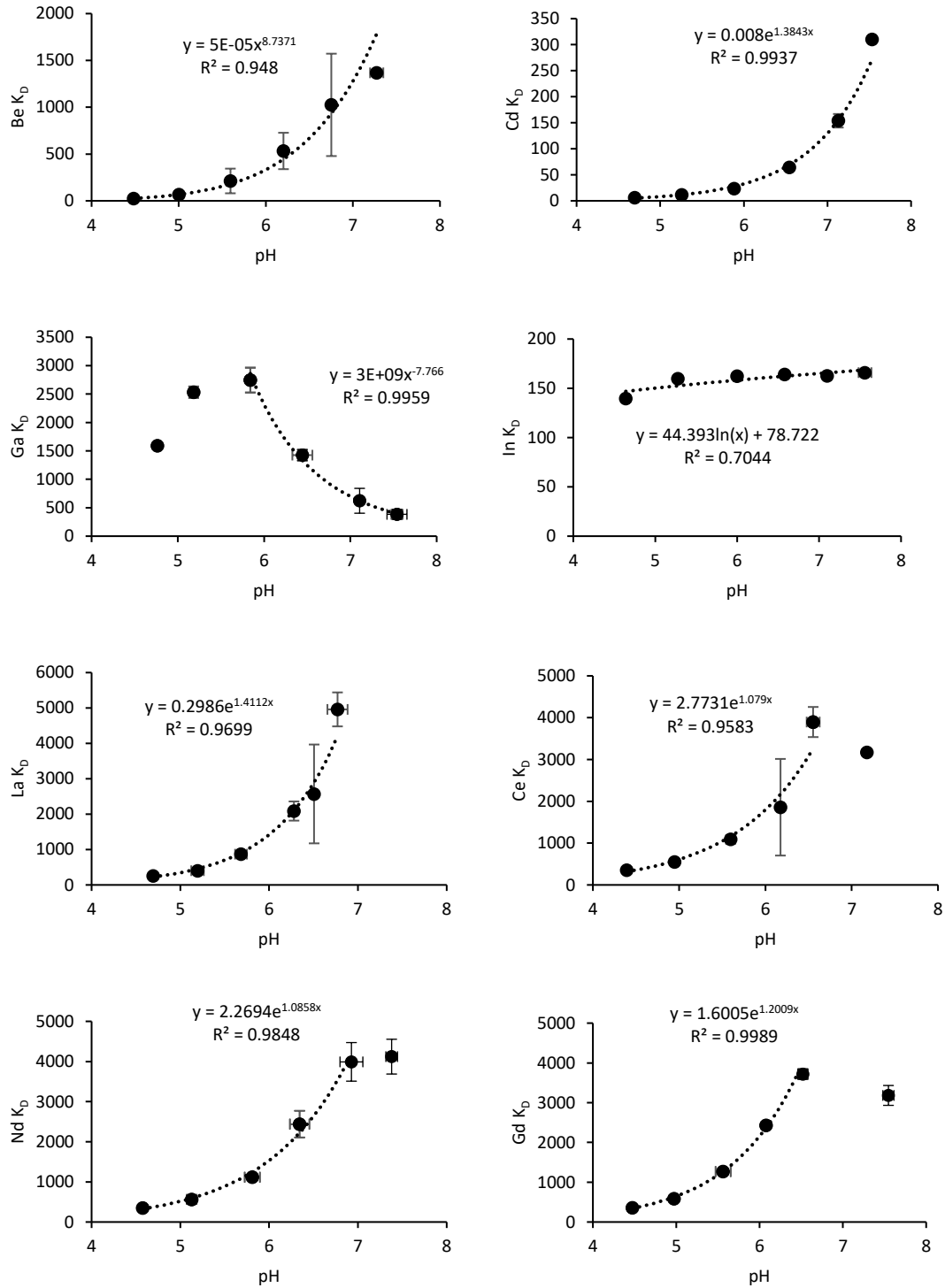
### 4.3.2. Effect of pH on $K_D$ of the ETECs and Cd

#### 4.3.2.1. *RFMW soil*

The increase in solution pH from 4.5-7 caused the  $K_D$  of Be, Cd, La, Ce, Nd and Gd to increase in the RFMW soil (Fig. 4.2).  $K_D$  values of Be and Cd increased from 23 and 6.1 to 1368 and 310, respectively. The  $\infty$ 5000% exponential increase in sorption occurred one pH unit lower for Be than Cd, but otherwise the elements behaved similarly.

$K_D$  of the REEs increased exponentially with increasing pH, but for Ce, Nd, and Gd  $K_D$  levelled off or decreased above pH 6.5. The exponential curves were similar between the REEs, but the key distinguishable difference is that the exponential increase in sorption for Gd occurred at a lower pH than for Ce, La, and Gd (Fig. C.5).

Sorption of Ga peaked at a lower pH range than Be, Cd, and the REEs, with the highest  $K_D$  value at pH 5.8. The change in soil solution pH had little effect on the sorption of In in the RFMW soil at pH 4.6-7.6;  $K_D$  did not vary along this range.



**Fig. 4.2. Effect of pH on the  $K_D$  of Be, Cd, Ga, In, La, Ce, Nd and Gd in the RFMW soil when 10 mg L<sup>-1</sup> ETEC added to solution.**

Error bars show standard error of  $K_D$  and pH, and the trendlines show the equations of best fit for pH versus  $K_D$ .

#### 4.3.2.2. RFT and GOO soils

The  $K_D$  of Be and Cd exponentially increased in the RFT (Fig. C.3), like in the RFMW, but the maximum  $K_D$  values were higher for both elements in the RFT. In the GOO soil (Fig. C.4),  $K_D$  of Be and Cd increased linearly as the solution pH increased. At the lowest pH range tested (pH 4-5)  $K_D$  of Be and Cd were lower in the GOO soil than the other two soil types, and the GOO soil had the lowest percentage increase in the  $K_D$  of Be and Cd than the other two soil types.

pH had little effect on the  $K_D$  of Ga and In in the RFT (Fig. C.3). In the GOO soil the  $K_D$  of In was little-affected by pH but was higher than in the other two soil types. In both the GOO and RFMW soils, the maximum  $K_D$  of Ga occurred at pH 5.7.

#### 4.3.3. Comparison of $K_D$ of the ETECs and Cd

The ranking of the ETECs and Cd from low to high  $K_D$  varied with the concentration added to soil, solution pH, and soil type, but in general the  $K_D$  ranking was Cd<Be<In<La<Ce<Nd<Gd<Ga (Table 4.4 and Table 4.5). Gallium and the REEs had similar  $K_D$  but differed in the concentrations and pH that the  $K_D$  was the highest at.

$K_D$  of Ga was the highest in the RFMW soil, followed by the GOO then RFT, whereas In had the highest sorption in the GOO soil followed by the RFMW soil and RFT (Table C.9). Beryllium and Cd had the highest  $K_D$  values in the RFT in the pH gradient but had the lowest sorption in the RFT in the concentration gradient. In the concentration gradient which had low pH, the GOO soil had the highest  $K_D$  values for Be and Cd.

**Table 4.4 Effect of ETEC concentration added on the  $K_D$  of Be, Cd, Ga, In, La, Ce, Nd and Gd (standard error).**

RFMW					
Element	0 mg L <sup>-1</sup>	1 mg L <sup>-1</sup>	10 mg L <sup>-1</sup>	100 mg L <sup>-1</sup>	<sup>b</sup> 1 mmol kg <sup>-1</sup>
Be	<sup>a</sup>	71 (13)	23 (0.88)	2.6 (0.026)	77
Cd	<sup>a</sup>	10 (0.76)	6.1 (0.17)	4.1 (0.046)	5.6
Ga	<sup>a</sup>	180 (26)	<b>1,591 (26)</b>	807 (31)	<b>1648</b>
In	<sup>a</sup>	3.9 (0.076)	140 (0.36)	<b>895 (6.4)</b>	165
La	<sup>a</sup>	215 (21)	215 (21)	89 (1.7)	212
Ce	<sup>a</sup>	240 (27)	332 (8.4)	119 (2.5)	276
Nd	60,551 (3,191)	300 (22)	356 (7.4)	134 (2.8)	306
Gd	<sup>a</sup>	<b>370 (15)</b>	350 (12)	131 (3.3)	293
RFT					
Element	0 mg L <sup>-1</sup>	1 mg L <sup>-1</sup>	10 mg L <sup>-1</sup>	100 mg L <sup>-1</sup>	<sup>b</sup> 1 mmol kg <sup>-1</sup>
Be	<sup>a</sup>	<b>66 (2.2)</b>	35 (0.45)	4.5 (0.053)	73
Cd	<sup>a</sup>	5.2 (0.018)	3.7 (0.11)	2.7 (0.069)	3.5
Ga	<sup>a</sup>	3.3 (3.5)	<b>157 (15.7)</b>	<b>934 (65)</b>	<b>168</b>
In	<sup>a</sup>	0.41 (0.46)	17 (0.19)	152 (1.4)	30
GOO					
Element	0 mg L <sup>-1</sup>	1 mg L <sup>-1</sup>	10 mg L <sup>-1</sup>	100 mg L <sup>-1</sup>	<sup>b</sup> 1 mmol kg <sup>-1</sup>
Be	7,243 (347)	<b>154 (41)</b>	197 (22)	57 (4.8)	218
Cd	18 (5.1)	18 (5.1)	67 (2.3)	61 (2.3)	64
Ga	<b>171,189 (40,226)</b>	121 (18)	185 (19)	690 (42)	216
In	<sup>a</sup>	17 (0.13)	<b>237 (0.43)</b>	<b>994 (20)</b>	<b>275</b>

Highest value, lowest value. <sup>a</sup>Below detection limit; <sup>b</sup>Values calculated from the trendline in Fig. 4.1.

<sup>a</sup>Values calculated from isotherm (Fig. 4.1).

**Table 4.5 Effect of pH on the  $K_D$  of Be, Cd, Ga, In, La, Ce, Nd and Gd when 10 mg L<sup>-1</sup> ETEC added to solution.**

RFMW			
Element	pH 5	pH 6	pH 7
Be	64	315	1,210
Cd	8.1	32	129
Ga	<b>2,026</b>	<b>2,716</b>	821
In	150	158	165
La	346	1,420	<b>5,824</b>
Ce	599	1,755	3,377
Nd	517	1,532	4,012
Gd	649	2,155	3,469
RFT			
Element	pH 5	pH 6	pH 7
Be	140	<b>693</b>	<b>2,687</b>
Cd	16	109	552
Ga	<b>247</b>	241	236
In	18	18	19
GOO			
Element	pH 5	pH 6	pH 7
Be	254	425	<b>595</b>
Cd	78	157	319
Ga	<b>552</b>	<b>880</b>	394
In	246	205	171

Highest value, lowest value. All values calculated from trendlines (Fig. 4.2)

#### 4.3.4. Freundlich and Langmuir isotherms

The Langmuir isotherm represented the sorption of Be, La, Ce, Nd and Gd ( $R^2 \geq 0.67$  for Be, and 1.00 for the REEs) across the tested concentration range, while the Freundlich isotherm was the best fit for Cd and Ga ( $R^2 \geq 0.75$ ), and the logarithmic curve was the best fit for In, with  $R^2$  values  $\geq 0.75$  (Table 4.6, Table C.3, C.4 and C.5). In some of the soil-element combinations (Cd, Ga, and In in the GOO soil, Be in the RFMW and RFT soils, and Ga in the RFMW soil), the isotherm or equation accurately fit all the data points except that at the highest concentration (100 mg L<sup>-1</sup>) where  $Q_e$  exceeded the calculated value. Two of the soil-element combinations, Ga- RFT and In- RFMW, visually did not fit any of the isotherms or equations (sum of normalised error >0.9).

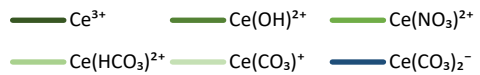
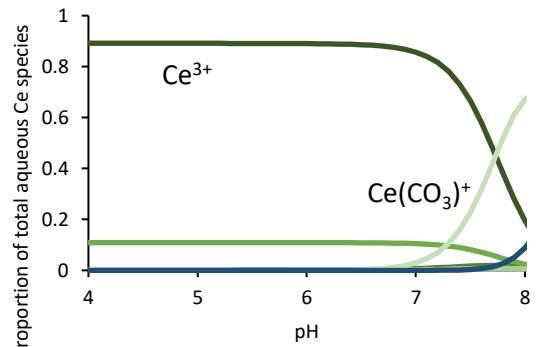
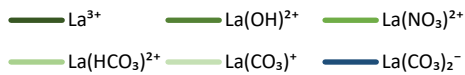
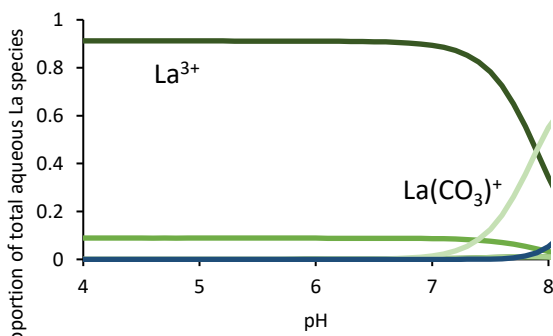
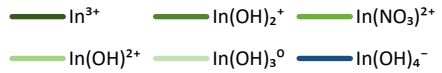
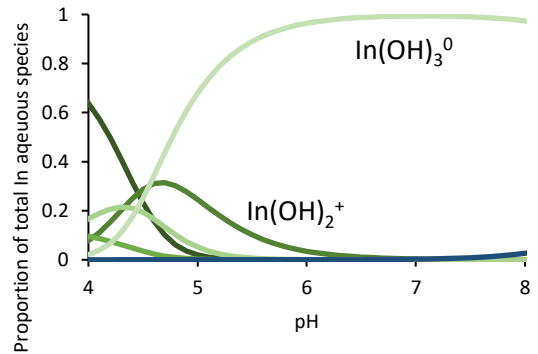
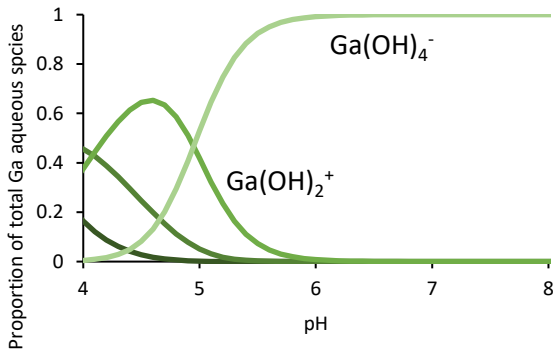
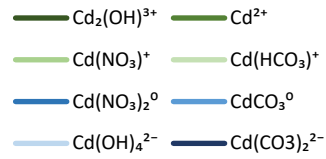
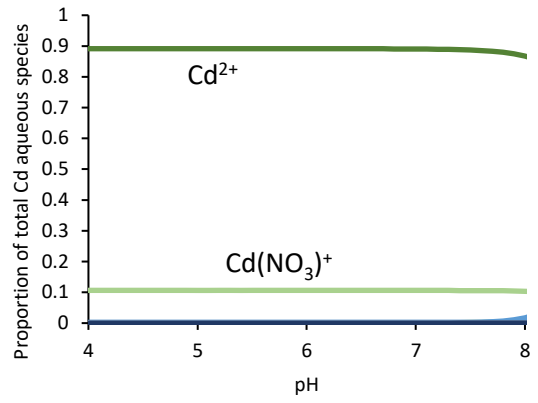
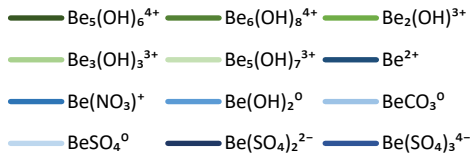
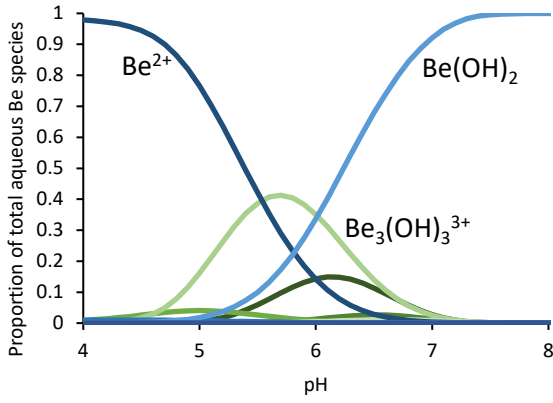
**Table 4.6 The fit of the Langmuir, Freundlich, linear and logarithmic models (as indicated by  $R^2$ ) to Be, Cd, Ga, In, La, Ce, Nd and Gd sorption data.**

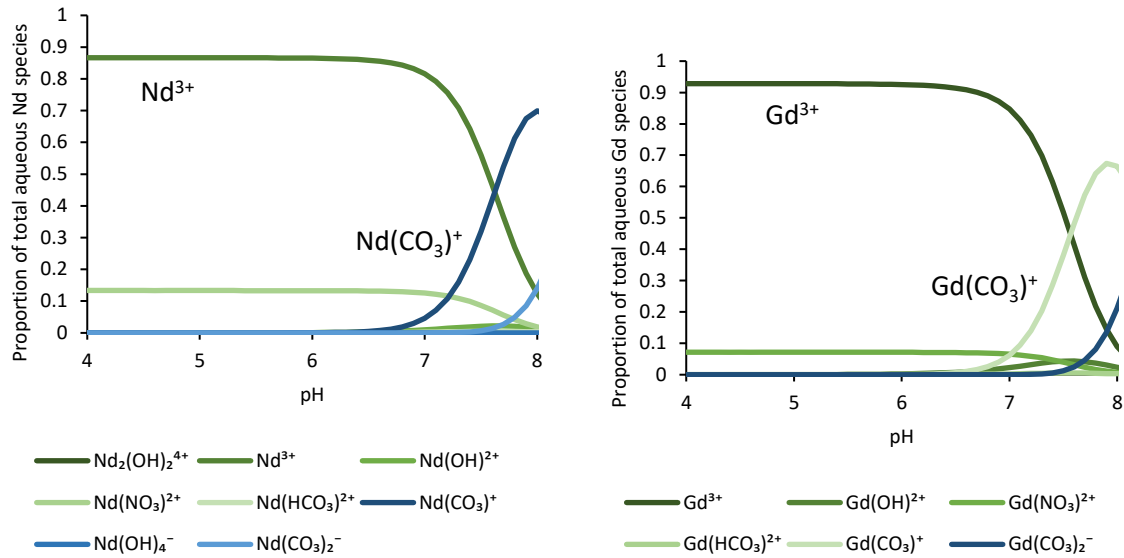
Element	Soil type	Model type			
		Langmuir	Freundlich	Linear	Logarithmic
Be	RFMW	<b>0.67</b>	<b>0.69</b>	0.72	0.68
	RFT	<b>0.75</b>	0.75	0.75	0.75
	GOO	<b>0.75</b>	0.75	0.75	0.75
Cd	RFMW	0.75	<b>0.77</b>	0.75	0.75
	RFT	0.76	<b>0.84</b>	0.75	0.75
	GOO	0.75	<b>0.75</b>	0.75	<b>0.75</b>
Ga	RFMW	0.75	0.75	0.75	<b>0.75</b>
	RFT	0.75	<b>0.75</b>	0.75	0.75
	GOO	0.75	<b>0.75</b>	0.75	0.75
In	RFMW	0.75	0.75	0.75	<b>0.75</b>
	RFT	0.75	0.75	0.75	<b>0.75</b>
	GOO	0.00	0.97	0.00	<b>0.83</b>
La	RFMW	<b>1.00</b>	0.99	0.96	0.28
Ce		<b>1.00</b>	0.99	0.96	0.36
Nd		<b>1.00</b>	0.99	0.96	0.24
Gd		<b>1.00</b>	1.00	0.99	0.68

Bold font indicates the line(s) of best fit, as determined by the sum of normalised error (Table C.3, C.4 and C.5).

#### 4.3.5. MINTEQ modelling

The numerical speciation found that Ga and In hydrolyse at pH <4, hydrolysing to  $\text{Ga}(\text{OH})_4^-$  and  $\text{In}(\text{OH})_3^0$  by pH 5.5, which remain the dominant aqueous species in an ETEC-salt solution until pH 8 (Fig. 4.3). Dominant species of Be transition from  $\text{Be}^{2+}$  to  $\text{Be}(\text{OH})_2$  from pH 5-7, with the higher-charged cations  $\text{Be}_3(\text{OH})_3^{3+}$  and  $\text{Be}_5(\text{OH})_6^{4+}$  present at >5% as Be hydrolyses from the divalent to neutral forms. The REE stay as trivalent cations until pH 7, then they hydrolyse to  $(\text{REE})(\text{CO}_3)^+$  then  $(\text{REE})(\text{CO}_3)_2^-$ . Hydrolysis of the REEs occurs at the lowest pH range for Gd, followed by Nd, Ce, and La. In the discussion, this modelling will be linked to the batch sorption data.





**Fig. 4.3 Modelled speciation changes with for Be, Cd, Ga, In, La, Ce, Nd and Gd.**

The line colours are ranked from the species with the highest positive charge to neutral to the highest negative charge, from dark green to light green to dark blue to light blue.

Graphs display pH 4-8 as this is the common pH range of soils. Some species listed in the legend are present outside of this pH range.

## 4.4. Discussion

As with other trace elements (Shaheen et al., 2013; Sohlenius et al., 2013; Watmough, 2008), the experiments showed that variation in pH, concentration and soil OM content changed the  $K_D$  values of the ETECs by up to 95%. In particular, pH is dynamic and can change after the ETECs enter soil, through liming, use of acidic fertilisers (e.g. urea, ammonium-containing fertilizers and elemental sulphur), further contamination, or release of  $H^+$  by plant roots. The effect of the concentration added to soil on  $K_D$  is an important factor to consider for contaminants, as higher concentrations added to soil could result in disproportionately greater solubility (due to sorption sites becoming saturated at higher concentrations).

### 4.4.1. Effect of soil solution pH on $K_D$

For the REEs La, Ce, Nd and Gd,  $K_D$  increased exponentially as the pH increased above pH 6, which is consistent with other studies (Fang et al., 2007; Shan et al., 2002; Sohlenius et al., 2013; G. Tyler & T. Olsson, 2001). The increase in sorption occurred at a lower pH range for Gd than the other REEs, followed by Nd and Ce, then La, at pH >5.5 in B.16. This ranking is consistent with the order the REEs hydrolyse in-Gd at the lowest pH and La at the highest pH-and at the IP of the elements-Gd has the highest and La has the lowest. The exponential 900-1800% increase in sorption occurred 2-3 pH units lower than the pH where hydrolysis occurs, thus the differences in sorption between the REEs are



unlikely to be a result of the hydrolysis products, but show that along the lanthanide group, ions with a higher ionic potential begin increasing in sorption at a lower pH, which may be a result of outcompeting other ions or increased capacity to sorb to hydroxide oxygen-based functional groups on soil colloids. As a result, Gd usually had the highest or near-highest  $K_D$  of the four REEs throughout the pH and concentration variations, followed by Nd and Ce, then La.

The effect of increasing pH on the sorption of Ga and In differed to the other elements, but is consistent with the transitions in the visual speciation modelling (Fig. 4.3). Gallium transitions from  $Ga^{3+}$  to  $Ga(OH_4)^-$  within the pH range of soils, and between these two species it is briefly present as  $Ga(OH)_3^0$ , which has low solubility and readily precipitates. This precipitation is likely to have caused the  $K_D$  of Ga to reach a maximum at pH 5.84 and 5.73 in the RFMW and GOO soil types, after which it transitions to the anion that is more soluble.  $Ga(OH)_3^0$  was not able to be selected in Minteq to put on the graph, but it was modelled as a small peak by Wood and Samson (2006) at pH 5, and the highest saturation index of  $Ga(OH)_3$  was modelled to occur at pH 4.5-5. Bernstein (1998) supports these findings, as stated that the two Ga hydroxide precipitates reach minimum solubility at pH 5.2. Sorption of Ga likely did not rapidly increase when the REEs did because  $Ga(OH_4)^-$  is an anion, which are repelled by and outcompeted for negative sorption sites.

There was little change in In sorption between pH 4.5 and 7.5. In has a large period of maximum  $In(OH)_3^0$  production and  $In(OH)_{3(s)}$  insolubility between pH  $\approx$ 5.5-8.5, which is similar to the pH range of 4-7 used in the batch sorption experiments. The soil where the sorption of In increased slightly with pH had the lowest pH range (RFT at 4.1-6.5), and the soil where In sorption decreased with increasing pH (GOO) had the highest pH range at 4.8-7.1, suggesting that the aforementioned pH ranges bordered the periods of peak In precipitation. The In anion is unlikely to be present until pH 9.5 (Kabata-Pendias & Mukherjee, 2007). The differences in  $K_D$  with soil type may be due to the variation in other ligands such as DOM,  $PO_4^{3-}$ , and  $SO_4^{2-}$  forming soluble or insoluble complexes with In.

Sorption of Be increased when the soil solution pH increased, like Cd, La, Ce, Nd and Gd, but the curve and pH range at that the  $K_D$  of Be increased was the same as the formation of poorly-soluble  $Be(OH)_2$  in the modelling (Fig. 4.3) in the RFMW and RFT soils. This is consistent with the previous findings that  $Be(OH)_2$  formation and precipitation is responsible for the rise in  $K_D$  of Be above pH 6 (Aldahan et al., 1999; Islam et al., 2021). There was a similar increase in Cd sorption, but is unlikely to hydrolyse within the pH range tested in this study (Alloway, 2013), thus like the REEs its increase in sorption is due decreased  $H^+$  competition and the increasingly negative surface charge of soils (Alloway, 2013).

Sorption of Be and Cd differed significantly in the GOO soil, where Be had a linear response and Cd almost had a linear response to increasing pH and less change in  $K_D$ . This is likely due to the high OM content in that soil; sorption to OM increases at a lower rate than to minerals, as sorption to minerals rapidly increases as they precipitate, but sorption to OM usually increases with pH due to deprotonation of  $\text{OH}^-$  groups (Boschi & Willenbring, 2016b; Dube et al., 2001). Also, many of the organic complexes created are soluble (Ashworth & Alloway, 2007). If a lower pH range was tested in the three soil types, it could be determined if Be and Cd have similar  $K_D$  at pH before the exponential increase in sorption, or if Be consistently had the capacity to bind to more soil sorption sites than Cd. Be had the lowest maximum  $K_D$  values in the GOO soil, which had the highest concentration of OM (Table 4.1), which indicates that soluble OM is complexed with Be, limiting formation and precipitation of  $\text{Be}(\text{OH})_2$ , as has been shown for other trace elements (Ashworth & Alloway, 2007). The same is likely true for Cd, with DOM reducing the rapid increase in sorption with precipitation of minerals, as observed in the other two soil types; other studies have recorded the strong affinity of Cd with OM (Fan et al., 2015; Wong et al., 2007).

The modelling provides a useful indication of what happens in the aqueous system including the transitions between different-charged hydroxide or carbonate species, and the pH range at that an exponential increase in  $K_D$  is due to precipitation and not adsorption. Flaws are that this approach but does not account for removal of ions to the solid phase, and soluble ions (especially P, which varied in concentration between the soil types) and DOM from soil that can complex with the ETECs and Cd, and limit adsorption and precipitation.

#### 4.4.2. Effect of added ETEC and Cd concentration on $K_D$

The  $K_D$  values of Be and Cd followed a saturation curve in the RFMW and RFT soils (Shaheen et al., 2013), where easily accessible adsorption sites quickly become occupied by ions, thus at higher concentrations more ions remain in solution, decreasing the  $K_D$ . Beryllium had a higher  $K_D$  than Cd at 1-3  $\text{mg L}^{-1}$  Be or Cd added (Fig. 4.1 and Fig. C.1), which indicates that the smaller size and/or higher IP of  $\text{Be}^{2+}$  caused more specific adsorption sites to be available for Be, but by 100  $\text{mg L}^{-1}$  of ETEC added, at saturation, the  $K_D$  of the two elements were similar, at 2.6-4.5. This is despite the lower Mr of Be (10  $\text{mg L}^{-1}$  of Be and Cd is 1.11 mM Be and 0.09 mM Cd); on a mass basis, Cd is likely to have a higher  $K_D$  than Be, as there are fewer molecules of Cd competing for a limited number of sorption sites. Therefore, at saturation when both elements had the same  $K_D$  range, more Be particles were sorbed than Cd, hence the soil had a greater capacity to bind Be. Perhaps the higher ionic potential caused

Be to outcompete other elements for sorption sites, which Cd was unable to do, or the large Cd atoms blocked sorption sites from other Cd atoms in the limited surface area of the soil colloids. In Shaheen et al. (2015) Zn was smaller and had a higher IP than Cd, and was more strongly sorbed, albeit some soils had a stronger affinity for Cd than Zn, which could be due to hardness versus softness, the strong affinity of Cd for dissolved OM (Kubier et al., 2019), and other soil properties.

Precipitation of Be is unlikely to have occurred in the environmental conditions the 1-100 mg L<sup>-1</sup> Be concentration gradient was conducted in, as the pH of the solution was too low. The maximum solution pH in the concentration gradient was 4.8 (Table C.6), and >pH 5 is where the formation of Be(OH)<sub>2</sub> is considered likely in soil (Islam et al., 2021). The K<sub>D</sub> values in the concentration gradient in this study were 1-2 scales lower than that by Islam et al. (2021), but their experiments were conducted at a higher pH (pH 5) with more sorption sites in the solid phase, with a longer shaking time (24 hr) and to soils rich in Al and Fe oxyhydroxides. Alloway (2013) stated that Cd precipitation is possible at high concentrations, >100 mg kg<sup>-1</sup> (the 30 and 100 mg L<sup>-1</sup> solution samples are equivalent to 180 and 600 mg kg<sup>-1</sup> ETEC in soil), which could explain the different effect of the GOO soil on the K<sub>D</sub> of Cd, though unlikely as the solutions were three pH units below the Cd hydrolysis range (Fig. 4.3).

The K<sub>D</sub> values of the REEs were consistently higher than Be despite their lower ionic potential, which shows that the trivalent cations can access more sorption sites than divalent. Maximum and minimum K<sub>D</sub> values of the REEs followed the ionic potential gradient of Gd>Nd>Ce>La, however, for the minimum K<sub>D</sub> at 100 mg L<sup>-1</sup> ETEC added Nd had a higher K<sub>D</sub> than Gd. This occurred for Be and Cd, where within the same valency, ions with a higher IP had a higher K<sub>D</sub> at the concentration of maximum sorption.

As with pH, the K<sub>D</sub> of Ga and In increased in response to increasing the concentration added to the system to precipitation, as hypothesised in Chapter 3. The pH ranges of the concentration gradients were within the ranges for production of the neutral hydroxides as calculated by Minteq (Fig. 4.3). Hou et al. (2005) reported that In had higher mobility than Sb, Ag and Sn, but added a lower concentration of In to soil (1.8 mg kg<sup>-1</sup> In versus 6 mg kg<sup>-1</sup>), thus the K<sub>D</sub> was likely lower. Tyler and Olsson (2002) and Hou et al. (2005) reported that In has strong associations with OM, indicating that mobility may have been initially increased by sorption to soluble organic complexes, and perhaps saturation of those lead to sorption to non-soluble OM and/or hydroxide precipitation.

#### 4.4.3. Fit of Langmuir and Freundlich isotherms to ETEC sorption

Langmuir and Freundlich isotherms fit well ( $R^2 > 0.75$ ) for half of the soil-element combinations, but poorly for the other half. The REEs and Be fitted the Langmuir model well in the RFT and GOO soils, which shows that sorption of these elements rapidly increases as the concentration increases but will hit a plateau. The sorption gradient of these elements was much lower between 30-100 mg L<sup>-1</sup> than at lower concentrations, implying that a plateau is likely slightly beyond the range tested. However, the Langmuir model underestimated sorption of Be for the highest concentration of Be added to soil (100 mg L<sup>-1</sup>) by 33-77% in the RFMW and RFT soils. Islam et al. (2021) also reported that for Be, the isotherm was best described by the Langmuir equation. The Freundlich fit of Cd and Ga sorption implies that sorption will continuously increase as the concentration added to soil increases. Neither of the soil sorption models were suitable fit for In, thus further work is required to investigate the sorption patterns of In.

Sorption of Cd, Ga, and In did not fit any of the curved well in the GOO soil, due to sorption at the highest concentration added to soil being higher than the other data points and the fit of the trendline, but Be data fit the Langmuir curve well. The addition of 100 mg L<sup>-1</sup> of Cd, Ga and In reduced the pH of the solution to 4.65-4.76 (Table C.6), whereas 100 mg L<sup>-1</sup> Be reduced the solution pH from 4.81 to 4.23. This suggests that sorption of the ETECs to OM decreased as the pH decreased. You et al. (1999) found that soil DOC concentrations increased with pH, but little change was observed between pH 4-5.

Langmuir and Freundlich can be good predictors of soil sorption, as seen with the REEs in this study, and are feasible to be used in many environments as the only data required to be inputted is sorption data, and they provide clear visualisation of what is happening to total sorption. Islam et al. (2021) suggest they are particularly useful for high concentrations associated with contamination, as saturation and thus the decreased rate of sorption is more likely to occur, which is consistent with the finding that the linear equation was not the best fit for any data according to the sum of normalized error. However, Langmuir and Freundlich curves need to be recalibrated for each soil type (Selim & Zhang, 2013), and within this study, accuracy was lower at high concentrations (>30 mg L<sup>-1</sup> solution in this study), soil properties such as OM may alter the curve, and some elements deviate from the increase in sorption with concentration that the Langmuir and Freundlich isotherms assume. The capacity of some elements to precipitate and further immobilise at high concentrations in soil, such as Ga and In, further contributes to reducing their suitability for the sorption isotherms, as they

assume sorption will decrease at high concentrations, and precipitation causes  $K_D$  to continuously increase.

#### 4.4.4. Comparison of $K_D$ between the elements

The results show that elements from different areas of the periodic table have contrasting behaviour to environmental perturbations (soil solution pH and the concentration added to the system). Although an overall ranking was created for the sorption of the ETECs and Cd, it will differ based on the concentration added to soil and the pH of the soil solution, thus a ranking that is accurate across all soil types cannot be created. In this study, the elements that had similar reactions to the pH and concentration perturbations (and thus their ranking stayed similar across the perturbations) were Be and Cd, which are both divalent cations, and the REEs La, Ce, Nd and Gd. Despite both being in group 13, Ga and In had different reactions to each other to the pH increasing, but the mechanisms responsible for the variation between the two elements are the same, as both elements hydrolysed and precipitated, but In had a higher pH range of hydrolysis and a larger pH range of maximum hydrolysis. Therefore, it may be possible to use an element as a benchmark for others who have been tested to behave similarly (e.g. using Nd to estimate the  $K_D$  and responses of other lanthanides), but the use of benchmarks is limited and not feasible in many cases (e.g. using Cd estimate the  $K_D$  of Ga).

#### 4.4.5. Management of ETEC-contaminated soil

The effect of changes in ETEC concentration added and solution pH on the  $K_D$  of the ETECs varies between the elements. Thus, the elements at risk of contamination should all be investigated further and tested on a wide range of soil types, because as shown in this study the behaviour can differ significantly. If the aim of the system is to store ETECs with little risk of migrating to plants or groundwater, the data shows that the relative solubility of Ga and In will be low if high concentrations of these elements are added to soil, or if the pH of the soil is in the In precipitation range or near maximum Ga precipitation. If Be, Cd or REE contaminants are present in soil, the pH should be raised through liming (to >pH 6, or higher for Cd) to immobilise these elements, and reduce uptake by plants and leaching. There is a moderate risk of these elements leaching at high concentrations, particularly in acidic soils. The  $K_D$  of Cd, across the concentration and pH variations, is the lowest of the elements, followed by Be.  $K_D$  of In was usually lower than Ga. Gallium and the REEs usually had high  $K_D$ , albeit dependent on the soil conditions. Soluble ETECSs can potentially be taken up by plants and translocated into material that is eaten by animals and humans, which is toxic at high concentrations, thus the effect of the variation in solubility on the differences in plant uptake of the ETECs should be investigated, e.g. if the higher soil  $K_D$  of Be causes it to have lower plant uptake than Cd.

The insolubility of Bi and Te in  $\text{Ca}(\text{NO}_3)_2$  and water means that these elements are unlikely to be taken up by plants and upon entry to soil will rapidly be incorporated into the solid phase. Therefore, the  $K_D$  values of Bi and Te are higher than the other ETECs and Cd measured. Like the other ETECs, they may be soluble in acidic solutions, but this was not tested as it would be at a pH below the normal soil, and plant growth, pH range.

#### 4.5. Conclusions

The  $K_D$  of the selected ETECs and Cd in soil had the ranking of  $\text{Cd} < \text{Be} < \text{In} < \text{La} < \text{Ce} < \text{Nd} < \text{Gd} < \text{Ga} < \text{Bi} = \text{Te}$ . The ETECs and Cd had contrasting responses to changes in concentration and soil solution pH; sorption of Be and Cd increased with increasing pH and decreased with the concentration of the elements added to the system. Although both are divalent, the larger IP of Be caused it to have a higher  $K_D$  than Cd, and exponentially increase in sorption at a lower pH range, although that is likely attributed to precipitation of  $\text{Be}(\text{OH})_2$ . The REEs La, Ce, Nd and Gd had similar variation in  $K_D$ , with higher  $K_D$  due to their trivalent species; Gd had a higher ionic potential than the other REEs, thus sorption occurred at a lower pH range. Gallium and In precipitate within the soil pH range, thus  $K_D$  in response to pH reflected this, and their  $K_D$  increased with the concentration added to soil. The Freundlich and Langmuir models of sorption fit well for Be, Cd, La, Ce, Nd, and Gd some element-soil combinations but are not good predictors for Ga and In, which may be related to the aforementioned precipitation. Future work should find how the variation in solubility affects the uptake of these elements by plant roots.

## 5. The tolerance and uptake of ETECs by perennial ryegrass (*Lolium perenne*)

### Abstract

Technological development has increased use of unusual trace elements. Such elements are ultimately released into the environment as Emerging Trace Element Contaminants (ETECs). Soil contamination with ETECs may lead to leaching or plant uptake, increasing human and ecological exposure. This study aimed to determine the capacity of *Lolium perenne* (a common pasture species) to tolerate and accumulate the ETECs Be, Ga, In, La, Ce, Nd and Gd in a RFMW soil. Cadmium was used as a reference as a well-studied contaminant that is relatively mobile in the soil-plant system. Soil was spiked with 2.5-283 mg kg<sup>-1</sup> of solubilised ETEC or Cd salts, representing 5, 10, 20 and 40 times their background concentrations in soil. The addition of Be, Ce, In and La did not reduce plant growth at any of the concentrations tested. The maximum no-biomass reduction concentrations of the target ETECs and Cd in perennial ryegrass were 0.061 mg kg<sup>-1</sup> for Cd, 0.11 mg kg<sup>-1</sup> for Gd, 7.1 mg kg<sup>-1</sup> for Nd, and 11 mg kg<sup>-1</sup> for Ga. Bioaccumulation coefficients ranged from 0.0030-0.95, and increased Ce<In<Nd≅Gd<La≅Be≅Ga<Cd. Beryllium and La are the elements most at risk of entering the food chain via perennial ryegrass, as their toxicity thresholds were not reached in the ranges tested, and the trendlines suggested that uptake and bioaccumulation would continue to increase at higher concentrations added to soil. Cadmium, In and Ce are the elements least likely to be passed up the food chain. Further research should repeat the experiments in different soil types or with different plant species to test the robustness of the findings.

### 5.1.1. Introduction

Technological developments have led to new uses for ETECs, which hitherto have not been emitted into the environment at high concentrations. Soil contamination via disposal of mining and extractions waste, rudimentary recycling of electronic waste (Robinson et al., 2009) and leaching of materials from landfills has increased rapidly with the industrial utilisation of ETECs (Ha et al., 2009; Ha et al., 2011; Jinxia et al., 2010; Tokumaru et al., 2017). Beryllium, Ga, In, La, Ce, Nd and Gd are ETECs of concern that are used across several industrial sectors at the rate of tens or hundreds of tonnes per year (Table 2.1).

Upon entry to soil, these ETECs either become associated with the solid phase through specific or non-specific adsorption to organic or inorganic matter, precipitation, or remain in solution (Bradl, 2004). In the soil solution, ETECs may leach downwards through the soil profile or be taken up by plants

(Hooda, 2010). Ions associated with the solid phase of the soil age to less-soluble forms the longer they are in soil (Alloway, 2013). As ETECs are non-essential for plants with background concentrations in soil of 0.26-56 mg kg<sup>-1</sup> (Kabata-Pendias & Mukherjee, 2007), plants are unlikely to have evolved specific mechanisms affecting tolerance or uptake. In soil, soluble ETECs will migrate toward plant roots via mass flow and diffusion (Banuelos & Ajwa, 1999). Inside the root cortex, they are transported to the xylem tissues via the apoplastic or symplastic pathways (Reid & Hayes, 2003). Transportation across membranes into the symplast may occur, via the pathways of chemically similar ions (Banuelos & Ajwa, 1999), e.g. Ga<sup>3+</sup> may be taken up via the same mechanism as Fe<sup>3+</sup> in strategy II plants because the ions are similar in size and electronegativity (Bernstein, 2005), La, Ce, Nd and Gd can replace Ca<sup>2+</sup> (Tyler, 2004b), and Be can replace Ca<sup>2+</sup> and Mg<sup>2+</sup> (Shah et al., 2016). Once in the roots, ETECs may be translocated around the plant, and if they enter the above-ground biomass or the edible organs, animal and human ingestion may occur. If ETECs are retained by soil, they can be ingested through soil retained on the surfaces of plant material (Laaouidi et al., 2020), which is more common in erosion-prone areas where the contaminated soil can migrate, and on root crops such as potatoes that are directly in contact with the contaminated soil.

Most plant species have foliar concentrations of <1 mg kg<sup>-1</sup> of the selected ETECs (Table A.2), even when growing in contaminated soil. The ETECs are taken up and translocated by plants if they are present in the soil solution, such as in hydroponic systems or acidic soils where elements such as Ga and In have not been hydrolysed to insoluble forms (Su et al., 2018; Syu et al., 2017; Yu et al., 2015). Hydroponic rice seedlings contained 74 mg kg<sup>-1</sup> Ga without toxicity (Syu et al., 2017). The phytotoxicity of these elements when added to soil depends on solid-phase retention and thus bioavailability, which vary between soil types (Sheppard et al., 2009; Su et al., 2018; Syu et al., 2021). Plants can tolerate similar concentrations of the ETECs and Cd, with tolerable concentrations ranging from <2 to >10 mg kg<sup>-1</sup> plant material. These studies spike one or a few elements with similar chemical properties (e.g. Ga and In) and spike the plants at various stages of growth and in various growing conditions, which hinders the capacity to accurately compare the toxicity of elements.

Bioaccumulation coefficients (BACs), defined as the plant/soil concentration coefficient, are used to assess and compare the capacity of plants to take up ETECs from the soil and translocate them to above-ground biomass (Buscaroli, 2017). Bioaccumulation coefficients for the ETECs typically range from <0.1-1.0 (Cao et al., 2000; Su et al., 2018; Wang et al., 2021; Waterlot et al., 2013; Wen et al., 2001), but in rare instances can be >1.0 in plants which have strategies to take up and mitigate the phytotoxicity of ETECs, such as wild species growing in contaminated locations in Khan et al. (2017).



There is a lacuna of studies comparing plant uptake and bioaccumulation of ETECs to each other and to common contaminants such as Cd. For example, the concentrations of the ETECs in *Fagus sylvatica* beech leaves increased In<Gd<Be<Ga<La<Nd<Ce, from 0.0002 to 0.066 mg kg<sup>-1</sup> (Tyler, 2005), and in Browntop grass Gd<Be<Nd<La<Ce, from 0.0031-0.025 to 0.051-0.13 mg kg<sup>-1</sup> (Germund Tyler & Tommy Olsson, 2001). Bioaccumulation coefficients in wheat/barley stems and grains increased Nd<La<Ga<Be<Ce, ranging from 0.0022-0.48 in stems and 0.00053-0.14 in grains (Omberg et al., 2011). However, the plants in the aforementioned studies were grown in uncontaminated soil. In soils contaminated with the ETECs, ETECs are usually less strongly sorbed to soil and thus more bioavailable (Alloway, 2013). Two studies used contaminants, e.g. root-shoot translocation of In was higher than Ga in Vietnamese wild plants growing in contaminated soil (Ha et al., 2011), and perennial ryegrass growing in spiked soil had higher uptake and bioaccumulation of Ga than In, but (Chapter 3), but these studies only measured two of the selected ETECs, and did not compare the solubility to that of other contaminants.

Due to the lack of data ranking the elements, it is hypothesised that the uptake and bioaccumulation of the ETECs Be, Ga, In, La, Ce, Nd and Gd in perennial ryegrass growing in soil spiked with these elements will follow the rankings for *Fagus sylvatica* leaves in Tyler (2005) and wheat/barley in Omberg et al. (2011).

The aim was to measure the uptake and tolerance of *Lolium perenne* to Be, Ga, In, La, Ce, Nd and Gd soil contaminants, to determine the potential risks of these elements in contaminated soils. This will be achieved through pot trials of perennial ryegrass (*Lolium perenne*) grown in soils spiked with various concentrations of these elements, with Cd used to act as a benchmark for a mobile trace element contaminant.

## 5.1.2. Materials and methods

### 5.1.2.1. Soil spiking

A mottled-weathered fluvial recent soil (RFMW) was collected from Christchurch (-43.5229981 S, 172.5873929 E). The soil was an acidic loamy sand, with high Olsen P, a moderate CEC and low concentrations of organic C (Table 5.1 and 5.2). Soil had stones removed and was dried and sieved to <2 mm.

**Table 5.1 Soil properties of the RFMW soil**

pH	5.3
Olsen P (mg L <sup>-1</sup> ) <sup>a</sup>	27
CEC (cmol(+) kg <sup>-1</sup> ) <sup>a,d</sup>	13
Base saturation (%) <sup>a</sup>	61
Total C (%) <sup>a</sup>	1.9
Texture <sup>b</sup>	Loamy sand
Sand (%) <sup>e</sup>	80.6
Silt (%) <sup>e</sup>	16.3
Clay (%) <sup>e</sup>	3.1

<sup>a</sup>Analysis from Hill's Laboratories; <sup>b</sup>Details in the appendix; <sup>c</sup>Determined in H<sub>2</sub>O, 1:2 v/v soil:water; <sup>d</sup>Sum of extractable cations and extractable acidity; <sup>e</sup>Particle size distribution measured in a Saturn DigiSizer II 5205 V1.03, soil textures classified by the texture diagram in McLaren and Cameron (1996).

**Table 5.2 Pseudo-total and Ca(NO<sub>3</sub>)<sub>2</sub> extractable concentrations of elements in the RFMW soil (mg kg<sup>-1</sup>) (standard error)**

Element	Total concentration	Extractable concentration
Na	383 (21)	-
Mg	4,708 (21)	-
Al	23,673 (195)	2.3 (0.11)
P	599 (7.9)	0.91 (0.11)
K	6,615 (50)	-
Ca	885 (11)	-
Cr	24 (0.14)	0.075 (0.00090)
Mn	337 (5.6)	3.2 (0.044)
Fe	17,183 (116)	1.4 (0.17)
Co	6.2 (0.031)	0.039 (0.00078)
Ni	12 (0.060)	0.080 (0.0020)
Cu	8.0 (0.057)	0.014 (0.00075)
Zn	57 (0.32)	0.22 (0.011)

- Not detected

**Table 5.3 Background concentrations of the ETECs and Cd used for reference in the treatments (standard error)**

Element	Pseudo-total concentration in RFMW soil (mg kg <sup>-1</sup> )	Reference background concentration (mg kg <sup>-1</sup> ) <sup>a</sup>
Be	13 (0.55)	1.9
Cd	0.064 (0.0018)	0.5
Ga	89 (1.1)	28
In	0.31 (0.0081)	0.26
La	308 (1.5)	22
Ce	60 (0.53)	57
Nd	256 (4.0)	18
Gd	39 (0.56)	3.0

<sup>a</sup>Reference concentrations from Kabata-Pendias and Mukherjee (2007)

Soil was spiked with 5 (T1), 10 (T2), 20 (T3) and 40 (T4) times the reference ETEC and Cd-background concentrations (Table 5.3), with the ETECs and Cd spiked in separate samples. The spiked concentrations were relative to the background concentrations of the ETECs and Cd in soil, as they vary by orders of magnitude, from 0.255 mg kg<sup>-1</sup> In to 56.6 mg kg<sup>-1</sup> Ce, thus the addition of the same concentrations of the elements would almost certainly cause toxicity by some elements and have no

effect on others, and the aim is to identify the toxicity thresholds of each element (toxicity calculations explained later), and find how perennial ryegrass takes up and translocates each element, relevant to what it has evolved to.

Cadmium and all ETECs were added as nitrate salts, except for Be, which was added as sulphate. The mass of salt required to achieve the ETEC or Cd concentration in T4, in 2 kg of soil, was solubilised in 100 mL of deionised water, which was transferred to a spray bottle and made up to approximately 200 mL. The solution was evenly incorporated into 2 kg of soil, 1 kg was taken out, and 250 g of that soil was placed into three pots, and 1 kg of uncontaminated soil was added to the remaining 1 kg of spiked soil to create a dilution. Dilutions were repeated to prepare each treatment. Three pots with uncontaminated soil were used as a control. The pots were square, with a height of 100 mm, a diameter of 70 mm across the top, and 50 mm across the bottom. Three replicates of each sample type were placed in a shared saucer to prevent contamination between sample types from water, and the big saucers were placed in a randomised design in a greenhouse. Pots were watered, and the ETECs and Cd were left to equilibrate for seven weeks.

#### 5.1.2.2. *Plant growth*

Perennial ryegrass (*Lolium perenne*) was used for this experiment. Perennial ryegrass is a type of grass grown in temperate areas of Asia, Australia, Europe, New Zealand, North America, South Africa, and South America. It is a member of the Poaceae family, thus shares physiological similarities to wheat, barley, and the other grains which are present in this family, which are important food crops (Cunningham et al., 1994; Grogan & Gilliland, 2011). Therefore, it is a suitable species for analysing the capacity of the ETECs to be taken up and translocated to above-ground biomass. There are currently no studies that have compared the mobility of the ETECs to each other and Cd in contaminated soil.

On the 9<sup>th</sup> of October, 2019, 50 seeds of perennial ryegrass, variety Nui obtained from Luisetti seeds, Rangiora, were sown into each pot. Pots were watered three times a week for 15 minutes each time for the duration they were in the greenhouse, from 8 overhead sprinklers at a rate of 0.47 L hr<sup>-1</sup> for each sprinkler. Pots were placed in a randomised design in a room with similar exposure to light from a window covering one side of the room. One week later, most of the seeds had germinated. The ryegrass was harvested twice, on the 17<sup>th</sup> of December 2019 and the 13<sup>th</sup> of January 2020. Ryegrass was placed into separate paper bags and dried at 60°C for 24 hours for measuring dry weight.

#### 5.1.2.3. *Digestion and measurement*

In 15 mL glass vials, 0.05-0.5 g of dried ryegrass was added to 5 mL of concentrated HNO<sub>3</sub> and left overnight. The next day, the samples were digested in a Milestone UltraWAVE single reaction chamber microwave digestion system at 220°C for 25 minutes using the General digestion method for environmental samples. After they had been cooled and stored, samples underwent a 21x dilution in 10 mL of ultrapure 1% HNO<sub>3</sub>. Samples were then analysed using ICP-MS, which measured the concentrations of Be, Na, Mg, Al, P, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Cd, In, Te, I, La, Ce, Nd, Gd, and Pb (listed in order of atomic number). The concentrations of the elements in perennial ryegrass are all reported in a dry weight (DW) basis. National Institute of Standards and Technology (NIST1573a-SRM “tomato leaves”) Certified Reference Material was used, and the measurements of were 60-140% of the certified value.

Soil digestions were completed in the same way, with 0.2-0.3 g of RFMW soil added to concentrated HNO<sub>3</sub> and digested, to measure the pseudo-total concentration (Table 5.2), and Ca(NO<sub>3</sub>)<sub>2</sub> extractable concentrations were found using the method in Al Mamun et al. (2016).

#### 5.1.2.4. *Data analysis*

Bioaccumulation coefficients (BACs) were calculated by dividing the concentration of the ETECs or Cd in each of the perennial ryegrass samples (mg kg<sup>-1</sup> DW) by the concentration of the ETEC or Cd in soil. In the treatments, the total concentrations of the elements in soil were assumed to be the pseudo-total concentration in the RFMW soil (Table 5.3) plus the concentrations added to the treatments which were gained from (Kabata-Pendias & Mukherjee, 2007) (Table 5.3). Averages and standard errors were found, based on the variation in the concentrations of the ETECs and Cd in the perennial ryegrass samples.

Biomass indexes were calculated by dividing the dry weight of the perennial ryegrass in each sample against the average dry weight in the control. When the biomass indexes of the treatments were significantly lower than the control, it is assumed that adding the ETECs and Cd to soil reduced the biomass production of perennial ryegrass, and thus phytotoxicity occurred. The toxicity threshold for each ETEC was established as the concentration at which the plant biomass was significantly lower than the control (as determined by least significant differences).

The biomass indexes for the ETECs and Cd at the same concentration added to soil were calculated by adding trendlines to graphs with the concentration added to soil versus BAC, and inputting the same concentration added to soil into the trendlines for each of the elements.

#### 5.1.2.5. Statistical analysis

Data were processed in Excel. Graphs and trendlines were produced, standard errors were calculated through Descriptive statistics data analysis, Single-factor ANOVA analysis was performed and the least significant differences (LSD) were calculate (Eq. 1), and data were logged, underwent Pearson Correlation analysis, then the correlations were tested for significance (Eq. 2 and 3). The thresholds for significance were when the difference between values was greater than the LSD (Eq. 1.), or  $p < 0.05$ .

$$LSD = \sqrt{(MSWG \cdot 2/n_r)} \cdot t \quad (\text{Eq. 1})$$

In Equation 1, MSWG is the mean squares within groups,  $n_r$  is the number of replicates in a sample (3), and  $t$  is the  $t$  value.

$$Cor2 = ABS (Cor \cdot \sqrt{(n_d - 2)} / \sqrt{1 - Cor^2}) \quad (\text{Eq. 2})$$

$$p = T.DIST.2T (Cor2, (n_d - 2)) \quad (\text{Eq. 3})$$

Where in equation 2,  $Cor$  is the correlation  $r$ -value, and  $n_d$  is the number of observations.

### 5.1.3. Results

#### 5.1.3.1. Effect of ETECs and Cd on the dry weight of perennial ryegrass

In T2 Be and T1 Gd the biomass of perennial ryegrass was significantly higher than in the control. The biomass was significantly lower than the control for Cd T1, T3 and T4, Ga T3, Ce T1, Nd T3 and T4, and Gd T3 (Table 5.4). Biomass of perennial ryegrass did not significantly deviate from the control when In and La were added to soil. The toxicity thresholds of the ETECs increased  $Cd < Gd < Nd < Ga$ , and the maximum concentrations of Be, Ce, In, and La did not cause consistent significant reductions to biomass within the range tested. The maximum concentrations of the ETECs in perennial ryegrass found in this study without reductions to biomass (thus T4 or the highest treatment without reductions to growth) increased  $Cd < In < Gd < Be < Nd < Ga < Ce < La$  on a mass basis, and the ranking was the same on a molar basis except Be had the highest safe uptake, and safe uptake of Ga within the range tested had a higher molar concentration than Ce.

**Table 5.4 Treatment ETEC and Cd concentrations, biomass indexes, and plant toxicity thresholds gained from biomass index significance, for perennial ryegrass. Brackets show standard error to the mean, treatments with the same letter are statistically similar to each other, from a (lowest biomass index) to c (highest).**

ETEC or Cd added to soil	Treatment and concentration added (mg kg <sup>-1</sup> )	Biomass index	Significance (LSD) <sup>a</sup>	Toxicity threshold in plant biomass		
				(mg kg <sup>-1</sup> )	(μmol kg <sup>-1</sup> )	
Be	Control	0	1	ab	>7.1	>790
	T1	9.5	1.1 (0.28)	abc		
	T2	19	1.9 (0.52)	c		
	T3	38	1.6 (0.053)	bc		
	T4	76	0.56 (0.11)	a		
Cd	Control	0	1	c	0.06-0.30	0.54-2.6
	T1	2.5	0.70 (0.046)	b		
	T2	5	0.81 (0.078)	bc		
	T3	10	0.76 (0.012)	b		
	T4	20	0.47 (0.11)	a		
Ga	Control	0	1	bc	11-21	159-300
	T1	140	1.3 (0.27)	c		
	T2	280	0.83 (0.061)	ab		
	T3	560	0.56 (0.056)	a		
	T4	1120	0.69 (0.060)	ab		
In	Control	0	1	a	>0.11	>0.98
	T1	1.275	1.1 (0.42)	a		
	T2	2.55	1.0 (0.20)	a		
	T3	5.1	1.3 (0.20)	a		
	T4	10.2	0.84 (0.064)	a		
La	Control	0	1	ab	>50	>362
	T1	109.25	0.88 (0.18)	ab		
	T2	218.5	1.5 (0.25)	b		
	T3	437	1.2 (0.43)	ab		
	T4	874	0.71 (0.22)	a		
Ce	Control	0	1	b	>12	>87
	T1	283	0.37 (0.058)	a		
	T2	566	0.87 (0.081)	b		
	T3	1132	0.85 (0.22)	b		
	T4	2264	0.84 (0.22)	b		
Nd	Control	0	1	c	8.7-9.0	60-62
	T1	92.25	0.80 (0.019)	bc		
	T2	184.5	0.75 (0.10)	abc		
	T3	369	0.51 (0.041)	a		
	T4	738	0.72 (0.15)	ab		
Gd	Control	0	1	b	1.1-2.1	6.0-14
	T1	15.075	1.7 (0.31)	c		
	T2	30.15	0.58 (0.045)	ab		
	T3	60.3	0.44 (0.069)	a		
	T4	120.6	0.69 (0.025)	ab		

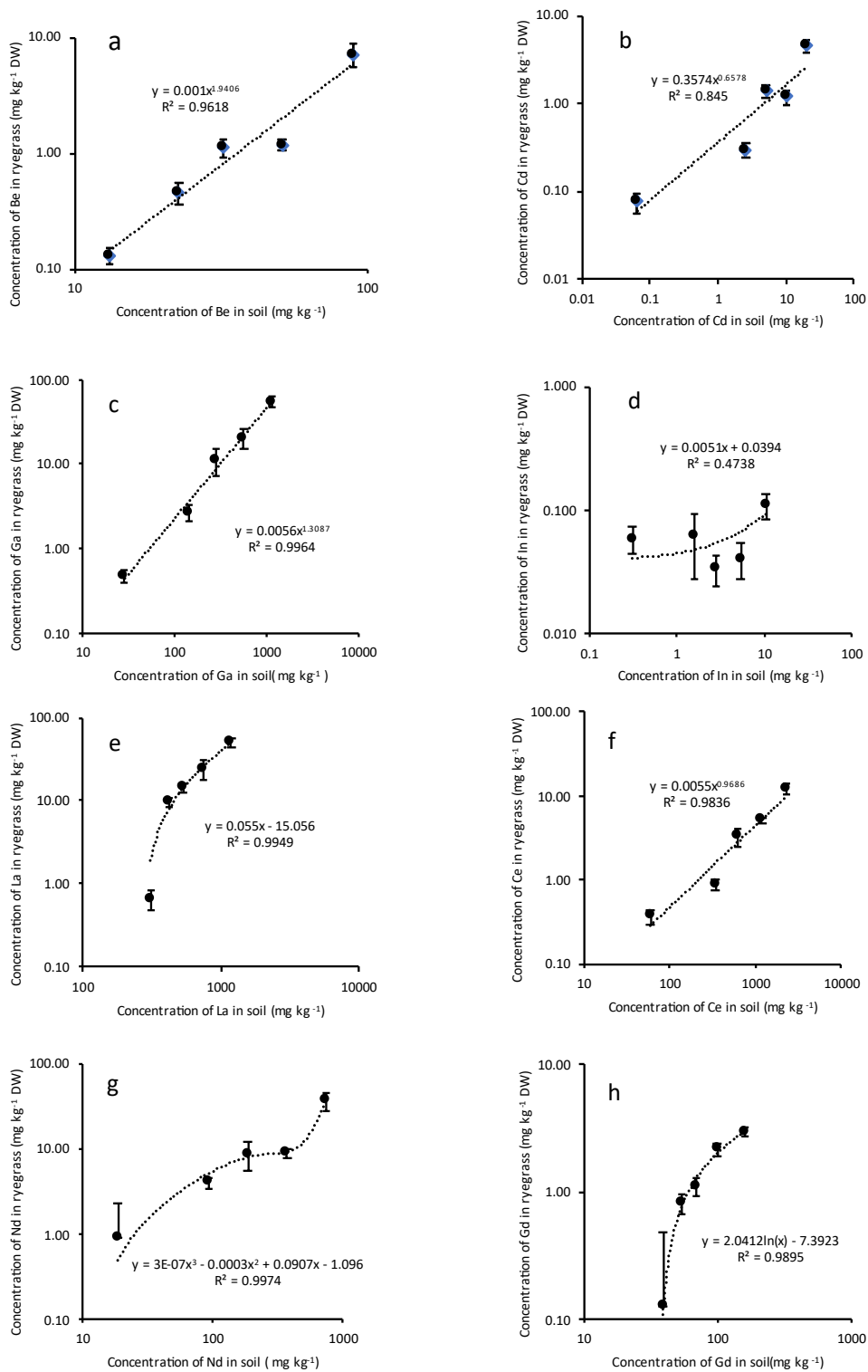
<sup>a</sup>Significance gained from LSD, with a for the significantly smallest dry weight.

### 5.1.3.2. Uptake and bioaccumulation of ETECs in perennial ryegrass

In the control, the concentrations of the ETECs and Cd in perennial ryegrass increased In<Cd<Be<Cd<Gd<Ga<Nd<La on a mass basis, and In<Cd<Ce<Gd<Nd<La<Ga<Be on a molar basis (Table D.2). Lanthanum, Ga, and Nd were taken up at the highest concentrations in the control and in all the treatments on a mass basis, and on a molar basis Ga, Be, and La were taken up at the highest

concentrations. Indium consistently had the lowest uptake by ryegrass, with  $0.05 \text{ mg kg}^{-1}$  In in the control, and a maximum of  $0.11 \text{ mg kg}^{-1}$  In in T4 when  $10.2 \text{ mg kg}^{-1}$  In was added to soil.

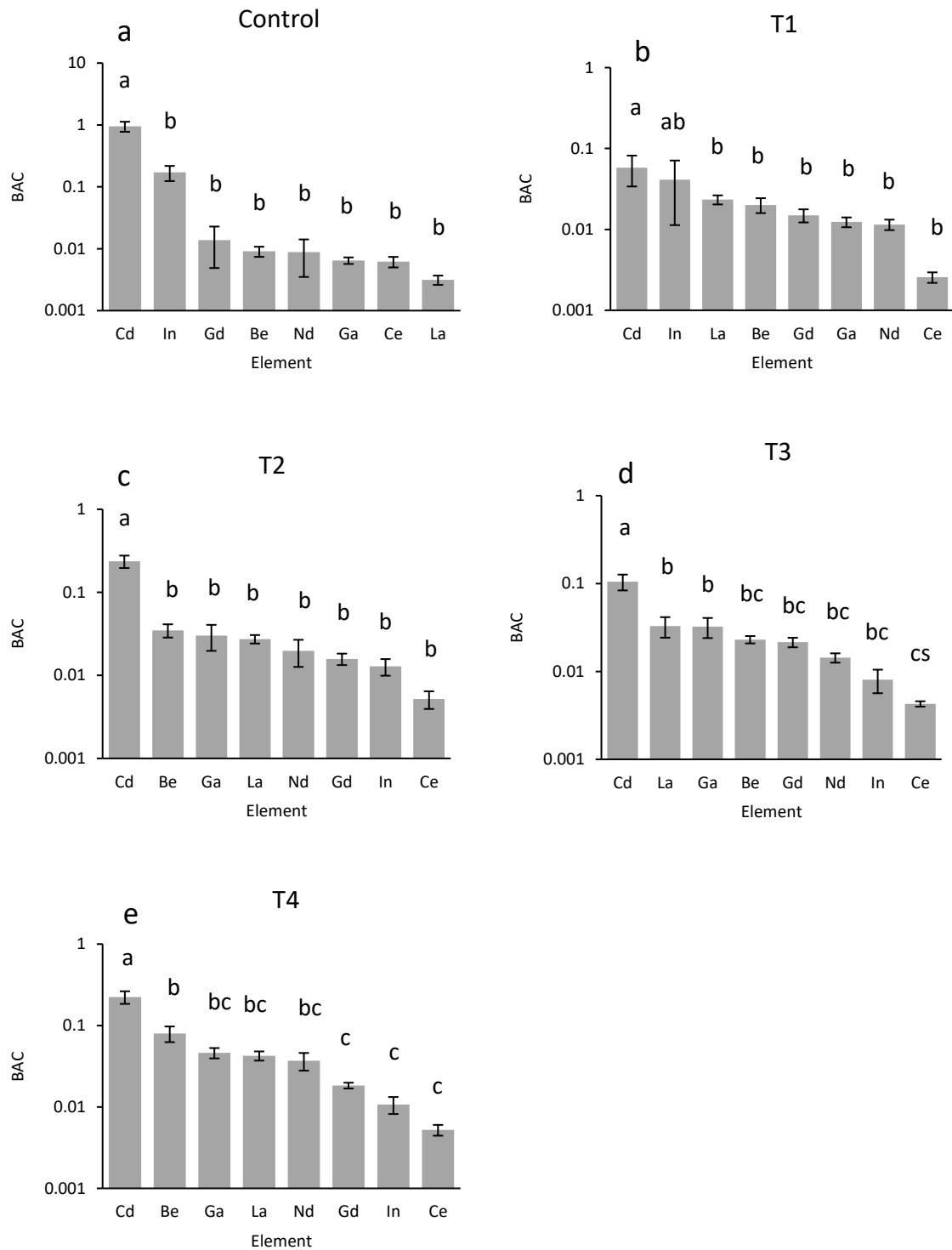
Apart from In, uptake of the ETECs and Cd by perennial ryegrass increased with increasing concentrations of the ETECs and Cd added to soil (Fig. 5.1). The uptake of Be and Cd in T4 was high and did not fit the trendlines well (Fig. 5.1(a) and (b)). Perennial ryegrass Ga and La concentrations increased linearly with the concentrations of these elements added to soil. Uptake of Nd had a sigmoid response, which like Be and Gd is due to the inordinately high uptake of these elements in T4.



**Fig. 5.1** Concentrations of Be, Cd, Ga, In, La, Ce, Nd and Gd in the shoots of ryegrass growing in contaminated soil.



BACs of the ETECs and Cd in perennial ryegrass varied from 0.0031-0.95 in the control (Fig. 5.2 (a)) to 0.0052-0.22 in T4 (Fig. 5.2 (e)). Across all the treatments, BACs increased  $Ce < In < Nd \cong Gd < La \cong Be \cong Ga < Cd$ . When BACs were calculated at the same concentration of ETEC or Cd added to soil, at 5 mg kg<sup>-1</sup> ETEC or Cd added to soil the ranking of the ETECs and Cd was the same as T1 except Gd had a higher BAC than Be and La, and at 1 mg kg<sup>-1</sup> added to soil the ranking of the BACs was  $La < Nd < Ce < Ga < Gd < In < Be < Cd$ .



**Fig. 5.2 Bioaccumulation coefficients for the uptake of Be, Cd, Ga, In, La, Ce, Nd and Gd in perennial ryegrass grown in soil spiked with none (a), or low (b) to high (e) concentrations of the respective ETEC or Cd.**

The letters denote significant differences in the BACs of the elements in each treatment type through LSD.

The concentration of Be in perennial ryegrass was significantly positively correlated with the concentrations of Al, Cd, Gd, La, Mg, Na, Nd, and Zn (Table 5.5). The concentrations of Gd, In, and La taken up by perennial ryegrass did not affect the uptake of many of the other elements in ryegrass.

**Table 5.5 r values and significance of significant correlations between the concentrations of Be, Cd, Ga, In, La, Ce, Nd or Gd in perennial ryegrass grown in soil spiked with the respective element and the controls, and the concentrations of other elements in perennial ryegrass.**

	Be	Cd	Ga	In	La	Ce	Nd	Gd
Be								
Na	0.50 S		0.48 S				0.48 S	
Mg	0.69 S**					0.52 S*		
Al	0.67 S**							
P			-0.54 S*		-0.47 S			
K								
Ca						0.53 S*	0.51 S	
Cr						0.54 S*		
Mn		-0.53 S*						
Fe		-0.14 S				0.62 S*	0.60 S*	
Co			0.58 S*			0.56 S*	0.47 S	
Ni		0.59 S*				0.58 S*		0.53 S*
Cu						0.49 S	0.42 S	
Zn	0.78 S**	0.44 S	0.58 S*			0.55 S*		
Ga				0.50 S				
As		-0.82 S**						
Cd	0.49 S		0.57 S*		0.50 S*	0.50 S	0.42 S	0.45 S
In								
Te								
I		-0.76 S**						
La	0.49 S		0.52 S			0.65 S**	0.72 S**	
Ce							0.64 S**	
Nd	0.44 S		0.58 S*	0.37 S		0.77 S**		
Gd	0.41 S		0.53 S*			0.79 S**	0.56 S*	

S =  $p < 0.05$ , S\* =  $p < 0.01$ , S\*\* =  $p < 0.001$ ; Shaded cells are correlations between the same element thus not applicable, blank cells are where the correlation is insignificant.

#### 5.1.4. Discussion

##### 5.1.4.1. *Effect of the ETECs and Cd contaminants on the biomass of perennial ryegrass*

The addition of Be and Gd to soil significantly increased the biomass of perennial ryegrass, likely due to hormesis, an increase in growth in response to stress (Poschenrieder et al., 2013), as both elements are non-essential to plants, and the biomass consistently decreased from the peak when higher concentrations of these elements were present in the soil. The anions added to the soil as the counterion in the ETEC and Cd salts added to soil,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are unlikely to have contributed to the increase in dry weight; the soil was rich in sulphate sulphur (Table 5.2) thus perennial ryegrass was not deficient in it, and the grass in the pots spiked with high concentrations of  $\text{NO}_3^-$  salts did not significantly increase in biomass, even when the cations did not significantly decrease the biomass within the range tested (e.g. La and Ce). Nitrate is unlikely to have mitigated the toxicity of La and Ce, as they are different sizes and charges thus unlikely to have followed the same uptake pathway.  $\text{NO}_3^-$  was added to soil at higher concentrations in the Ga, La, Ce, and Nd spiked-samples and the grass in these pots did not increase in dry weight with the concentration added, hence growth increases related to nitrate would have also been found in the samples spiked with those elements.

Cadmium, Ga, Nd, and Gd caused significant reductions in the biomass of perennial ryegrass. Cadmium ryegrass concentrations at toxicity were usually low, below the 3-30  $\text{mg kg}^{-1}$  plant Cd toxicity threshold range (Table D.1), but the concentration of Cd added to soil in T1 was close to the soil Cd toxicity threshold of 5  $\text{mg kg}^{-1}$  (Ismael et al., 2019). The soil used in this study was an acidic sandy soil (pH 5.3) with a relatively low CEC (13  $\text{cmol}(+) \text{kg}^{-1}$ ), thus is expected to have high solubility and bioavailability of ETECs and Cd (Su et al., 2018; Syu et al., 2021), which may have contributed to the low soil toxicity threshold of Cd. For the other elements, whether they experienced toxicity or not in this study, the toxicity thresholds and/or safe uptake fell within or were close to the ranges in Table D.1 for Be, Ga, In, La, Ce and Nd. The concentrations of the ETECs added to soil which induced toxicity were similar to other studies (Bohn & Seekamp, 1979; Carpenter et al., 2015; Hao et al., 2021; Kaplan et al., 1990; Rezaee et al., 2018).

For Be, Ce, La, and In, no toxicity occurred within the range tested. The soil and conditions (e.g. pH) in this study may have caused high retention of some elements, but not others, e.g. Ga and In precipitate and thus are bioavailable at different pH ranges in soil (Wood & Samson, 2006). Future research should test the relative phytotoxicity of Be, Ce, La, and In at higher soil concentrations and in different soil types. In the KFR [soil type], it was determined that Be, Ce, In, and La are less toxic than the other ETECs in soil, in respect to the natural background concentration.

#### 5.1.4.2. Uptake of the ETECs and Cd in perennial ryegrass

The ranking of uptake of the ETECs and Cd by perennial ryegrass differed from the ranking which was hypothesised, which may be due to the physiological differences between *Lolium perenne* and *Fagus sylvatica* (Germund Tyler & Tommy Olsson, 2001). Cerium was hypothesised to be taken up at the highest concentrations by ryegrass, but was only the fourth highest, but had the lowest BACs of the ETECs and Cd. Compared to the ranking of the ETECs in Tyler (2005), uptake of Ga and La were higher than the other ETECs. Uptake of the ETECs in ryegrass was similar to that (within the same order of magnitude) of grasses and other members of the Poaceae family (Kabata-Pendias & Mukherjee, 2007; Laul et al., 1979; Li et al., 1998); it is useful to compare within this family if possible, as they have physiological differences to other plant species which affect uptake and translocation, e.g. they are monocotyledonous plants, and use Strategy II for Fe acquisition (Wairich et al., 2019), which helps them to acquire higher concentrations of Cu, Mn, and Zn (Graham & Stangoulis, 2003). In studies that spiked soil with similar concentrations of the ETECs, uptake of Be and Ga in ryegrass were similar to that in oat plants, collards, cabbage, wheat and rice seedlings (Bohn & Seekamp, 1979; Hara et al., 1977; Kaplan et al., 1990; Su et al., 2018; Syu et al., 2021).

Grass (Ryegrass and *Leersia hexandra* Sw.) growing in soil that had been contaminated previously (with sufficient time for residential development and wild species to grow) contained concentrations of Ga and In, which were more similar to the control versus the grass growing in contaminated soil (Ha et al., 2011; Waterlot et al., 2013). This suggests that ageing quickly reduced the bioavailability of the contaminants, or the most bioavailable fraction was quickly taken up by plants and passed up the food chain, thus the concentrations of the ETECs found in perennial ryegrass in this study are only comparable for environments where recent contamination has occurred.

#### 5.1.4.3. Bioaccumulation coefficients of the ETECs and Cd in perennial ryegrass

Cadmium had the highest BACs, and since it is a relatively mobile trace element (Smolders, 2001), the ETECs are thus moderately or poorly mobile in the soil-ryegrass system. In contrast to the findings of Omberg et al. (2011), Ce had a lower BAC than the other ETECs. Those experiments utilised natural soils, but even in the control Ce had a lower BAC than all of the elements except for La, thus Ce had less mobility in this study than Omberg et al. (2011). Aside from Ce, the ranking of the ETECs by their bioaccumulation coefficients is consistent with Omberg et al. (2011) in T4, when 40x the background concentrations of the elements were added, but in the control Gd and In had higher BACs than Be and Ga, which is unexpected as the control is more similar to the natural soil used in Omberg et al. (2011) than T4.

The BAC values were, for the most part, similar to that of Poaceae species in Laul et al. (1979), Germund Tyler and Tommy Olsson (2001), and Kotelnikova et al. (2020), in contaminated and uncontaminated soil. BACs for In in perennial ryegrass were higher than that for In in rice and wheat (Chang et al., 2020), but higher concentrations of In were added to the soil in that study, which is consistent with the BAC of In decreasing with increasing concentrations added to soil (Fig. D.2).

#### *5.1.4.3.1. Effect of concentration of ETECs and Cd added to soil on the bioaccumulation in perennial ryegrass*

As the concentration of ETEC added to soil increased, the BACs of Be, Ga, La, and Nd increased (Fig. B.18), thus the exogenous solubilised ions (ions from the ETEC and Cd salts added to soil) were more bioavailable than the endogenous ions (ions present in soil before the salts were added). This was expected, as most of a ETEC in soil is sorbed to the solid phase, as shown in Sheppard et al. (2007), and ageing further decreases the mobility of elements. Surprisingly, endogenous Cd and In was more bioavailable than exogenous (spiked) elements. Cerium and Gd had little significant change in BAC with the concentration added to the soil.

The first step into understanding the differences in BAC trends of the ETECs and Cd was to investigate if exogenous Cd and In were more rapidly immobilised in soil than the other elements, as that would limit bioavailability. Speciation modelling was conducted with Visual MINTEQ 3.1 (Gustafsson, 2013). The details of how the model was used are in Table 4.3. The model was used to provide a preliminary indication of the ionic species the elements would form in an aqueous solution free of other elements (soil is a complex mixture of insoluble and soluble organic and inorganic compounds, and it was not feasible to accurately model the soil system). The pH of the studied soil was 5.3, thus the graphs show the calculated species from pH 4.3-6.3 to allow for variation, as pH is a dynamic variable. Fig. 5.3 indicates that at this range, Cd, La, Ce, Nd and Gd would be present as their respective divalent and trivalent ions (86-93% of the aqueous species),  $\text{Be}^{2+}$  would begin to hydrolyse to  $\text{Be}(\text{OH})_3^{3+}$  ( $\text{Be}^{2+}$  decreases from 97% to 6% of the aqueous Be species along the pH range of 4.3-6.3), and Ga will have almost finished hydrolysis to  $\text{Ga}(\text{OH})_4^-$  ( $\text{Ga}(\text{OH})_4^-$  increases from 3% to 100% along that range). Indium was calculated to be predominantly as  $\text{In}(\text{OH})_3^0$ , which readily precipitates into poorly soluble  $\text{In}(\text{OH})_{3(s)}$  (Wood & Samson, 2006) that has low bioavailability. This finding is consistent with Fig. 5.1, where In uptake by ryegrass did not significantly increase when In was added to the system and is consistent with the findings by Chang et al. (2020) in rice and wheat.

That does not explain why the endogenous In was more bioavailable than exogenous In. It could be that the concentration of  $\text{In}(\text{OH})_3^0$  in the soil solution had already reached the maximum soluble concentration, thus any extra added precipitated. Alternatively, some endogenous In was held in exchangeable sorption sites, limiting precipitation in solution. This fraction may have been in equilibrium with In in solution, replenishing the In that was removed via plant uptake. Indium has a strong association with OM (Tyler & Olsson, 2002), thus soluble or insoluble complexation may also have limited precipitation, retaining availability.

The behaviour of Cd could not be explained by MINTEQ modelling, which calculated high concentrations of the free ion,  $\text{Cd}^{2+}$ , which is consistent with the finding that divalent cations do not undergo hydrolysis at  $\text{pH} < 6$  (Grzybkowski, 2006). Thus, a different mechanism is responsible, which is not applicable to the ETECs. In literature states that Cd is taken up by plants easily because it is more soluble in soil than other trace elements (Sarwar et al., 2010), which has been verified by the lesser solid-phase retention (Sheppard et al., 2009). Plant uptake of Cd linearly increased between the control and T4; therefore, it seems unlikely that uptake and translocation of Cd was limited by the plants.

Cadmium, a 'soft' Lewis acid, binds more strongly to soft functional groups such as  $\text{S}^{2-}$  and  $\text{I}^-$  than hydroxide groups (Kinraide, 2009); The soft functional groups may have been present at high concentrations in soil, which Cd bound to, limiting the availability of exogenous Cd to plants, particularly at the lower concentrations of Cd added to soil. This was not directly measured in the soil properties however, so it cannot be confirmed.

The change in the BACs with increasing soil concentration was different for Ce and Gd than La and Nd. In the control, Ce and Gd had higher BACs than La and Nd and thus had higher uptake than expected relative to the sum of the REEs in the soil. It cannot be explained why the bioavailability of endogenous Ce and Gd was higher than endogenous La and Nd, and the existing high uptake may have limited the increase in bioaccumulation factors.

Another process that may have increased the uptake of the elements is following the uptake pathways of essential ions, which would result in a significant negative correlation with the essential ion, as the ETEC would occupy spaces in the molecules responsible for the uptake and translocation of essential elements. There were few negative correlations across the elements (Table 5.5), and those often occurred with anions (Ga and La with P, Cd with As and I) which the cations would not substitute for

in biological molecules. Uptake of Be was positively correlated with the uptake of Mg, but this could be a strategy to ameliorate toxicity by taking up higher concentrations of essential elements to maintain the physiological processes which Be may disrupt (Shah et al., 2016). Beryllium was one of the ETECs that did not cause toxicity within the range tested in this study, which supports the above theory. Two of the four REEs had significant positive correlations with Ca, which the REEs have physiological similarities to (Tyler, 2004b), but they were Ce and Nd, elements whose BACs were little affected and increased with the concentration added to soil respectively, thus it is unknown the significance of this correlation on plant uptake. Uptake of Be was positively correlated with uptake of the REEs, thus Be stress may increase the uptake of Mg and Ca, resulting in a net increase in growth.

The concentrations of each element added to the soil in the treatments were relative to the concentrations of the elements naturally in soil and may not represent concentrations in contaminated soils. If the same concentration of each ETEC and Cd were added to soil, at  $>750 \text{ mg kg}^{-1}$  BAC of Nd would be higher than Ga, Gd and La, and Be would be higher than Cd if the patterns in Fig. B.18 extrapolate without saturation.

#### 5.1.4.4. *Risk of entering the food chain*

By discussing the mobility, the relative risks of the ETECs entering the food chain can be evaluated. Of the ETECs and Cd tested in this study, Be and La have the highest risk of entering the food chain via perennial ryegrass. Beryllium and La did not cause significant phytotoxicity within the concentration range tested, and the BACs of these elements increased with the concentration added to soil, thus uptake of Be and La will likely continue to increase.

Only Cd, Ga, Nd, and Gd had toxicity thresholds, which occurred at plant concentrations of 0.3, 21, 9.0, 2.1  $\text{mg kg}^{-1}$  respectively. Thus, relative and non-relative to the background concentrations of the elements in soil, Be and La have the highest risk of being taken up and translocated to above-ground biomass at high concentrations by perennial ryegrass.

Contrastingly, Cd had a higher BAC than the ETECs, but had a low toxicity threshold, with reductions to growth occurring in T1. The low toxicity threshold contrasts with previous findings of Cd being a mobile and easily transferable contaminant to animals (Kopittke et al., 2010), thus the cultivar of perennial ryegrass used (Nui) should be regrown in different environments to confirm its low tolerance to Cd. The ETECs least likely to be taken up and translocated by perennial ryegrass, variety Nui, are In, as uptake did not increase with the concentration added to soil, and Ce due to the low



BACs. Cerium was safely taken up at the second-highest concentration in ryegrass due to the high concentrations naturally in and thus added to soil.

Unlike other crop types such as grains and vegetables, perennial ryegrass does not need to survive reproduction or be harvested to enter the food chain. In the field, reductions in ryegrass growth by ETECs could be mistaken for symptoms of drought, nutrient deficiency, disease, or insufficient aeration, increasing the feasibility of animals eating contaminated ryegrass. Currently, there are no food safety standards in place for these ETECs, thus the implications of animals ingesting the ryegrass grown in this study are unknown.

#### 5.1.5. Conclusions

Addition of Be, Ce, In, and La to soil at 40x the background concentration did not cause significant reductions to the biomass of perennial ryegrass. Cadmium and Gd had the lowest toxicity thresholds of the selected ETECs. The bioaccumulation coefficients of the ETECs and Cd increased  $Ce < In < Nd \cong Gd < La \cong Be \cong Ga < Cd$ . The elements with the highest overall mobility in the soil-perennial ryegrass system are La and Be, as they were present at 50 and 7.1 mg kg<sup>-1</sup> respectively in perennial ryegrass in the highest treatment, and the BACs of these elements are likely to continue to increase beyond the range tested. The least mobile elements in the variety of perennial ryegrass tested were Cd, as it had a low toxicity threshold, Ce, as it had low BACs, and In, as uptake did not increase with the concentration added to the system. Therefore, data showed there is a low risk of ryegrass uptake being a significant source of Cd, Ce, and In to animals, but there is a higher risk of perennial ryegrass being a source of Be and La to animals and humans. Further research should test if the trends identified in this study are robust in a range of soil types, plant species and climates, to better evaluate the mobility of these ETECs in the soil-plant system. Then the rates of transfer of these elements to animals and their ecotoxicology should be determined. The maximum concentrations of the ETECs that can be in perennial ryegrass that can successfully reproduce and continuously grow, despite slight phytotoxicity, should also be determined.

## 5.2. Addendum: The concentrations of ETECs in commercial Tea (*Camellia sinensis*)

### Abstract

As an addendum to Chapter 5, a preliminary survey of trace elements in *Camellia sinensis* (tea bush) was undertaken because this species is known to hyperaccumulate Al (to concentrations of 1000 - 10,000 mg kg<sup>-1</sup>) and therefore may also accumulate some of the trivalent ETECs. Eleven samples of tea were analysed for a suite of ETECs and the results were compared to those obtained with perennial ryegrass grown in unspiked soil (Chapter 5.1) and various other terrestrial plant species (Table A.2). Tea from *Camellia sinensis* contained 0.02-8.2 mg kg<sup>-1</sup> of the ETECs, with La present at the highest concentrations and In at the lowest. The mean concentrations of Be, La, Ce, Nd, and Gd in *Camellia sinensis* were higher than the concentrations in perennial ryegrass, and all of the *Camellia sinensis* samples contained more In, La, Ce, and Nd than perennial ryegrass. Tea grows best in acidic soil, thus the elevated concentrations of the ETECs in tea could be due to increased solubility and bioavailability of the ETECs, therefore future work should compare the concentrations of ETECs in *Camellia sinensis* and other terrestrial species grown in the same soil type.

### 5.2.1. Introduction

*Camellia sinensis*, common tea, is mostly grown in Africa and Asia but is consumed worldwide (Han et al., 2018). Variation in the timing and the types of leaves harvested, degree of fermentation, and cultivar of *Camellia sinensis* has given rise to different types of tea such as black, white, green, oolong, pu'erh, and rooibos tea (Sharangi, 2009).

*Camellia sinensis* differs from other plant species in that it accumulates aluminium (Al) to concentrations >10,000 mg kg<sup>-1</sup> (1%) in old leaves (Zhang et al., 2018). Soil normally contains 1-4% Al (10,000-40,000 mg kg<sup>-1</sup>), but it readily precipitates in neutral-basic soils, limiting bioavailability (Kabata-Pendias & Mukherjee, 2007). In acidic soils, the increased Al solubility can limit the growth of some species, but *Camellia sinensis* thrives in acidic soils and can contain up to 30,000 mg kg<sup>-1</sup> Al without toxicity (Li et al., 2017), with an optimal soil pH of 5-5.6 (Wang et al., 2009). Aluminium is in the same group of the periodic table as the ETECs Ga and In, and forms a trivalent cation in solution like La, Ce, Nd, and Gd.

The concentrations of the ETECs and Al in various commercial teas will be compared to that in the perennial ryegrass grown in unspiked soil in Chapter 5.1. The perennial ryegrass in Chapter 5.1 contained concentrations of the ETECs similar to geometric mean of various other terrestrial plants

grown in unspiked soil (Table 5.7), hence is used as a benchmark in this chapter. However, we do not know the properties of the soils the teas were grown in, e.g. low pH soils may increase the bioavailability of the elements and contribute to increased uptake, but most plants have a limited range of soil conditions in that they can sustainably grow, hence increased availability in particular soil conditions will not result in increased uptake if plants cannot grow in the soil.

The aim of this section is to find if *Camellia sinensis* contains higher concentrations of the ETECs Ga, In, La, Ce, Nd, and Gd than typical terrestrial species such as perennial ryegrass. A variety of commercially available will be digested, and the concentrations compared to that of perennial ryegrass from unspiked soil in Chapter 5.1, and various other terrestrial plant species (Table A.2).

## 5.2.2. Materials and methods

### 5.2.2.1. Tea (*Camellia sinensis*)

Eleven types of loose or bagged tea were purchased from the New World Ilam supermarket (Table 5.6). Black, white, and green tea leaves are from the *Camellia sinensis* plant; black and green tea is from fully-fermented, and unfermented *Camellia sinensis* leaves respectively, white tea from buds and young leaves of *Camellia sinensis* (Sharangi, 2009), and Furong tea is from a different plant. Tea was removed from the teabags where applicable and ground to a fine powder.

**Table 5.6 Description of the tea samples analysed**

Sample	Type of tea	Brand	Name of tea
T1	Black	Dilmah	100% Pure Ceylon tea
T2	Green	Dilmah	Naturally Pure Green tea (leaf)
T3	Green	Dilmah	Green tea (bags)
T4	Green	Bell	Mellow Pure Green Tea
T5	Black	Bell	Original Tea Leaf
T6	White	Bell	White tea bags
T7	Black	Chanui	English Breakfast tea
T8	Black	Twinings	English Breakfast tea
T9	White	China White	Organic Jasmine - from <i>Camilla senensis</i>
T10	Green	Red seal	Green tea (bags)
T11	Furong	-	(Chinese tea)

In separate 15 mL glass tubes, 0.2-0.3 g of tea or grass was added to 5 mL of concentrated HNO<sub>3</sub> and left overnight. The next day, the samples were digested in a Milestone UltraWAVE single reaction chamber microwave digestion system at 220°C for 25 minutes using the General digestion method for environmental samples. Samples were diluted 21x in 10 mL of ultrapure 1% HNO<sub>3</sub> then run through an ICP-MS, which measured the elements in the first half of this chapter. Three replicates were

completed for each sample. NIST1573a certified reference material was used, and the measurements of 6/7 elements fell within 60-140% of the CRM.

#### 5.2.2.2. *Perennial ryegrass*

The perennial ryegrass samples that were compared to the tea samples were the controls from Chapter 5.1, thus were grown in unspiked soil.

#### 5.2.2.3. *Other terrestrial species*

Data of the concentrations of the ETECs in various terrestrial species were compiled in Table A.2, and the minimum, maximum, and geometric mean were calculated. This data is useful to provide a general idea of the concentrations of the ETECs typically in plants, but some of the plants included were accumulators or growing on contaminated soil (Ha et al., 2011; Khan et al., 2017), and the studies differed in environmental conditions and the elements measured.

#### 5.2.2.4. *Data processing*

Data were processed as in Part 1 of this chapter. Correlation analysis was completed with the tea and ryegrass samples.

### 5.2.3. Results

#### 5.2.3.1. *Concentrations of the ETECs in Camellia sinensis*

*Camellia sinensis* leaves contained up to 8.2 mg kg<sup>-1</sup> of the ETECs, with La present at the highest concentrations in *Camellia sinensis*, and In at the lowest. The concentrations of the ETECs in *Camellia sinensis* averaged across the different tea types were higher than perennial ryegrass for all of the ETECs, and higher than the geometric mean of other terrestrial plants for Be, La, Ce, Nd, and Gd. The minimum concentration in *Camellia sinensis* was higher than the concentration in perennial ryegrass for In, La, Ce, and Nd, and higher than the geometric mean for Be, La, Nd, and Gd.

**Table 5.7 Concentrations of Be, Ga, In, La, Ce, Nd, and Gd in *Camellia sinensis* leaves, perennial ryegrass grown in unspiked soil (Chapter 5.1), and various terrestrial spiked grown in unspiked soil (Table A.2) (mg kg<sup>-1</sup>)**

Element	<i>Camellia sinensis</i>			Perennial ryegrass	Various terrestrial species growing in unspiked soil		
	Mean	Minimum	Maximum	Unspiked soil	Geometric mean	Minimum	Maximum
Be	0.17	0.020	0.71	0.12	0.016	0.000018	0.42
Ga	0.62	0.28	0.94	0.58	0.66	0.0014	6.8
In	0.15	0.053	0.28	0.053	0.34	0.0002	7.5
La	3.3	1.1	8.2	0.97	0.38	0.0032	1568
Ce	0.93	0.61	1.4	0.37	0.61	0.0056	2290
Nd	2.7	0.95	6.3	0.91	0.28	0.0028	1499
Gd	0.58	0.17	1.4	0.55	0.067	0.0002	176

#### 5.2.3.2. Comparison with Al, perennial ryegrass and between tea types

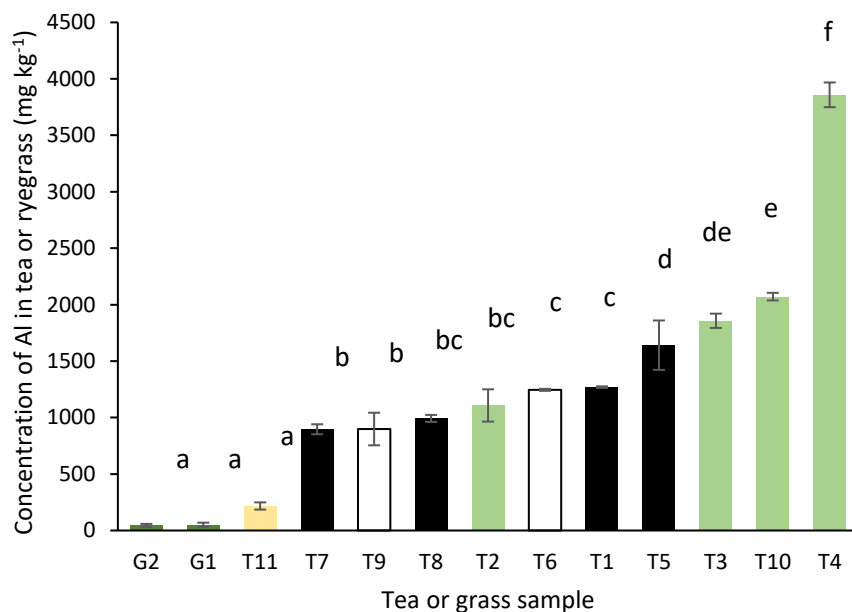
*Camellia sinensis* leaves contained 896-3859 mg kg<sup>-1</sup> Al, which is much higher than the ETECs, but Al is more abundant in the environment. *Camellia sinensis* contained more Al than perennial ryegrass and Furong tea, which was not produced from *Camellia sinensis* (Fig. 5.3).

Aluminium concentrations across the tea leaves and perennial ryegrass were significantly correlated to the concentrations of In, La, Ce, Nd, and Gd, but not significantly correlated to the concentrations of Be and Ga (Table 5.8), which further implies higher concentrations of In, La, Ce, Nd, and Ga in *Camellia sinensis* than in other terrestrial plants.

**Table 5.8 Correlations of Be, Ga, In, La, Ce, Nd, and Gd with Al in tea and perennial ryegrass.**

Element	r value	p-value	Significance
Be	0.1152	0.48	NS
Ga	0.2367	0.15	NS
In	0.5698	0.0002	S**
La	0.7384	0.0000	S**
Ce	0.7423	0.0000	S**
Nd	0.6940	0.0000	S**
Gd	0.4571	0.0034	S*

Significance levels: S = p<0.05, S\* = p<0.01, S\*\* = p<0.001



**Fig. 5.3 Concentrations of Al in each type of tea and uncontaminated perennial ryegrass.**

Error bars denote standard error, letters denote least significant differences (LSD).

Samples are in order from low to high Al concentration.

The colours of the bars denote the types of tea; ● green tea, ● black tea, ○ white tea, ● Furong tea (from China), ● ryegrass

#### 5.2.4. Discussion

There is little data on the concentrations of the ETECs in tea to compare this data to. The concentrations of Ce in black and green tea were similar to Kara (2009), while La concentrations in this study were higher. Lanthanum and Ce concentrations in green tea were similar to that in tea shrubs in Hung et al. (2011). Black tea leaves measured in this study contained higher concentrations of Be and the REEs than in ØDEGÅRD and Lund (1997) and Matsuura et al. (2001), but this is likely due to variation in where the *Camellia sinensis* plants were grown as well as the fermentation process. In 2005, China had a limit of 2.0 mg kg<sup>-1</sup> total REE oxide in tea (Butterworth & Bugang, 2006), which many of the teas sampled in this study would exceed, but this was likely to monitor the foliar application of REE fertilisers (Pang et al., 2002), and has not been included in the recent food safety standards (2013 onwards).

*Camellia sinensis* has the best growth rates in acidic soils, with an optimal pH range of 5-5.6 (Wang et al., 2009). In this pH range, the  $K_D$  values of Be, La, Ce, Nd, and Gd are much lower than at pH >6.5 (Chapter 4), which increases their bioavailability and thus could be responsible for the elevated concentrations of these elements in tea. However, La, Ce, Nd and Gd form trivalent cations in solution like Al, thus the uptake pathways utilized by Al could be utilized by other trivalent cations.

#### 5.2.4.1. *Effect of fermentation on the concentrations of the ETECs in tea*

The concentrations of the ETECs in black tea, where the *Camellia sinensis* leaves have been fully fermented, and green tea, where the leaves are unfermented, were compared (Table D.3). The tea bushes were grown in different locations thus the original concentrations of the ETECs in the black tea leaves are unknown, but when averaged the black tea contained lower concentrations of all the ETECs and Al than the green tea, which suggests that significant concentrations of the ETECs and Al were lost to fermentation. Two of the four tea samples that contained lower concentrations of Be than the uncontaminated perennial ryegrass were green teas, which further verifies that *Camellia sinensis* did not take up significantly higher concentrations of Be than perennial ryegrass. The concentrations of the ETECs in tea that pose risk to human health are thus far unknown, but data suggests there is a greater risk to health from green tea than black tea. Concentrations will be much lower in brewed tea.

#### 5.2.5. Conclusions

Commercial tea (*Camellia sinensis*) contained higher concentrations of In, La, Ce, Nd, and Gd than perennial ryegrass, but it is thus far not known if it is due to the increased bioavailability of the ETECs in acidic soils, or if *Camellia sinensis* can utilize the pathways utilized by Al to take up and translocate higher concentrations of the ETECs than some other terrestrial species. Future work should compare the concentrations of the ETECs in *Camellia sinensis* and other terrestrial plants grown in the same soil.

## 6. Iodine

### 6.1. Understanding the distribution of I in New Zealand pastures

The material in this part of the chapter was successfully published (Jensen et al., 2019).

#### Abstract

Iodine (I) is an essential trace element commonly deficient in agricultural systems. Whereas there is much information on I in food crops, there is a lacuna of knowledge on the environmental factors that affect pasture I concentrations. We aimed to identify the most important environmental factors affecting the concentration of I in New Zealand pastures, and the consequences to agricultural systems. Soil and pastoral samples were collected throughout the country and analyzed for I and other elements. The soils contained 1.1 to 86 mg I kg<sup>-1</sup>, with 0.005 to 1.4 mg kg<sup>-1</sup> in the pasture. In 26% of pastures, I concentrations were insufficient for sheep nutrition, whereas 87% contained insufficient I for cattle nutrition. Pasture I concentrations were negatively correlated with the distance from the sea, and the concentration of oxalate-extractable amorphous Al, Fe, and Si oxides, which immobilize soil I. Soil organic C and clay increased I retention in soil but did not significantly affect pasture I concentrations. Future work should investigate how soil properties affect pasture I uptake in inland areas.

#### 6.1.1. Introduction

More than two billion humans are deficient in iodine (I), an essential trace element for animals (Mottiar, 2013), and many agricultural systems suffer deficiencies, thereby reducing productivity. Deficiencies cause mental and physical retardation, goiter, and potentially death (Zimmermann, 2009). Sheep and cattle require feed I concentrations of 0.05 to 0.2 and 0.3 to 0.5 mg kg<sup>-1</sup> respectively, for which pasture is the predominant source in many grazing systems (Flachowsky, 2007; Grace & Knowles, 2012; Suttle, 2005). The prevalence of I deficiency is due to low concentrations in inland soils, low soil bioavailability, and nonessentiality for terrestrial plants (Fuge, 1996; Medrano-Macías et al., 2016; Zimmermann, 2009). Iodine deficiency is exacerbated by goitrogens, which are thyroid I-limiting compounds commonly found in brassicas (*Brassica* spp.) and clover (*Trifolium* spp.) (Suttle, 2005). These are predominantly organic glucosinolates (Hurrell, 1997). Iodine deficiency is potentially exacerbated by selenium (Se) deficiencies, which are common worldwide, including in New Zealand (Arthur et al., 1999; Grace & Knowles, 2012). Consequently, iodized salt has been extensively supplied



to humans, with iodized salt licks, oil, drenches, and boluses provided to animals (Ershow et al., 2018; Grace & Knowles, 2012; Lee et al., 2002; Miller, 1979).

The background concentrations of I in soil typically range from 0.1 to 100 mg kg<sup>-1</sup> (Fuge, 1996; Fuge & Johnson, 2015), with a mean concentration of 5.1 mg kg<sup>-1</sup> (Johnson, 2003). Concentrations in Northern Ireland, which is geographically similar to New Zealand, averaged 10.6 mg kg<sup>-1</sup> (Smyth & Johnson, 2011). Concentrations of 56 mg kg<sup>-1</sup> were reported in the United Kingdom peat soils, whereas soils in both Norway and the United Kingdom ranged from 4.2 to 14.7 mg kg<sup>-1</sup> (Fuge, 1996). Relatively little soil I originates from the parent material (Whitehead, 2000). In contrast, seawater, which contains 0.06 mg I L<sup>-1</sup> (Wright & Colling, 1995), is a major reservoir of the element in the biosphere, with seaspray and subsequent wet and dry deposition of volatilized I being important processes for supplying the element to soils. It follows that elevated I concentrations are often found in soils close to the sea (Fuge & Johnson, 2015; Medrano-Macías et al., 2016). Johnson (2003) reported geometric means of 11.6 and 2.6 mg kg<sup>-1</sup> <50 and >50 km from the sea, respectively. Iodine may be lost from soil via removal in crops, volatilization, and leaching (Medrano-Macías et al., 2016). Therefore, soil I concentrations are also a function of the capacity of the soil to immobilize I (Fuge & Johnson, 2015).

Speciation, pH, redox potential, organic carbon (C), and clay content influence the mobility of I in soil (Kaplan et al., 2000). The predominate soil forms of I are organic, followed by iodide (I<sup>-</sup>) and iodate (IO<sub>3</sub><sup>-</sup>), which are present at various proportions (Fuge, 1996; Hu et al., 2009). Labile electrostatic adsorption to positive functional groups is higher under acidic conditions, though as the pH increases, I<sup>-</sup> oxidizes to IO<sub>3</sub><sup>-</sup> thus it has more specific adsorption and less volatilization potential—albeit partially hindered by anion repulsion (Fuge, 1996; Yoshida et al., 1992; Zou et al., 2018). Soil sorption decreased as the pH increased from approximately 4.5 to 7 (Söderlund et al., 2017; Yoshida et al., 1992), and liming caused I losses in English soil (Bowley et al., 2017). However, there was no significant relationship between pH and total I in an extensive Northern Irish database (Smyth & Johnson, 2011), with reports of high-I soils formed from heavily weathered limestone and other high pH areas (Fuge, 1996). Solubility increases with waterlogging and decreasing redox potential when iron (Fe) and manganese (Mn) oxides dissociate and IO<sub>3</sub><sup>-</sup> is reduced to I<sup>-</sup> (Medrano-Macías et al., 2016; Qian et al., 2017). Iodine is firmly retained by clay-sized particles and particularly organic matter (Humphrey et al., 2018; Medrano-Macías et al., 2016; Shetaya et al., 2012), with Johnson (2003) finding that peat followed by clay soils contained the most I.

Iodine concentrations in pasture are sometimes insufficient to sustain grazing animal health. Much of the international pasture concentration data fall within the range of 0.1 to 1.0 mg I kg<sup>-1</sup>, which encompasses the ruminant requirement range of 0.05 to 0.5 mg kg<sup>-1</sup>, with as little as 0.026 and >3 mg I kg<sup>-1</sup> recorded (Grace & Waghorn, 2005; Smith et al., 1999; Travnicek et al., 2004). Plant roots take up I<sup>-</sup> more rapidly than IO<sub>3</sub><sup>-</sup>, as I<sup>-</sup> likely follows the same pathway as chloride (Cl<sup>-</sup>) (White & Broadley, 2009; Whitehead, 2000), with recent evidence that plants convert IO<sub>3</sub><sup>-</sup> to I<sup>-</sup> (Humphrey et al., 2019). Iodine enters the leaves via stomata and cuticular waxes, though it is often fixed by the waxes and hence retained in exposed leaves with reduced translocation throughout the plant (Humphrey et al., 2019; Medrano-Macías et al., 2016). Solubility and atmospheric concentrations affect plant uptake. Pakchoi (*Brassica chinensis* L.) I concentrations across three different soils were negatively correlated with their degree of I immobilization (Hong et al., 2012). In field conditions, *Hylocomium splendens* (Hedw.) Schimp. (moss) and willow (*Salix* spp.) shrub leaves contained significantly more I near the sea in Norway (Sivertsen et al., 2014; Steinnes et al., 1994). English plot trials demonstrated that pasture I was positively correlated with soil I and negatively correlated with soil pH (Bowley et al., 2017). In Northern Ireland, 20 predominantly pasture vegetation and soil samples from various locations found that pasture I negatively correlates with the distance from the sea, soil pH, and Fe or Mn oxides and is positively correlated with soil I and organic C (Bowley, 2013).

Widespread agricultural I deficiencies have been identified in NZ (Grace & Knowles, 2012; Hercus et al., 1925). Nevertheless, some recent work has shown that soil I concentrations are not unusually low in some areas, with a mean of 20.9 mg kg<sup>-1</sup> found in the Waikato region (McNally, 2011). New Zealand's intensive grazing systems use pasture as the first source of I for ruminants. There has not yet been investigation into the effect of the aforementioned soil properties and proximity to the sea on the concentration of I in New Zealand pastures, how they may be affected by major and trace elements such as Mo, N, P, S, and Se in the soil–plant system, and how they affect the potential for ruminant I deficiencies. We hypothesized that pasture I concentrations decreased with increasing yield, were higher close to the sea, and were lower in organic C and clay-rich soils via reduced availability. We aimed at identifying the environmental factors that significantly influenced the concentration of I in New Zealand pasture and the consequences to agricultural systems.

## 6.1.2. Materials and methods

### 6.1.2.1. *Sampling and processing*

About 0.2 m<sup>2</sup> of pasture, predominantly perennial ryegrass (*Lolium perenne* L.), was sampled from intensively grazed pastures at 69 locations throughout New Zealand during December 2009 to January 2010. The sampling locations are provided in the Supplemental Table E.1 (Reiser et al., 2014). Samples were collected throughout New Zealand, but were focused on the South Island, and varied in soil type, parent material and land use. Pasture was cut 2 to 3 cm from the surface to avoid contamination with soil. From the same paddock, 10 to 15 soil cores were collected at 0-10 cm depth and then combined as one composite sample for each site.

Locations were determined via GPS, and minimum distances to the sea (DFS) were estimated using Google Earth. The soil was dried at 105°C for 24 h then sieved to 2 mm and stored. The pasture samples were rinsed with deionized (DI) water, dried at 60°C for 24 h, then milled and stored.

### 6.1.2.2. *Chemical analysis*

The soil particle size composition was determined with the pipette method, and pH measured with a Mettler Toledo pH meter after addition of DI water (Milli-Q at 18.2 MΩ) (Reiser et al., 2014). Soil and vegetation C and N were measured with an Elementar Vario MAX CN element analyzer; in most New Zealand soils, all the measured C is organic if the pH is <7, which was true in all soils, hence the total C will be referred to as organic C.

The concentrations of many elements in the soils were measured: pseudo-total Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, and Zn via digestion of 0.5 g soil in 5 mL aqua regia (BDH Aristar nitric acid 69%, BDH Aristar hydrochloric acid 37%), oxalate extractions were completed for Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, S, Si, and Zn using the method adapted from (Blakemore et al., 1987), and soluble concentrations of Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, P, S, and Zn were measured via extraction and filtration with 0.05 M calcium nitrate (Reiser et al., 2014). Samples were stored at 4°C then measured by inductively coupled plasma optical emission spectroscopy (ICP–OES) with a Varian 720 ES. Certified reference materials (CRMs) Wageningen ISE 921, IPE 100, and NIST 1573a were used to confirm acceptable recovery by the digestion. Recoveries ranged from 89 to 108% of the CRMs.

Soil and pasture were analyzed for total I, following standard methods (Fecher et al., 1998; Tagami et al., 2010; Whitehead, 1984; Yamada et al., 1996). Subsamples of each were dried at 103°C for 4 h (prepAsh 129 machine, Precisa Instruments). The soil was milled further, then 0.25 g was added to 4 mL of DI water (Milli-Q at 18.2 MΩ) and 1 mL of 25% tetramethylammonium hydroxide (TMAH) in a 25-mL volumetric flask, in 90°C water for 3 h. When cooled, flasks were filled to volume with DI water, transferred and centrifuged at 2620g for 20 min (HiCen21, Herolab), then filtered (0.45-μm syringe filter; Sartorius Stedim). The procedure was repeated for pasture, except 4.5 mL DI water and 0.5 mL 25% TMAH was added to flasks, with a centrifuge speed of 5897 g. Samples were measured with a Varian inductively coupled plasma mass spectrometry (ICP–MS) type 820. Iodine calibrations at 0, 1, 5, 10, 25, and 50 μg L<sup>-1</sup> were completed. The machine detection limit was 0.032 μg L<sup>-1</sup>, giving a sample detection limit of 0.0032 mg kg<sup>-1</sup>. Certified reference materials included five soils (GSS 4, 6, 8, 10, and 14) from the Institute of Geophysical and Geochemical Exploration in Hebei, China, and hay powder (BCR-129) and skim milk powder (BRC- 063R) from the Community Bureau of Reference in Brussels, Belgium. Recoveries ranged from 78 to 118% (Table E.2).

#### 6.1.2.3. *Data analysis*

Several authors have reported that soil and dust particles become incorporated into the leaves of field sampled plants, thereby changing the measured concentration (Robinson et al., 2008). Iron was used as an indicator for soil contamination of the sample. Although Fe is an essential plant micronutrient, plant uptake is strongly regulated, hence high values can indicate some contribution from soil. In our survey, pasture Fe concentrations ranged from 44 to 740 mg kg<sup>-1</sup>. There was a strong correlation ( $r = 0.790$ ,  $p < 0.001$ ) with chromium (Cr), which is usually found at low concentrations in vegetation. Corrections for soil contamination were completed using Eq. [1] and [2], adapted from Robinson et al. (2008). First, the concentration of contaminating soil,  $[s]$  (kg kg<sup>-1</sup>), was estimated, using Eq. [1]:

$$[s] = ([Fe]^1 - [Fe])/([Fe]_s - [Fe]) \quad [1]$$

Where  $[Fe]^1$  is the concentration of Fe measured in pasture (mg Fe kg<sup>-1</sup> dry wt.),  $[Fe]$  is the regulated concentration of 40 mg Fe kg<sup>-1</sup> dry wt. assumed in pasture, and  $[Fe]_s$  is the concentration of Fe measured in soil (mg kg<sup>-1</sup>). After this, the actual concentration of the element in vegetation,  $[x]$ , was calculated using Eq. [2]:

$$[x] = ([x]^1 - [x]_s[s])/(1 - [s]) \quad [2]$$

where  $[x]^1$  and  $[x]_s$  are the concentrations of the elements in soil and vegetation ( $\text{mg kg}^{-1}$ ), respectively.

Data were tabulated using Microsoft Excel (Office 365). Pearson correlation analyses were performed using the Excel Analysis ToolPak, with data log-transformed before analysis if skewed with the geometric mean closer to the median than the mean. Graphs and tables were produced in Excel to display data.

### 6.1.3. Results and discussion

#### 6.1.3.1. *Factors affecting soil I concentrations*

There was no significant correlation between soil I and the DFS (Table 6.1) This may be because soil I also depends on the capacity of the soil to retain the I that it has received (Fuge & Johnson, 2015). Our data showed significant correlations between soil I and clay ( $p < 0.01$ ) and organic matter (total C) ( $p < 0.005$ ) (Table 6.2), which is consistent with strong retention on the solid phase (Medrano-Macías et al., 2016). The maximum soil I concentration decreased as the distance from the sea increased (Fig 6.1), and the mean annual rainfall was high, at 1838 mm (Reiser et al., 2014); thus, it is likely that weakly and nonbound material was leached beyond the 0- to 10-cm sampling depth, producing the range of concentrations. The four sites that did not fit this trend were N04 and the three locations between 46.5 and 62 km with the second to fourth highest concentrations of I. Supplement contamination is a possible cause; soil sodium (Na) concentrations (a constituent of salt licks) at three of the locations were within the highest 20%. There was a significant positive correlation between soil I and soil Na (Table 6.1). Our findings were similar to those of other authors (Bowley, 2013; Johnson, 2003; Smyth & Johnson, 2011), who reported the highest soil I concentrations close to the sea, but with a large variation. McNally (2011) verified that leaching is likely, with significantly more I at the 10- to 20- than the 0- to 10-cm depth in soils from the Waikato region of New Zealand. Leaching is reduced in soils where I is retained by organic C and clay (Bowley, 2013; Johnson, 2003; Smyth & Johnson, 2011; Whitehead, 2000). Most of our samples were influenced by seawater as they were within 50 km of the sea. The sea has a negligible influence on soil I concentrations >50 km inland (Fuge, 1996; Johnson, 2003). Only 12 of our sampled locations (17% of the samples) were >50 km from the sea.

The amorphous Fe and aluminum (Al)-silicate (oxyhydr)oxide fraction sorbed and retained I in soil (Shetaya et al., 2012). Soil I was positively correlated with Al, Fe, and silicon (Si) oxalate ( $r = 0.652\text{--}0.843$ ) (Table 6.1). There was no significant correlation between soil pH and soil I, which is consistent with the findings of other authors measuring I in field soils (Bowley, 2013; Smyth & Johnson, 2011). However laboratory-based studies have reported a positive correlation between pH and I sorption (Yoshida et al., 1992; Zou et al., 2018).

#### 6.1.3.2. Factors affecting pasture I concentrations

Total soil I did not significantly affect pasture I, with an  $r$  value of  $-0.207$ . Our findings stand in contrast with other studies (Bowley, 2013; Bowley et al., 2017) that have reported significant positive correlations between soil I and plant I. Our study had 69 locations throughout New Zealand, whereas Bowley et al. (2017) used just one location and Bowley (2013) used 20 locations. Therefore, it is likely that our study incorporated many more soil types and climatic zones (Tait & Zheng, 2007) which are critical determinants of plant I uptake (Hong et al., 2012).

Distance from the sea had the strongest effect on the concentration of I in pasture. Analysis (Table 6.1) found a strong correlation between these two factors ( $p < 0.001$ ,  $r = 0.546$ ). Pasture concentrations within 15 km from the sea were highly variable, ranging from 0.10 to 0.85 mg kg<sup>-1</sup>, whereas at DFS >40 km, most samples were <0.12 mg kg<sup>-1</sup> except for four sites that may have received anthropogenic I (Fig 6.2). Similar trends were observed with barley (*Hordeum vulgare* L.), pasture, wheat (*Triticum aestivum* L.), and willow shrub from Northern Ireland and Norway (Bowley et al., 2017; Sivertsen et al., 2014).

Iodine and other elements present in seawater may have been intercepted and retained by leaves or taken up by the roots, thus reducing their accumulation in the underlying soils. Several elements present at  $\geq 0.01$  mg L<sup>-1</sup> in seawater were measured for in soil and pasture, but only soluble S had a negative DFS–soil correlation, with B, I, Mg, Na, and S having negative DFS–pasture correlations (Table 6.2). The critical leaf area index of pasture is high, at approximately 4 to 6 for perennial ryegrass and 3 for white clover (Martin et al., 2017), hence high rates of sea-derived I interception is likely. Bowley (2013) found that washing did not significantly decrease vegetation I concentrations, which indicates that I was not superficially retained, but inside the leaves, a finding replicated by Humphrey et al. (2019). Karunakara et al. (2018) showed that pasture can potentially intercept large quantities of I, with mass interception factors of 0.25 to 7.7 m<sup>2</sup> kg<sup>-1</sup>, although decreasing with rainfall and total I.

Competition for soil sorption sites from other seawater anions, particularly halogens, may increase the potential for plant uptake and leaching (Sheppard et al., 1995). The increased solubility of I resulting from these competitive effects may contribute to the observed differences in the relationships between soil and pasture concentrations and the DFS (Table 6.2). The Fe and Al-silicate (oxyhydr)oxides fractions were negatively correlated with pasture I ( $r = -0.241$  to  $-0.372$ ) (Table 6.1). Hence, though this fraction retained I in soil, it appeared to also reduce I availability to plants.

**Table 6.1 Variables significantly correlated with I concentrations in pasture and soil (n = 55-69).**

Pasture		Soil	
Zn soluble	0.344 **	Al oxalate	0.843 ***
S soluble	0.253 *	S oxalate	0.821 ***
Na total	0.253 *	Si oxalate	0.675 ***
Mn pasture	0.246 *	Cd oxalate	0.667 ***
B pasture	0.242 *	Fe oxalate	0.652 ***
Si oxalate	-0.241 *	C total	0.638 ***
P pasture	-0.244 *	Cr oxalate	0.636 ***
P total	-0.259 *	Se total	0.589 ***
K pasture	-0.263 *	N total	0.578 ***
P oxalate	-0.267 *	P total	0.553 ***
Ca total	-0.269 *	S total	0.525 ***
S oxalate	-0.279 *	Cd total	0.523 ***
Pb oxalate	-0.281 *	Al total	0.485 ***
N pasture	-0.288 *	Mo oxalate	0.426 ***
Al oxalate	-0.306 *	P oxalate	0.422 ***
Ca pasture	-0.310 *	Cu total	0.394 ***
Cr oxalate	-0.333 **	Mo total	0.391 ***
Fe oxalate	-0.372 **	Cr soluble	0.333 *
DFS	-0.546 ***	Fe total	0.322 **
		Na total	0.296 *
		Cu oxalate	0.276 *
		Cr total	0.271 *
		Clay	0.265 *
		Pb oxalate	0.264 *
		P soluble	-0.247 *
		Silt	-0.267 *
		Se pasture	-0.293 *
		Co soluble	-0.352 **

Total = pseudo-total soil concentration, oxalate = oxalate-extractable soil concentration, soluble = soluble/exchangeable 0.05 M Ca(NO<sub>3</sub>)<sub>2</sub> extractable soil concentration, and C total assumed to be all organic.

\* significant ( $p < 0.05$ ), \*\* highly significant ( $p < 0.01$ ), \*\*\* very highly significant ( $p < 0.001$ ).

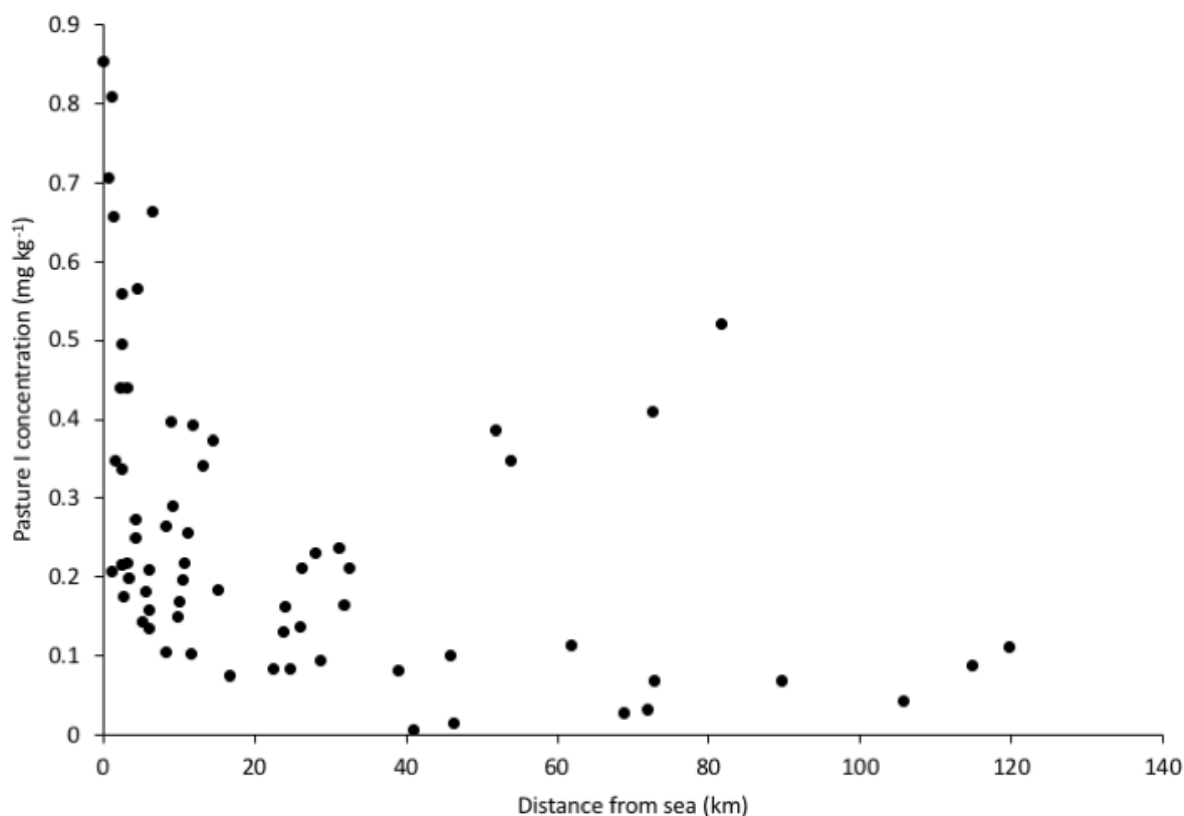


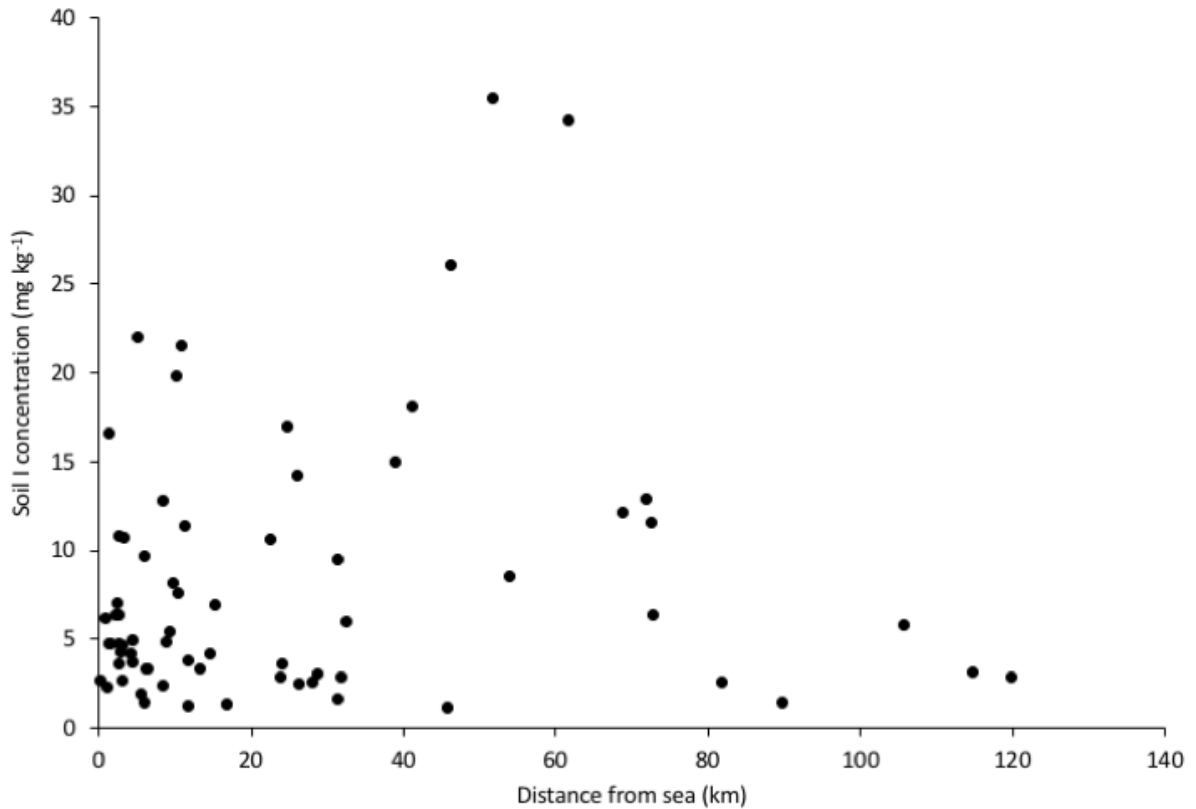
Fig. 6.1 Distance from the sea versus pasture I concentrations.

Table 6.2 Concentrations of predominant elements in seawater, and correlations between the distance from sea and their soil/plant concentrations (n = 44-69).

Element	Concentration in seawater (mg L <sup>-1</sup> ) <sup>a</sup>	Correlation between soil concentration and distance			Correlation between pasture concentration and distance
		Total	Oxalate	Soluble	
Na	10,770	-0.080			-0.256 **
Mg	1,290	0.129			-0.240 *
S	905	-0.063	0.219	-0.367 **	-0.245 *
Ca	412	0.231			0.200
K	380	0.140			0.022
C	28	0.072			0.357 **
N	11.5	0.076			0.046
B	4.4	0.010			-0.257 *
Li	0.18	-0.017			0.056
P	0.06	0.157	0.221	-0.056	-0.051
I	0.06	0.123			-0.546 ***
Mo	0.01	-0.154	0.060		-0.082

<sup>a</sup>Bearman (1995). Total = pseudo-total soil concentration, oxalate = oxalate-extractable soil concentration, and soluble = soluble/exchangeable soil concentration.





**Fig. 6.2 Distance from the sea versus soil I concentrations.**

#### 6.1.4. Conclusions

This study indicates that without supplementation, sheep and cattle will become deficient in I on 26 and 87% of the pastures tested. There was no correlation between soil I and DFS, nor was there a correlation between soil I and pasture I. However, the critical factors affecting I in pasture were the DFS and the presence of amorphous oxides, with the highest pasture concentrations occurring next to the sea in soils with low amorphous oxides. Therefore, the risk of I deficiency in stock is higher away from the sea and in amorphous-oxide-rich soils. Future research should test the effect of soil properties including organic C and clay on pasture I >50 km away from the sea, include the soil soluble I fraction in similar datasets, and replicate studies of this nature, to determine whether our conclusions are applicable in contrasting environments, in particular tropical soils and arid soils.

## 6.2. Mobility of I in soils and perennial ryegrass

### Abstract

Proximity to the source has a large effect on the concentration of I in grass in the field, but it is important to understand the factors that can manage the mobility of I within a single location, particularly those that can be easily modified such as soil solution pH, and it is useful to understand the mobility of I in comparison to other elements. It was hypothesised that I was more mobile than the ETECs Be, Ga, In, La, Ce, Nd, and Gd in the soil-plant system. Soil and plant experiments aimed to quantify the effect of pH, concentration and OM on the mobility of I independent of location (Chapter 5.1) and determine the mobility of I compared to the ETECs Be, Ga, In, La, Ce, Nd, and Gd, and the common contaminant Cd. The  $K_D$  of I decreased as the concentration added to soil increased.  $K_D$  values decreased with increasing pH in the RFMW and RFT soils; increasing the soil pH had little effect on the  $K_D$  of I in the organic-rich GOO soil. Iodine had lower  $K_D$  than Be, Cd, Ga, In, La, Ce, Nd, and Gd in the RFMW and GOO soils. The uptake of I by perennial ryegrass increased with the concentration of I added to soil, then plateaued at 1900-2271 mg kg<sup>-1</sup> DM, with higher BACs than Be, Cd, Ga, In, La, Ce, Nd, and Gd. This section showed that the monovalent anion I is more mobile than the cations Be, Cd, Ga, In, La, Ce, Nd, and Gd in the soil plant system, and is readily taken up by perennial ryegrass when bioavailable in the soil-plant system, although mobility can be altered by soil properties within a location.

### 6.2.1. Introduction

Since in the field the proximity to the supply of I has the biggest effect of the concentration of I in grass (Chapter 6.1), batch sorption and plant pot trial experiments were conducted to examine the effect of factors such as pH, soil OM content and the concentration of I added to soil on the mobility of I in the soil-plant system, independent of location. This information can be used to support management practices to supplement I to animals. In comparison to common TE contaminants which are often divalent, such as Cd, Cu, Ni, Zn (Burgos et al., 2006; Robinson et al., 2009), I forms a monovalent anion in solution, which is likely to affect its mobility in the soil-plant system.

While the radionuclide <sup>129</sup>I has often been investigated due to its presence in nuclear waste and long half-life (Sheppard, 2003; Shetaya et al., 2012), the focus of this study was the stable, isotope <sup>127</sup>I (>99% abundance). References to <sup>129</sup>I are limited due to the difference in mass and thus physical properties between the two isotopes, which can affect adsorption and plant uptake, and the difference in concentration, which, as shown in Chapter 4, can significantly affect  $K_D$ .

It was hypothesised that the  $K_D$  of I will decrease with increasing soil solution pH, decreasing soil OM content, and increasing I concentration added to soil in batch sorption experiments (Kaplan et al., 2000), and that the  $K_D$  of I will be less than the ETECs Be, Ga, In, La, Ce, Nd, and Gd, but similar to Cd (Sheppard et al., 2009). Thus, the uptake of I by perennial ryegrass will increase with the concentration of I added to soil, and I will have higher BACs than the selected ETECs, but similar BACs to the mobile TE contaminant Cd. This section aims to find the effect of pH, concentration added and soil OM content on the  $K_D$  of I and compare the  $K_D$  of I in soil and BACs of I in perennial ryegrass with the ETECs Be, Ga, In, La, Ce, Nd, and Gd, and Cd.

### 6.2.2. Materials and methods

The methodology, soils, and perennial ryegrass seed used were the same as in Chapters 4 and 5, with RFT, RFMW and GOO soils used for the batch sorption experiments, and just the RFMW soil used for the plant pot trial. The salt  $KIO_3$  was used to spike soil with I. The concentrations added to soil in the batch sorption experiments were the same as in Chapter 4, but the reference background concentration from Kabata-Pendias and Mukherjee (2007) was  $2.8 \text{ mg kg}^{-1}$  I, thus the concentrations of I added to soil in the treatments were 14, 28, 56 and  $112 \text{ mg kg}^{-1}$ . A certified reference material was used, and statistical analysis was carried out, as per Chapter 5.1.2.5.

#### 6.2.2.1. Form of I added to soil

The batch sorption experiments were conducted using  $IO_3^-$  (iodate) and  $I^-$  (iodide). However, for the  $I^-$  samples the concentrations of I were higher in the samples that had soil added than the samples without, indicating that the  $Ca(NO_3)_2$  extractant solution removed higher concentrations of endogenous I from the solid phase of the soil, than the concentrations of exogenous I that sorbed to soil. Thus, the  $K_D$  could not be calculated. Samples containing  $IO_3^-$  were not affected. These differences are likely linked to the oxidation states of the I. In  $I^-$  I has an oxidation state of -1 and in  $IO_3^-$  I has an oxidation state of +7, and the results imply that the higher oxidation state of I allowed it to overcome the  $Ca(NO_3)_2$  and sorb to soil, whereas  $I^-$  could not.

### 6.2.3. Results

#### 6.2.3.1. $K_D$ of I in soil

As the concentration of I added to soil increased, the  $K_D$  of I exponentially decreased (Fig. 6.3), similar to the saturation curves of Be, Cd, La, Ce, Nd, and Gd (Fig. 4.1). The  $K_D$  of I decreased as the pH of the

soil solution increased in the RFMW and RFT. In the GOO soil, increasing the pH had little net effect on the  $K_D$  of I (Fig. 6.4). The  $K_D$  of I was the highest in the RFT and similar in the other two soil types.

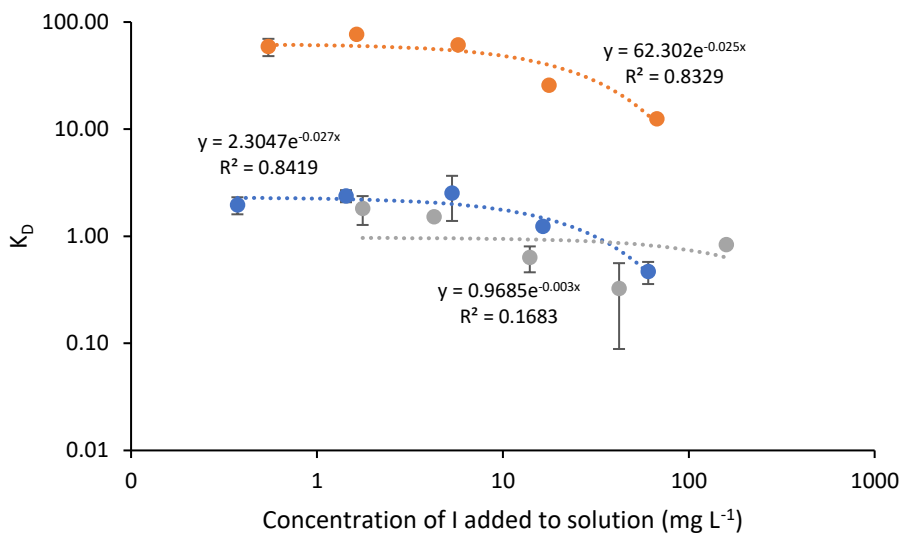


Fig. 6.3 Effect of the concentration of I added to the soil on the  $K_D$  of I in three different soil types.

• RFMW, • RFT, • GOO.

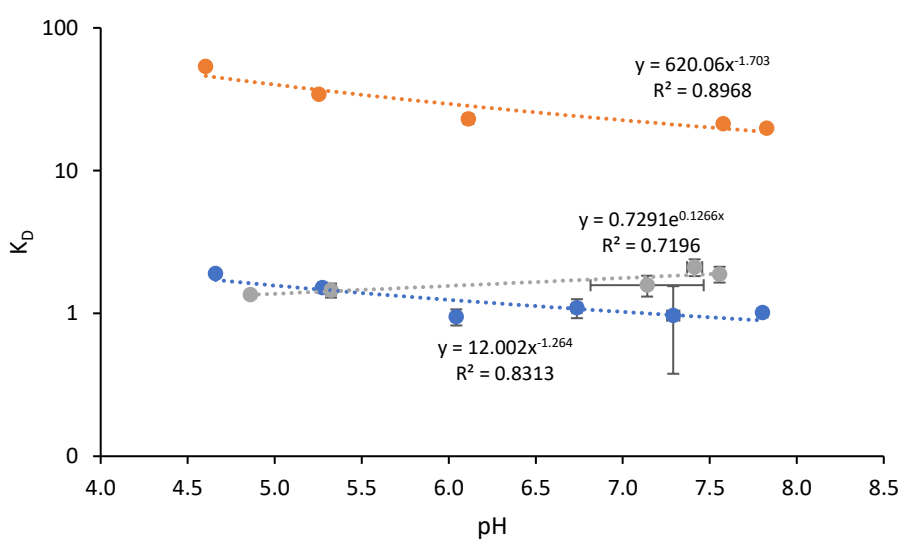


Fig. 6.4 Effect of the pH of the soil solution on the  $K_D$  of I in three different soil types.

### 6.2.3.1.1. Sorption of I to soil compared to Be, Cd, Ga, In, La, Ce, Nd, and Gd

The  $K_D$  of I was lower than the ETECs and Cd in the RFMW and GOO soils. In the RFT, where sorption of I was the highest, I had higher  $K_D$  than In in the pH gradient, and Cd and Be in the concentration gradient (Table 6.3 and Table 6.4).

**Table 6.3  $K_D$  of Be, Cd, Ga, I, In, La, Ce, Nd and Gd at 1, 10 and 100 mg L<sup>-1</sup> ETEC, Cd, or I added in solution, and 1 mmol kg<sup>-1</sup> added to soil (standard error), ranked from low to high.**

RFMW					
Element	0 mg L <sup>-1</sup>	1 mg L <sup>-1</sup>	10 mg L <sup>-1</sup>	100 mg L <sup>-1</sup>	<sup>b</sup> 1 mmol kg <sup>-1</sup>
I	688 (66)	2.0 (0.35)	2.5 (1.1)	0.47 (0.11)	0.28
Be	<sup>a</sup>	71 (13)	23 (0.88)	2.6 (0.026)	77
Cd	<sup>a</sup>	10 (0.76)	6.1 (0.17)	4.1 (0.046)	5.6
Ga	<sup>a</sup>	180 (26)	<b>1,591 (26)</b>	807 (31)	<b>1648</b>
In	<sup>a</sup>	3.9 (0.076)	140 (0.36)	<b>895 (6.4)</b>	165
La	<sup>a</sup>	215 (21)	215 (21)	89 (1.7)	212
Ce	<sup>a</sup>	240 (27)	332 (8.4)	119 (2.5)	276
Nd	60,551 (3,191)	300 (22)	356 (7.4)	134 (2.8)	306
Gd	<sup>a</sup>	<b>370 (15)</b>	350 (12)	131 (3.3)	293
RFT					
Element	0 mg L <sup>-1</sup>	1 mg L <sup>-1</sup>	10 mg L <sup>-1</sup>	100 mg L <sup>-1</sup>	<sup>b</sup> 1 mmol kg <sup>-1</sup>
I	529 (43)	59 (11)	61 (3.6)	12 (0.15)	9.6
Be	<sup>a</sup>	<b>66 (2.2)</b>	35 (0.45)	4.5 (0.053)	73
Cd	<sup>a</sup>	5.2 (0.018)	3.7 (0.11)	2.7 (0.069)	3.5
Ga	<sup>a</sup>	3.3 (3.5)	<b>157 (15.7)</b>	<b>934 (65)</b>	<b>168</b>
In	<sup>a</sup>	0.41 (0.46)	17 (0.19)	152 (1.4)	30
GOO					
Element	0 mg L <sup>-1</sup>	1 mg L <sup>-1</sup>	10 mg L <sup>-1</sup>	100 mg L <sup>-1</sup>	<sup>b</sup> 1 mmol kg <sup>-1</sup>
I	983 (75)	1.8 (0.55)	0.63 (0.17)	0.83 (0.047)	0.49
Be	7,243 (347)	<b>154 (41)</b>	197 (22)	57 (4.8)	218
Cd	18 (5.1)	18 (5.1)	67 (2.3)	61 (2.3)	64
Ga	<b>171,189 (40,226)</b>	121 (18)	185 (19)	690 (42)	216
In	<sup>a</sup>	17 (0.13)	<b>237 (0.43)</b>	<b>994 (20)</b>	<b>275</b>

**Highest value, lowest value.** <sup>a</sup>Below detection limit; <sup>b</sup>Values calculated from the trendline in Fig. 4.1 and Fig 6.3. Cells shaded green show the  $K_D$  values of I in comparison to the other elements.

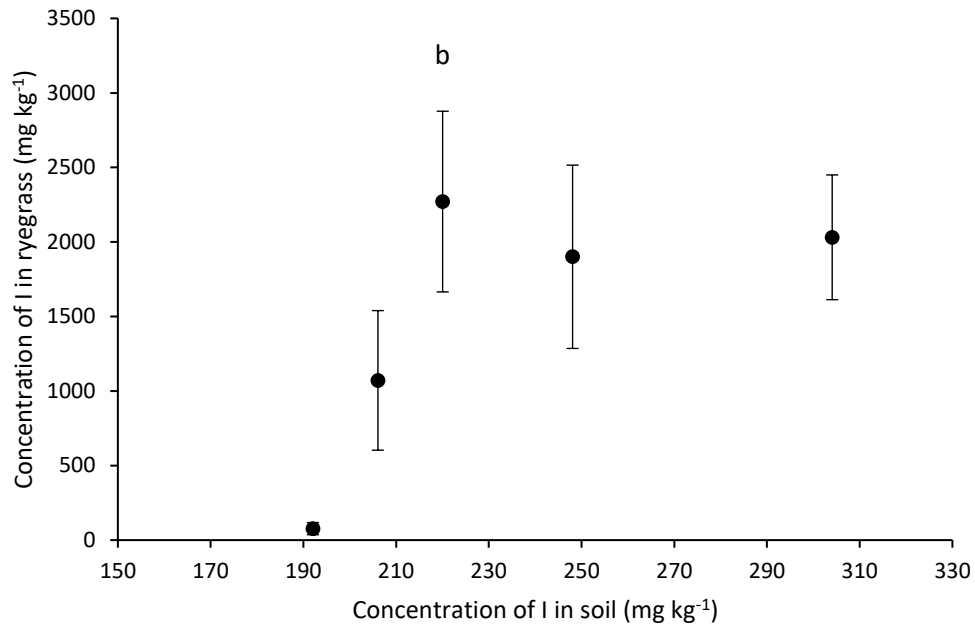
**Table 6.4**  $K_D$  of Be, Cd, Ga, I, In, La, Ce, Nd and Gd at pH 5, 6 and 7 when 10 mg L<sup>-1</sup> of ETEC, Cd, or I was added to solution, ranked in order from low to high.

<b>RFMW</b>			
<b>Element</b>	<b>pH 5</b>	<b>pH 6</b>	<b>pH 7</b>
I	1.6	1.2	1.0
Be	64	315	1,210
Cd	8.1	32	129
Ga	<b>2,026</b>	<b>2,716</b>	821
In	150	158	165
La	346	1,420	<b>5,824</b>
Ce	599	1,755	3,377
Nd	517	1,532	4,012
Gd	649	2,155	3,469
<b>RFT</b>			
<b>Element</b>	<b>pH 5</b>	<b>pH 6</b>	<b>pH 7</b>
I	40	29	23
Be	140	<b>693</b>	<b>2,687</b>
Cd	16	109	552
Ga	<b>247</b>	241	236
In	18	18	19
<b>GOO</b>			
<b>Element</b>	<b>pH 5</b>	<b>pH 6</b>	<b>pH 7</b>
I	1.4	1.6	1.8
Be	254	425	<b>595</b>
Cd	78	157	319
Ga	<b>552</b>	<b>880</b>	394
In	246	205	171

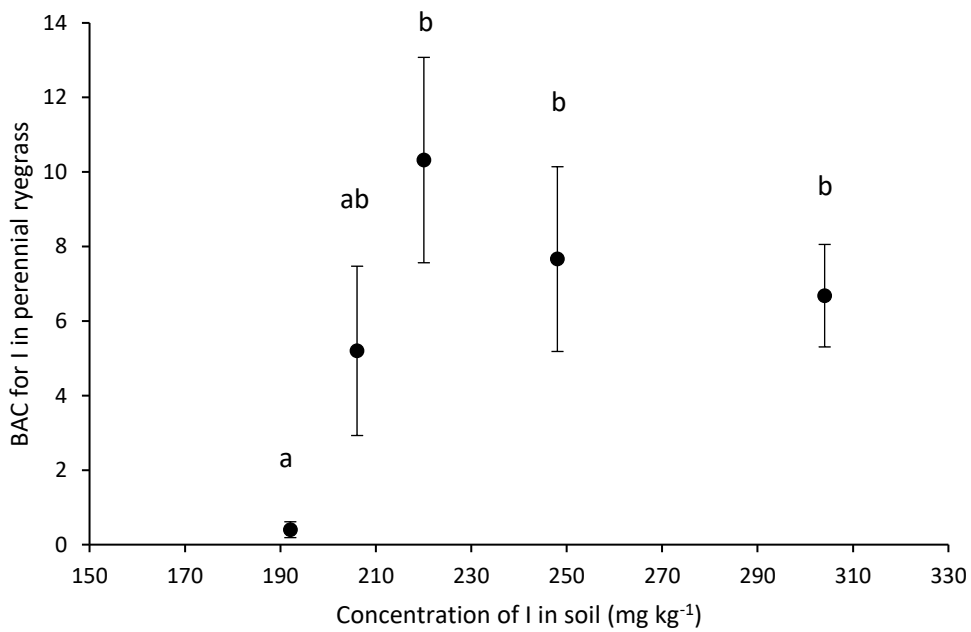
**Highest value, lowest value.** All values calculated from trendlines (Fig. 4.2 and Fig. 6.4)

### 6.2.3.2. Uptake and bioaccumulation of I in perennial ryegrass

The concentrations of I in perennial ryegrass increased from 192 mg kg<sup>-1</sup> to a plateau of 1900-2271 mg kg<sup>-1</sup> (Fig. 6.5). The BACs increased when the concentration of I added to soil increased, until the plateau in ryegrass I concentrations at 28 mg kg<sup>-1</sup> added to soil. Unlike the other elements, the concentration of I naturally in the RFMW soil was higher than the mean used to calculate the concentration to add to soil, hence the BACs increased when plant uptake increased (Fig. 6.6).



**Fig. 6.5 Concentrations of Be, Cd, Ga, In, La, Ce, Nd and Gd in the shoots of perennial ryegrass growing in I spiked soil.**



**Fig. 6.6 Bioaccumulation coefficients for the uptake of Be, Cd, Ga, In, La, Ce, Nd and Gd in perennial ryegrass grown in I spiked soil.**

6.2.3.2.1. *Uptake and bioaccumulation of I in perennial ryegrass in comparison with Be, Cd, Ga, In, La, Ce, Nd, and Gd*

The uptake of I by perennial ryegrass was higher than that of the ETECs and Cd, with 77 mg kg<sup>-1</sup> I in the control, compared with 56 mg kg<sup>-1</sup> Ga, which was the highest concentration across all the elements and treatments in Chapter 5. The high uptake of I was due to high concentrations in soil, and large BACs; the BACs of I were higher than the ETECs and Cd in all the treatments except the control, where I had a lower BAC than Cd (Table 6.5).

**Table 6.5 Bioaccumulation coefficients of Be, Cd, Ga, I, In, La, Ce, Nd and Gd in perennial ryegrass in each treatment (standard error), ranked from low to high.**

Element	Treatment				
	T0	T1	T2	T3	T4
I	0.40 (0.21)	<b>5.2</b> <b>(2.3)</b>	<b>10</b> <b>(2.8)</b>	<b>7.7</b> <b>(2.5)</b>	<b>6.7</b> <b>(1.4)</b>
Be	0.0091 (0.0017)	0.020 (0.0042)	0.035 (0.0063)	0.023 (0.0022)	0.080 (0.017)
Cd	<b>0.95</b> <b>(0.18)</b>	0.058 (0.024)	0.24 (0.040)	0.10 (0.021)	0.22 (0.039)
Ga	0.0065 (0.00078)	0.012 (0.0017)	0.030 (0.010)	0.032 (0.0083)	0.046 (0.0067)
In	0.17 (0.047)	0.041 (0.030)	0.013 (0.0030)	0.0081 (0.0024)	0.011 (0.0025)
La	0.0031 (0.00054)	0.023 (0.0030)	0.027 (0.0032)	0.033 (0.0086)	0.043 (0.0055)
Ce	0.0062 (0.0012)	<i>0.0026</i> <i>(0.00038)</i>	<i>0.0052</i> <i>(0.0012)</i>	<i>0.0043</i> <i>(0.00030)</i>	<i>0.0052</i> <i>(0.00079)</i>
Nd	<i>0.0030</i> <i>(0.0053)</i>	0.012 (0.0017)	0.020 (0.0070)	0.014 (0.0017)	0.037 (0.0090)
Gd	0.014 (0.0090)	0.015 (0.0028)	0.016 (0.0025)	0.021 (0.0027)	0.018 (0.0015)

Highest value, lowest value.

#### 6.2.4. Discussion

As hypothesised, the  $K_D$  of I in soil was lower than the ETECs and Cd. Iodine forms the anions I<sup>-</sup> or IO<sub>3</sub><sup>-</sup> in solution or complexes with soluble OM (Humphrey et al., 2018), and the anion exchange capacity is lower than the cation exchange capacity in soil, except for in volcanic soils, which none of the soil types were. Sorption of I in this study was lower than that reported by Almahayni et al. (2017) but was similar to Hong et al. (2012). In this study and Sheppard et al. (2009), the  $K_D$  values of I in spiked soil were similarly low, and in unspiked soil, the  $K_D$  values were high. This shows how animals can still experience I deficiency despite the low  $K_D$  values in this study, as trace elements increase in immobilisation with time (Chapter 5).

The soil OM content did not have the biggest effect on the sorption of I to soil, as seen by the similar  $K_D$  of I in the RFMW and GOO soils. Iodine had more sorption in the RFT soil, which had lower Olsen P



and base saturation than the other two soils, suggesting that P or the cationic bases may have outcompeted I for sorption sites.

As the concentration of I added to soil increased, I had a saturation curve consistent with Be, Cd, La, Ce, Nd, and Gd-ETECs that did not precipitate in the environmental conditions tested (Chapter 4). This finding is consistent with Hong et al. (2012). The decrease in the  $K_D$  of I with increasing pH is typical of anions and is consistent with the decrease in I sorption between pH 5-7 reported in Whitehead (1984). In the GOO soil, the lack of decreased  $K_D$  with increasing pH is likely due to an increased sorption to OM as the pH increased, especially as this soil has the highest OM content.

As with batch sorption experiments, the BACs of I in perennial ryegrass are higher than values in literature (Bowley et al., 2017; Omberg et al., 2011) due to the lower solubility and thus bioavailability of I in uncontaminated soil. In the control, the concentration of I in perennial ryegrass was within the range in the first half of this chapter, but at the higher end of the scale, which suggests that the RFMW naturally contained high concentrations of bioavailable I, hence this concentration was higher than some in literature (Whitehead, 1984) In the spiked soils, the concentrations of I in perennial ryegrass were similar to that of foliar-spiked grass in Geetha et al. (2012).

#### 6.2.5. Conclusions

Iodine is a relatively mobile trace element in the soil-plant system, and is more mobile than the cations Be, Cd, Ga, In, La, Ce, Nd, and Gd. Within a single location, the mobility of I in soil can be increased by increasing the soil solution pH and concentration of I added to soil and decreasing the base saturation and Olsen P. Perennial ryegrass can take up and translocate high concentrations of I from soil if available, up to approximately 2000 mg kg<sup>-1</sup>. Future work should compare the mobility of I with ETECs in a range of plant species, to identify if there are similar bioaccumulation differences.

## 7. General Discussion

### 7.1. Connections between the soil and plant mobility of ETECs

#### 7.1.1. Effect of concentration on their mobility in soil and plant

The ETECs had five contrasting effects on solubility and plant uptake, when their concentrations were increased in soil (Table 7.1). Beryllium, La, Nd and In had changes in BACs that were proportional to the change in  $K_D$  found in Chapter 4. As per Chapter 5, uptake of Ce and Gd by perennial ryegrass increased when the concentrations of these elements added to soil increased, but the endogenous and exogenous forms of Ce and Gd appeared to be equally taken up and translocated by the perennial ryegrass. It was also suggested in Chapter 5 that Cd is more bioavailable in the endogenous form. The increase in the BACs of Ga suggests that the Ga that was bound as the concentration and  $K_D$  increased was in equilibrium with the labile pool. Gallium was likely immobilised when excess  $Ga(OH)_3^0$  was formed and precipitated, thus when the  $Ga(OH)_3^0$  was taken up by perennial ryegrass,  $Ga(OH)_{3(s)}$  dissolved, increasing availability.

**Table 7.1 Effect of increasing the concentration of ETECs added to soil on solubility and plant uptake.**

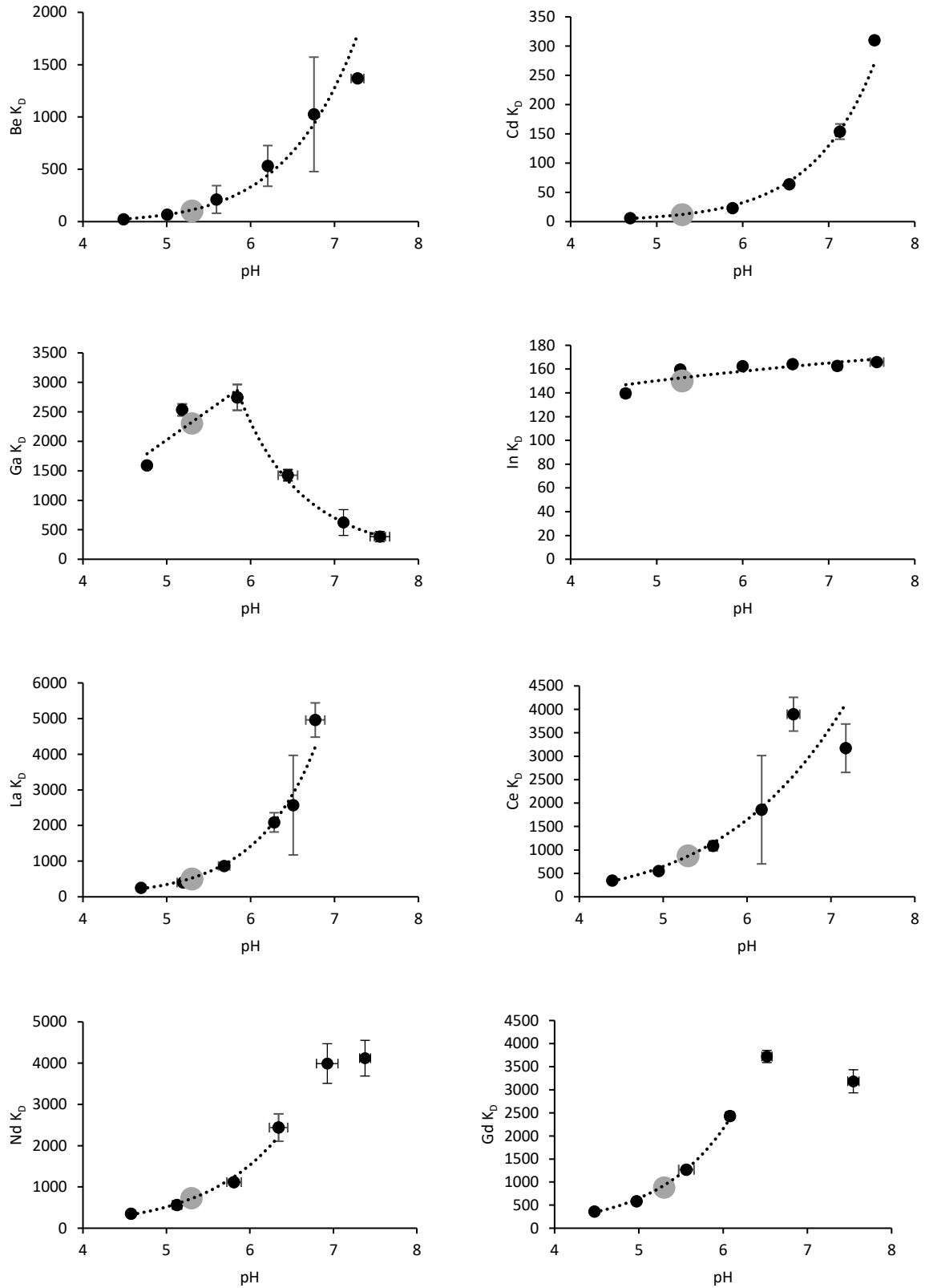
Elements	Effect
Be, La, Nd	$K_D$ decreased, BAC increased
Ce, Gd	$K_D$ decreased, little change in BAC
Cd	$K_D$ decreased, BAC decreased
Ga	$K_D$ increased, BAC increased
In	$K_D$ increased, BAC decreased

Addition of Ga to soil induced toxicity in perennial ryegrass in Chapter 5 but not Chapter 3, despite similar concentrations added in Chapter 3, which was due to the higher  $K_D$  of Ga in the soil in Chapter 3 versus Chapter 5 soil. This resulted in a lower bioavailability of Ga in the Chapter 3 soil, limiting uptake and the pool of bioavailable Ga ions induced toxicity. In Chapter 3, Ga had a  $K_D$  of 2021 in the granular silt loam, and in Chapter 4 Ga had  $K_D$  of 180-1591 in the RFMW soil used in Chapter 5. Similar concentrations were also used to calculate the  $K_D$  in both chapters. This demonstrates the potential for using  $K_D$  to assess the capacity for phytotoxicity between soil types.

#### 7.1.2. Effect of soil pH on the uptake of ETECs by plants

The ETECs have higher solubility in acidic soil (with the exception of Ga, which has the highest  $K_D$  values at pH 5-6). The soil used for the plant pot trials in Chapter 5.1 was an acidic sandy loam with a pH of 5.3, and the high solubility and thus bioavailability of the ETECs caused the soil toxicity thresholds to

be low. The approximate pH of the soil in the plant pot trials is plotted on the pH- $K_D$  graphs for the RFMW soil in Fig. 7.1, as shown by the grey dot. BACs were low for In, which could be due to the large pH range of maximum precipitation, which the pH of the RFMW soil fell within. Although Ga is also likely to have precipitated in the RFMW soil in Chapter 5.1, Ga has a steep  $K_D$  gradient either side of the maximum, thus  $\text{Ga(OH)}_3^0$  may have been in equilibrium with the dominant species either side of the peak ( $\text{Ga(OH)}_2^+$  and  $\text{Ga(OH)}_4^-$ ) that could be taken up by perennial ryegrass, thus causing Ga to have higher BACs than In.



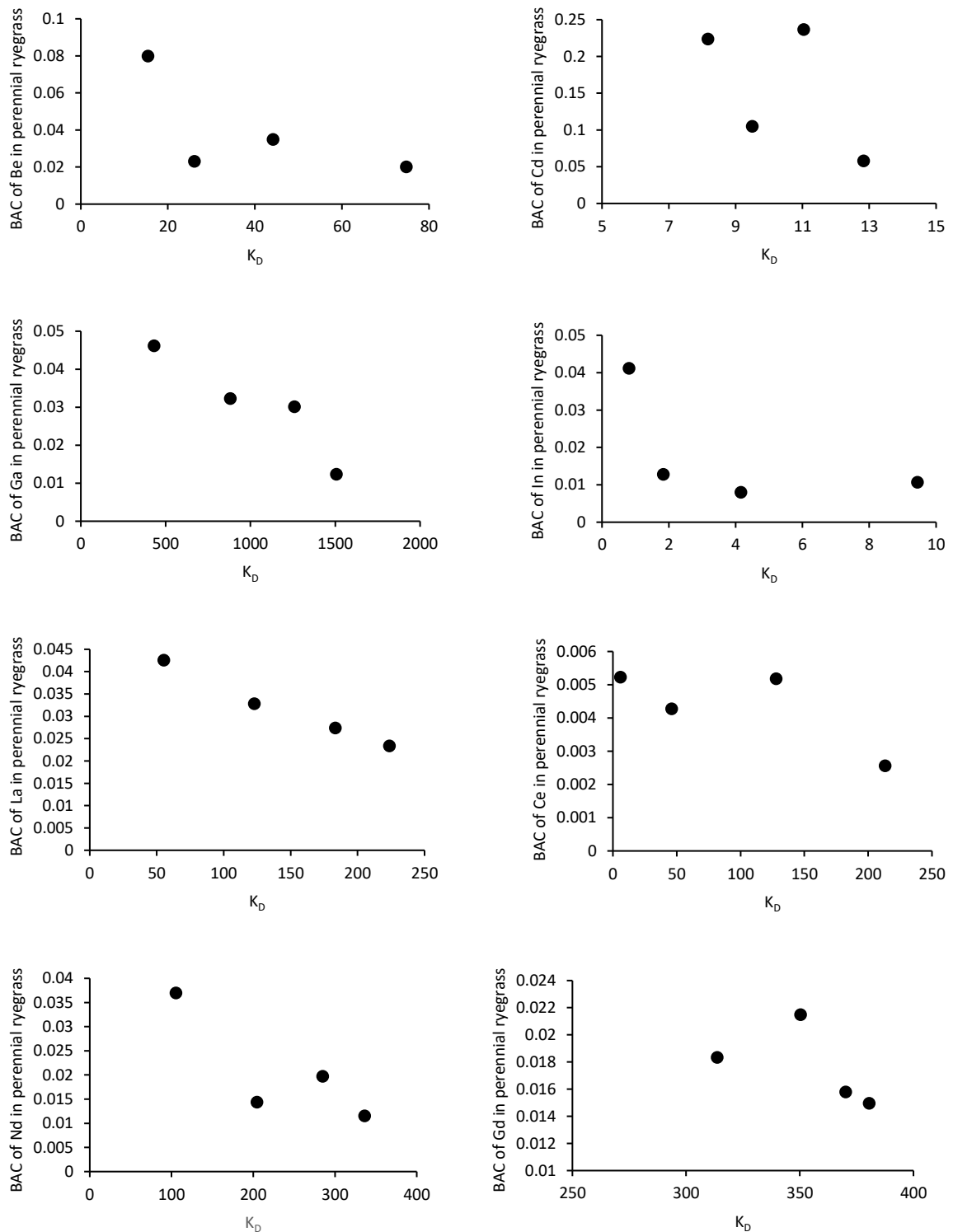
**Fig. 7.1** Effect of pH on the  $K_d$  of Be, Cd, Ga, In, La, Ce, Nd, and Gd.

● Approximate pH of the soil in the plant pot trials

### 7.1.3. Link between $K_D$ and BAC in data

The RFMW soil was used in the batch sorption experiments in Chapter 4 and the plant pot trials in Chapter 5.1, so the trendlines from the concentration vs  $K_D$  graphs (Fig 4.1) were used to calculate the approximate  $K_D$  of the ETECs in the soil of the plant pot trials (Fig. 7.2). These data show that as  $K_D$  of all of the ETECs in soil increase, BACs decrease. This pattern appears to be linear, but can be exponential for some elements such as In.

The actual  $K_D$  values will have differed from those calculated, as in Chapter 5.1 spiked soil was in the greenhouse, watered, for 7 weeks prior to sowing, thus aging and increasing  $K_D$ . In addition, for some of the ETECs the concentrations in the plant pot trials did not fit within the concentration range tested in Fig 4.1. These calculations assume that the rate of further immobilisation was the same for all the ETECs and Cd. But these data clearly show the relationship between  $K_D$  and BAC.



**Fig. 7.2 Effect of  $K_D$  on the BACs of the ETECs and Cd in perennial ryegrass.**

$K_D$  values calculated from Fig. 4.1.

## 7.2. Extrapolation of ETEC mobility data to other environments

### 7.2.1. Comparing the mobility of the ETECs to the common TE contaminant Cd

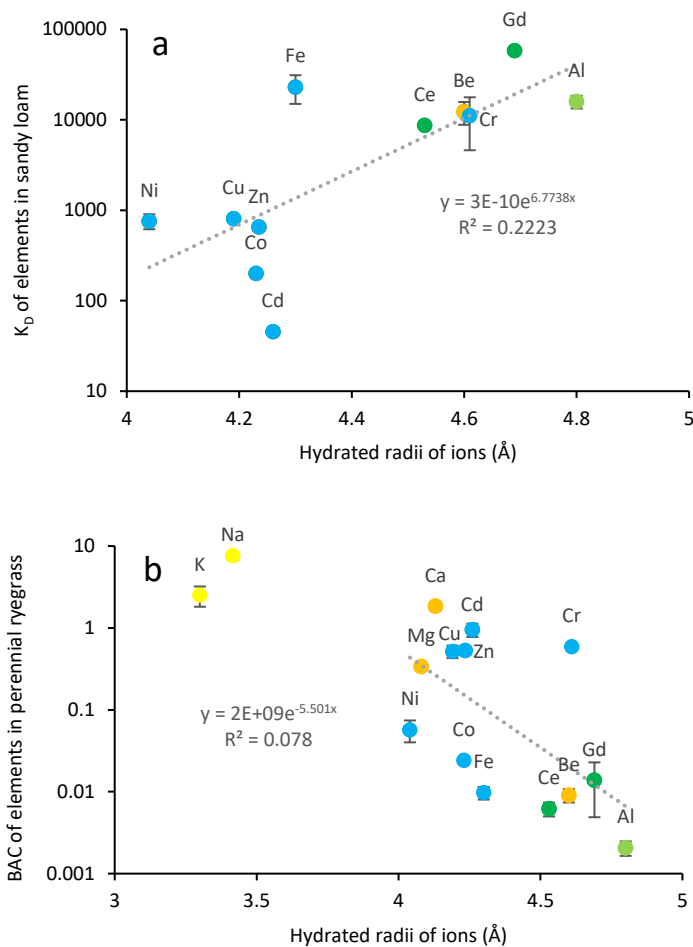
Cadmium was tested in the batch sorption and plant uptake experiments to be used as a benchmark of a relatively high mobility TE contaminant. Even though Cd typically has  $K_D$  values in the 100s, it has lower  $K_D$  values than many other trace element cations (Sheppard et al., 2007). Data in Chapters 4 and 5 show that the ETECs Be, Ga, In, La, Ce, Nd, and Gd have comparably low mobility in the soil-plant system.

As solubility and uptake varies between different soil types and plant species, there is the possibility of using Cd as a quantitative benchmark to estimate  $K_D$  and BAC of the ETECs in environments where Cd has been measured, but this is not feasible.  $K_D$  was the most likely use of Cd as a benchmark, but in Chapter 4 the effect of pH and concentration on the  $K_D$  of Ga and In was different to Cd, and the  $K_D$  of the REEs had different curve shapes in response to the perturbations. Beryllium sorption followed similar trendlines to Cd, but the difference between the two elements was not consistent, e.g., when the soil solution pH increased, the difference in the  $K_D$  of Be and Cd increased in the RFT and RFMW soils, but stayed relatively consistent in the GOO soil, which had a higher OM content.

### 7.2.2. Use of hydrated radii and Me-O bond length to calculate the relationship between $K_D$ and BAC

Cations become hydrated in solution; the  $\delta^-$  charge of O atoms in  $H_2O$  is attracted to the positive charge, forming a sphere of loosely-bound water molecules, with 4-9 often in the inner-sphere, and more water molecules loosely held in the outer-spheres. Ions with smaller ionic radii have higher effective nuclear charge, thus attract water more strongly and have larger hydrated radii.

It was tested whether the hydrated radii of the cations would be negatively correlated to  $K_D$  and thus positively correlated to BAC, as the more strongly attracted water molecules would limit specific adsorption to soil, thereby increasing the likelihood of plant uptake. A negative correlation was found between hydrated radii and BAC in perennial ryegrass in uncontaminated soil (Fig. 7.3b), but the correlation between hydrated radii and  $K_D$  was not significant (Fig. 7.3a).

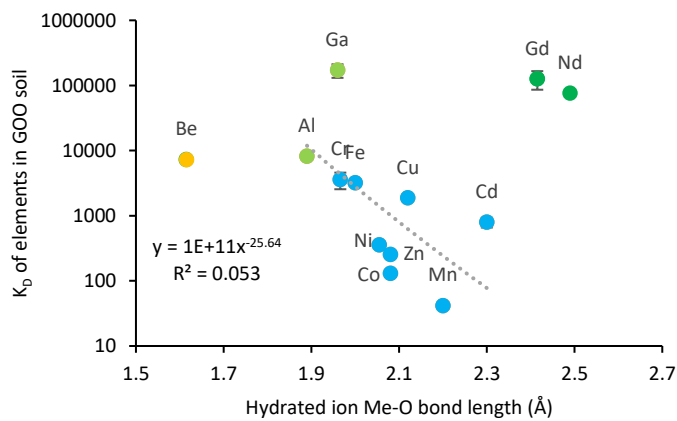
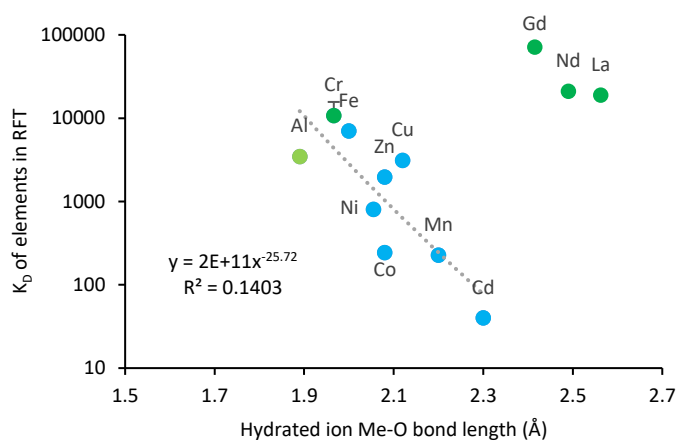
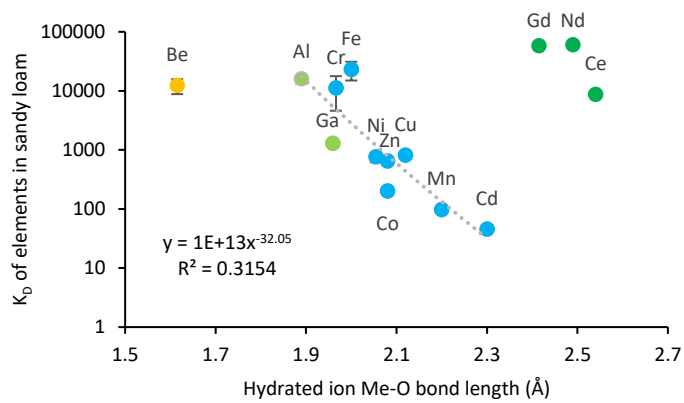


**Fig. 7.3 Effect of the hydrated radii of ions on the  $K_D$  and BACs of various elements in the RFMW soil**

Elements are coloured based on their position in the periodic table; ● group 1, ● group 2, ● transition elements, ● group 13, ● lanthanides.

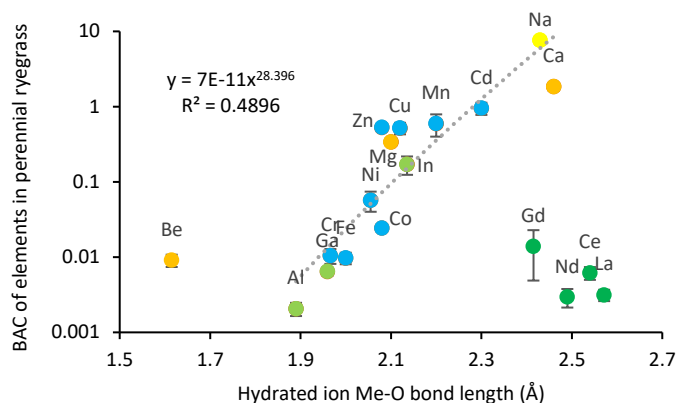
Correlating the hydrated radii to  $K_D$  and BAC has limited application, as data of the hydrated radii is lacking for many elements, such as Be, Ga, In, La, and Nd. However, data for a similar measurement is available for more elements-the length of the bond between the atom of the central element and oxygen atom in one of the inner-sphere water molecules (Me-O bond length)-and this data was plotted against  $K_D$  and BAC. For most of the elements measured, Me-O was negatively correlated with  $K_D$  in unspiked soil in the three soil types tested in Chapter 4 (Fig. 7.4), and positively correlated with the BACs of perennial ryegrass growing in unspiked soil in Chapter 5.1 (Fig. 7.5). Thus, if the  $K_D$  values or BACs of several elements are known and plotted against their Me-O bond length, the trendline can be used to calculate data for other elements.





**Fig. 7.4 Effect of hydrated ion Me-O bond length on the  $K_D$  of various elements in three different uncontaminated soil types**

Elements are coloured based on their position in the periodic table; ● group 1, ● group 2, ● transition elements, ● group 13, ● lanthanides.



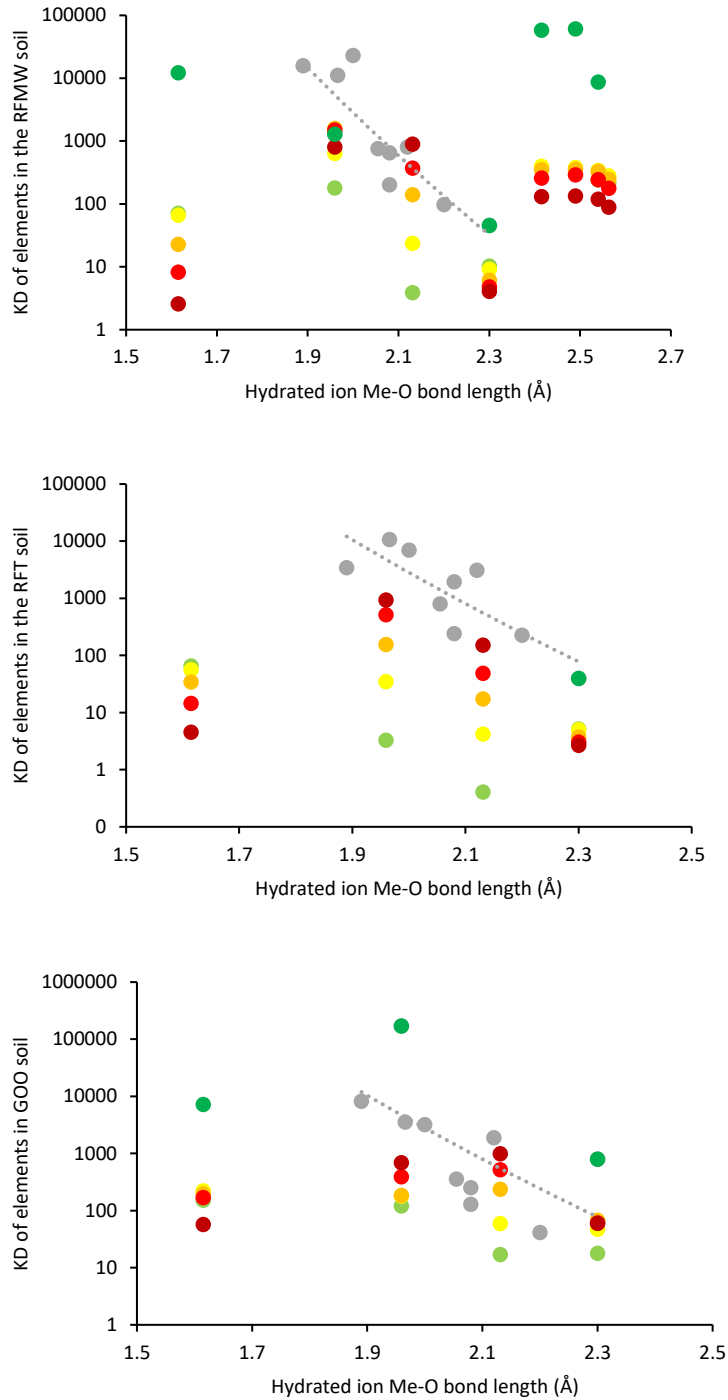
**Fig. 7.5 Effect of hydrated ion Me-O bond length on the BACs of various elements in perennial ryegrass growing in uncontaminated soil**

Elements are coloured based on their position in the periodic table; ● group 1, ● group 2, ● transition elements, ● group 13, ● lanthanides.

#### 7.2.2.1. Using Me-O to calculate the $K_D$ and BAC of contaminants

Using the Me-O bond length to estimate  $K_D$  and BAC is not suitable if the contamination causes the overall mobility of the element to change, as seen in Fig. 7.6 and Fig. 7.7.

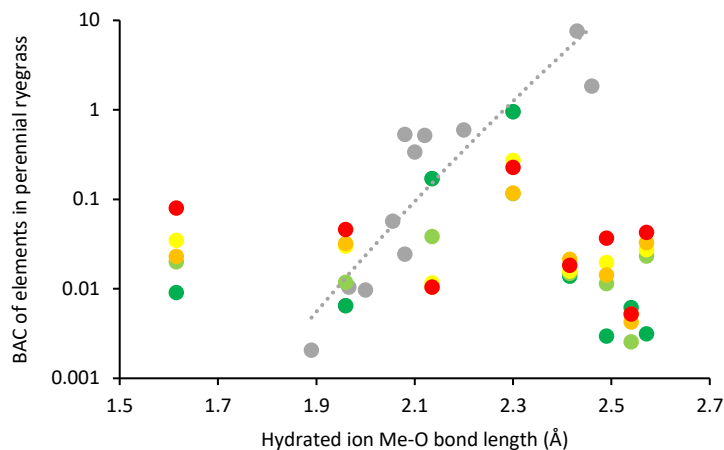
The Me-O bond length can be used to estimate the solubility and uptake of contaminants if the conditions cause the solubility of the contaminant to be similar to background levels. Examples of this are Ga and In added to soil at high concentrations (Fig. 4.1), Be, Cd, La, Ce, Nd, and Gd in soil with a high solution pH, and contaminants which have been in soil for several years thus have become strongly incorporated in the soil matrix. In spiked soils, the correlation between the Me-O and plant uptake is weaker than in the control (Fig. 7.6 and Fig. 7.7).



**Fig. 7.6 Effect of hydrated ion Me-O bond length on the  $K_D$  of various elements in three different soil types, at varying concentrations of Be, Cd, Ga, and In added to soil.**

Concentration added to soil solution: ● 0 mg L<sup>-1</sup>, ● 1 mg L<sup>-1</sup>, ● 3 mg L<sup>-1</sup>, ● 10 mg L<sup>-1</sup>, ● 30 mg L<sup>-1</sup>, ● 100 mg L<sup>-1</sup>, ● Elements which were not added to soil.

Me-O bond length of the ETECs and Cd listed in Table 7.2 to identify the elements.



**Fig. 7.7 Effect of hydrated ion Me-O bond length on the BACs of various elements in perennial ryegrass**

Multiple of the background concentration added to soil: ● 0 (control), ● 5 (T1), ● 10 (T2), ● 20 (T3), ● 40 (T4), ● Elements which were not added to soil.  
 Me-O bond length of the ETECs and Cd listed in Table 7.2 to identify the elements.

**Table 7.2 Me-O bond length of Be, Cd, Ga, In, La, Ce, Nd, and Gd, in order from shortest to longest**

Element	Me-O bond length (Å)
Be	1.615
Ga	1.9595
In	2.131
Cd	2.3
Gd	2.415
Nd	2.49
Ce	2.54
La	2.5629

#### 7.2.2.2. Elements that the Me-O bond length cannot be used for

There are some elements that do not fit the Me-O bond length versus  $K_D$  or BAC trendlines. In the data collected in Chapter 4 and 5.1, these elements were Be and the REEs. Beryllium has a small atom thus the Me-O bond length is short, however, it has a divalent charge thus sorption of Be to soil is distinct from the other elements. The REEs have large atomic masses thus long Me-O bonds but are trivalent, thus  $K_D$  is higher and bioaccumulation is lower than the trendline indicates.

Therefore, the trendlines for Me-O versus  $K_D$  and BAC are unlikely to fit ions which have small atoms thus short Me-O bonds (caused by the size small of the atom and not a high effective nuclear charge),

like Be and other elements with low atomic numbers, and large atoms which have large Me-O bonds but high effective nuclear charge, such as the REEs and other atoms with high atomic numbers.

To make this model inclusive for more elements, the  $K_D$  values and BACs could be measured for elements with high atomic numbers ( $\geq 55$ ) and identify if the pattern between Me-O and  $K_D$  and BAC is still applicable, as it would group elements where the main factor causing variation in the Me-O bond length is effective nuclear charge instead of atom size.

#### 7.2.2.3. *Environmental use of Me-O versus $K_D$ and BAC*

If the  $K_D$  values or BACs are found for some of the applicable elements identified in Fig. 7.4 and Fig. 7.5 (light transition or group 13), an exponential equation can be fitted and used to estimate solubility or bioaccumulation of other applicable elements in an environment. This method is easy to use, and does not require complex equations, specialised software, or measurements of other soil and plant properties.

It needs to be established which elements, or combinations of elements, can be used to create the equation of the relationship, and which elements have anomalous  $K_D$  values. This would require testing of more elements throughout the periodic table, and in different soil types, environments, and plant species, to identify potential limitations. Another limitation is that this method is not suited for contaminants, as their solubility deviates from the background concentrations of the elements.

### **7.3. The risk of recent contamination**

It has been reported in literature (Alloway, 2013) and demonstrated in the results that spiked ETECs are more mobile in soil than ETECs naturally in soil. In Chapter 4, most of the extractant concentrations were below the detection limit in unspiked soil, thus  $K_D$  could not be calculated but where it could, it was higher than all the spiked samples (Table 4.4.).

However, ETECs immobilise rapidly, and solubility and bioavailability is similar to background levels within a few years. The concentrations of Ga and In in the grasses in Ha et al. (2011) and Waterlot et al. (2013) were closer to the concentrations of Ga and In in the perennial ryegrass control than perennial ryegrass growing in the soil which had been spiked with Ga or In eight weeks previously (Chapter 5). Further research should analyse the effect of the time since spiking on the uptake of ETECs, ranging from months to years, to detect when the plant uptake and mobility of contaminants reaches background levels.

## 7.4. Effect of spatial distribution on plant ETEC concentrations

Soil I concentrations and properties affect the mobility of I in the soil-plant system, but the biggest factor affecting the concentration of I in grass in the field is the proximity to the sea, a source of I. It is therefore likely that for Be, Ga, In, La, Ce, Nd and Gd, which are less mobile in the soil plant system, the biggest factor affecting the concentration of these elements in plants in the field will be the proximity to and transport from a contaminant source. Plant ETEC concentrations could increase via increased plant uptake, but due to low BACs (Chapter 5.1, Table A.2) for a range of plant species ETEC concentrations are more likely to increase through sorption of contaminated soil to plant biomass (Fig. 7.8).

Therefore, it is recommended that contaminated soils should be managed to reduce erosion and thus transport other locations, or the transport pathways should be identified, and growth of edible biomass restricted in areas receiving the contaminated soil. Planting of non-edible plants is a good way to stabilise the soil and reduce erosion, but there is the risk of acidification through plant roots, which increases the solubility of most ETECs (Chapter 4) and risk of leaching and entering water bodies, thus the pH of the soil should be tested to make sure it is suitably high ( $\geq$  pH 6) before planting.

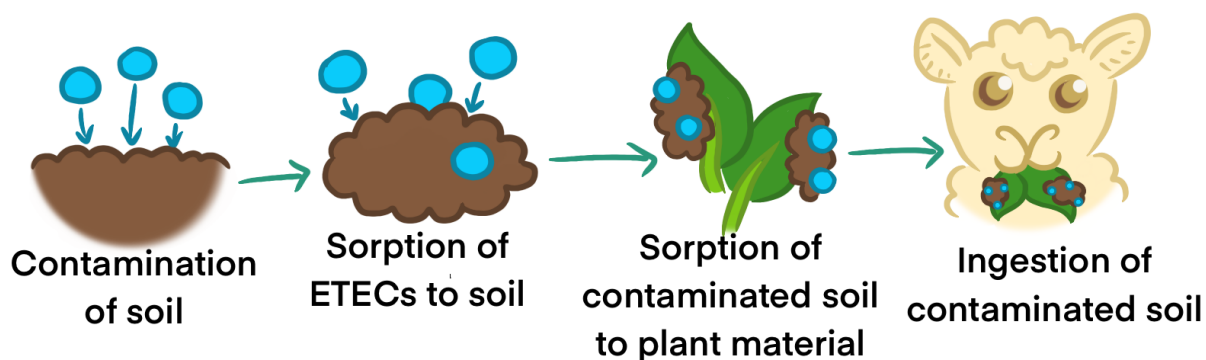


Fig. 7.8 Most likely pathway of the ETECs into the food chain.

## 7.5. Conclusions

### 7.5.1. Conclusions

The ETECs Be, Ga, In, La, Ce, Nd, and Gd have low mobility in the soil-plant system. Bismuth and Te could not be assessed, due to precipitation of soluble salts. Immobilization of the ETECs in soil increases in the order of  $Cd < Be < In < La < Ce < Nd < Gd < Ga$ .  $K_D$  decreases with increasing concentration added to soil and increases with increasing pH for Be, La, Ce, Nd, and Gd as hypothesised, but the  $K_D$  of Ga and In increases with increasing contaminant concentration due to precipitation within the soil

pH range. Gallium precipitation and thus  $K_D$  will peak at approximately pH 5.5-6, and In will peak at pH 5-9.

Gallium, Nd, and Gd are potentially phytotoxic to perennial ryegrass at  $\leq 40x$  the background concentration added to soil. Bioaccumulation of the ETECs in perennial ryegrass are lower than that of Cd. Of the ETECs, Be and La are most likely to be taken up by perennial ryegrass and translocated up the food chain.

In the environment, the source, soil concentration and properties that affect soil retention all affect the capacity of ETECs to be present in the above-ground biomass of plant material. Soil  $K_D$  is inversely proportional to the BACs in terrestrial plants, and for elements of similar atomic mass, the Me-O bond length of hydrated ions is correlated to  $K_D$  and BAC.

The ETECs Be, Ga, In, La, Ce, Nd, and Gd have a moderately low risk of entering the food chain via uptake by perennial ryegrass, but have a high risk through ingestion of soil sorbed to plant material. Contamination of the ETECs and migration of ETEC contaminated soil should be reduced where possible, and in contaminated soil mobility of the ETECs should be decreased by increasing the soil solution pH, adding OM, and planting species with low BACs of the ETECs.

#### 7.5.2. Recommendations for future work

##### *Measurement of absorption in human digestive systems*

As the ETECs except for Ga are soluble and bioavailable in acidic solutions, their absorption through the human digestive track should be measured, particularly in the stomach where the pH and thus likelihood of precipitation is the lowest. Bismuth and Te, which precipitated in the  $\text{Ca}(\text{NO}_3)_2$  extractant solution, should be tested in acidic solutions.

##### *Measurement of the concentrations of the ETECs in plants near a contamination source*

A study of the concentrations, bioaccumulation, and soil and environmental factors affecting the concentrations of the ETECs in plants near a contamination source e.g. mine tailings or e-waste should be conducted, to identify the factors other than proximity to the source that affect the concentrations of the ETECs in plant material e.g. as was completed for I in Chapter 6, with saltwater as the source.

*Measurement of uptake and bioaccumulation of the ETECs in Camellia sinensis grown in the same soil as perennial ryegrass*

Uptake and bioaccumulation of the ETECs should be compared between *Camellia sinensis* bushes and perennial ryegrass growing in the same conditions, to identify if it can take up and translocate higher concentrations of the ETECs.

*Comparison of the mobility of ETECs spiked at various time periods to background mobility*

$K_D$  values and BACs should be measured at various intervals since spiking and compared to the control, to identify when the mobility of ETEC contaminations is similar to their endogenous forms, to determine when the risk of increased plant uptake is significantly lessened.



## Appendix A

Table A.1 Solid-solution partition coefficients and sequential extraction soluble and exchangeable fractions of Be, Bi, Ga, Ge, In, Nd and Te.

Solid-solution partitioning							
Element	K <sub>0</sub> (L kg <sup>-1</sup> or mg kg <sup>-1</sup> /mg kg <sup>-1</sup> )			Calculated from data?	Contaminated?	Sample name/type (if multiple reported from one study)	Reference
	Mean	Minimum	Maximum				
Be	400	100	1,100				Sheppard et al. (2007)
	290					Peat, former fen	Sheppard et al. (2009)
	350					Clay gyttja, open fen	
	320					Mean	
	2,200			Yes			Tyler and Olsson (2002)
		2000	40,000				Watmough (2008)
Bi	39			Yes	Yes		Bhat et al. (2005)
	30,000	8,800	210,000				Sheppard et al. (2007)
	1,522			Yes			Tyler and Olsson (2002)
	307	40	973	Yes	Yes		Berthelot et al. (2008)
	8,040	2,736	13,888	Yes	Yes, experimental		Omouri et al. (2018)
		2,500	6,000		Yes		Dalvi et al. (2014)
Ce	44,000	440	3,700,000				Sheppard et al. (2007)
	39,000					Clayey till, fen	Sheppard et al. (2009)
	4,100					Peat, fen	
	1,700					Sandy till, oak forest	
	5,900					Clay gyttja, fen	
	3,800					Peat, former fen	
	4,400					Clay gyttja, open fen	
	88,000					Clayey till, arable	
	8,100					Mean	
	5,490			Yes			Tyler and Olsson (2002)
Ga	11,000	210	200,000				Sheppard et al. (2007)
	2,600					Clayey till, fen	Sheppard et al. (2009)
	1,300					Peat, fen	
	5,900					Sandy till, oak forest	
	9,400					Clay gyttja, fen	
	7,800					Peat, former fen	
	7,800					Clay gyttja, open fen	
	14,000					Clayey till, arable	
	5,500					Mean	
	14,211			Yes			Tyler and Olsson (2002)

		10,000	100,000						Watmough (2008)
Gd	17,000	390	340,000						Sheppard et al. (2007)
	22,000							Clayey till, fen	Sheppard et al. (2009)
	1,800							Peat, fen	
	1,200							Sandy till, oak forest	
	3,700							Clay gyttja, fen	
	2,400							Peat, former fen	
	5,100							Clay gyttja, open fen	
	51,000							Clayey till, arable	
	5,200							Mean	
	6,154								Tyler and Olsson (2002)
In	2,800	180	11,000						Sheppard et al. (2007)
	967				Yes				Tyler and Olsson (2002)
La	30,000	500	1,600,000						Sheppard et al. (2007)
	44,000							Clayey till, fen	Sheppard et al. (2009)
	2,600							Peat, fen	
	1,800							Sandy till, oak forest	
	5,900							Clay gyttja, fen	
	4,000							Peat, former fen	
	2,700							Clay gyttja, open fen	
	80,000							Clayey till, arable	
	7,200							Mean	
	5,305								Tyler and Olsson (2002)
Nd	29,000	430	1,100,000						Sheppard et al. (2007)
	46,000							Clayey till, fen	Sheppard et al. (2009)
	2,100							Peat, fen	
	1,500							Sandy till, oak forest	
	5,200							Clay gyttja, fen	
	3,200							Peat, former fen	
	7,300							Clay gyttja, open fen	
	76,000							Clayey till, arable	
	7,500							Mean	
	5,854				Yes				Tyler and Olsson (2002)
Te	1,100	750	1,700						Sheppard et al. (2007)
	115,714				Yes	Yes			Qin et al. (2017)
		0.32	2,443			Yes, experimental			Janik et al. (2015)
<b>Sequential extraction procedures</b>									
Element	Soluble and exchangeable fraction (%)			Not detected/ negligible?	Carbonate-bound fraction included?	Estimated from graph?	Contaminated?	Reference	
	Mean	Minimum	Maximum						
Be	3.9	1.2	7.4		Yes			Ovari et al. (2001)	
				Yes					

Be	3.92	1.56	12.5			Yes	Zádrapová et al. (2019)
Bi				Yes		Yes	Pueyo et al. (2003)
	20	3	70			Yes	Favas et al. (2011)
				Yes			Hou et al. (2006)
	1.8	-	5.7		Yes	Yes, experimental	Murata et al. (2018)
			Yes		Yes	Wen et al. (2013)	
Ce	1.2					Unknown	Hu et al. (2006)
	0.39	0.23	0.63	Yes			Li et al. (1998)
	0.73	0.38	1.47	Yes			
		0.15	4.3	Yes			Land et al. (1999)
		0.031	0.19	Yes			Stille et al. (2009)
		0.024	0.081	Yes			
	9.5				Yes		Xinde et al. (2000)
	3.7				Yes		
		0.3	7.6	Yes			Perelomov et al. (2012)
		1.9	6.7	Yes			
		5	13	Yes	Yes		Šmuc et al. (2012)
		0.0025	0.32				Fu et al. (2001)
	Ga	32.7	19.3	40.8			
28.6		14.7	38.5			Yes	
49.6							Pofedniok (2008)
23.8						Yes	
Gd	0.62						Wiche et al. (2017)
	1.1					Unknown	Hu et al. (2006)
	0.54	0.35	0.82	Yes			Li et al. (1998)
	0.83	0.25	1.35	Yes			
		0.31	5.8	Yes	Yes		Land et al. (1999)
		0.030	0.24	Yes			Stille et al. (2009)
		0.14	0.55	Yes			
	8				Yes		Xinde et al. (2000)
	1.5				Yes		
		0.5	15.8	Yes			Perelomov et al. (2012)
		3.6	13.8	Yes			
		13.5	29	Yes	Yes		Šmuc et al. (2012)
		0.0045	0.56				Fu et al. (2001)
In				Yes			Hou et al. (2006)
	21	2	42		Yes	Yes, experimental	Murata et al. (2018)
		5.5	59.5	Yes		Yes	Waterlot et al. (2013)
			4	Yes		Yes	
			3	Yes		Yes	Boughriet et al. (2007)
				Yes	Yes		Wen et al. (2013)

La	0.38			Yes					Wiche et al. (2017)
		0.3	0.5	Yes					Wiche et al. (2016)
	1.4						Unknown		Hu et al. (2006)
	0.59	0.35	0.94						Li et al. (1998)
	1.05	0.55	1.86						
		0.41	5.6	Yes					Land et al. (1999)
		0.026	0.085	Yes					Stille et al. (2009)
		0.018	0.083	Yes					
	9.5						Yes		Xinde et al. (2000)
	2.6						Yes		
		0.3	4.8	Yes					Perelomov et al. (2012)
		1.3	4.9	Yes					
		6.3	14.4	Yes	Yes				Šmuc et al. (2012)
		0.0067	0.68						Fu et al. (2001)
Nd	0.45								Wiche et al. (2017)
		0.4	0.5						Wiche et al. (2016)
	0.6						Unknown		Hu et al. (2006)
	0.89	0.42	1.74	Yes					Li et al. (1998)
	0.58	0.38	0.89	Yes					
		0.28	4.58	Yes					Land et al. (1999)
		0.0055	0.12	Yes					Stille et al. (2009)
		0.031	0.10	Yes					
	4.7						Yes		Xinde et al. (2000)
	<1						Yes		
		0.3	11.4	Yes					Perelomov et al. (2012)
		2.5	10.5	Yes					
		8.1	19.4	Yes	Yes				Šmuc et al. (2012)
		0.0032	0.53						Fu et al. (2001)

**Table A.2 Concentrations, soil bioaccumulation coefficients and translocation factors of Be, Bi, Ga, Ge, In, Nd and Te in various terrestrial plant species not exhibiting toxicity.**

Category <sup>a</sup>	Species	Concentration (mg kg <sup>-1</sup> DW)		BAC <sup>c</sup>		TF <sup>d</sup>		Experimentally contaminated?	Reference
		Mean	Range	Below DL? <sup>b</sup>	Mean	Range	Mean		
<b>Beryllium</b>									
Poaceae A	Barley	0.6						Yes	Davis et al. (1978)
	Wheat and barley				0.0029		0.035		Omberg et al. (2011)
	Oat	2						Yes	Bohn and Seekamp (1979)
	Grass		0.00099-0.0051			0.00033-0.0017			Germund Tyler and Tommy Olsson (2001)

Poaceae B	Wheat		0.0005			Eriksson (2001)		
	Barley		0.0005			Eriksson (2001)		
	Wheat and barley			0.0016	0.019	Omberg et al. (2011)		
Vegetable A	Collards	10		0.22		Yes	Kaplan et al. (1990)	
	Cabbage	2			0.0022	Yes	Hara et al. (1977)	
	Cabbage	0.000057	0.000013-0.000126				Filippini et al. (2019)	
	Lettuce		0.02-0.06	0.02-0.03		0.12-1.96	Wang et al. (2021)	
	Kale	0.07	0.03-0.23			Yes	Williams and Le Riche (1968)	
	Leafy vegetables	0.000436	0.000164-0.001583				Filippini et al. (2019)	
	Soybean	0.40	0.25-0.6			Yes	Sajwan et al. (1996)	
	Potato	30				Yes	Bohn and Seekamp (1979)	
	Mushroom		0.082-0.25				Agafonova et al. (2007)	
	Mushroom		0.02-0.18				Ivanić et al. (2019)	
	Mushroom	0.000081	0.000038-0.000082				Filippini et al. (2019)	
	Amaranth	0.1		0.06		1.96	Wang et al. (2021)	
	<i>Pachyrhizus erosus</i> (Linn.) Urb	0.17		0.07		6.8	Wang et al. (2021)	
	<i>Ipomoea aquatica</i> Forsk	0.04		0.04		0.32	Wang et al. (2021)	
	<i>Beta vulgaris</i> L		0.01-0.04		0.01-0.02		0.37-2.67	Wang et al. (2021)
	<i>Brassica oleracea</i> L	0.18		0.27		1.03	Wang et al. (2021)	
	<i>Allium fistulosum</i> L		0.02-0.06		0.05-0.26		0.05-0.47	Wang et al. (2021)
<i>Capsicum annuum</i> L	0.04		0.06		2.86	Wang et al. (2021)		
<i>Sonchus oleraceus</i>		0.07-0.20		0.08-0.21		0.36	Wang et al. (2021)	
<i>Cichorium endivia</i> L	0.07		0.04		1.15	Wang et al. (2021)		
Vegetable B	Potato		5			Yes	Bohn and Seekamp (1979)	
	Potato	0.000109	0.000019-0.000376				Filippini et al. (2019)	
	Tomato	0.000032	0.000001-0.000093				Filippini et al. (2019)	
	Onion and garlic	0.000052	0.000019-0.000121				Filippini et al. (2019)	
	Root vegetables	0.000057	0.000016-0.000275				Filippini et al. (2019)	
Other A	Beech	0.0065		0.12			Tyler (2005)	
	Spruce		0.1				Navrátil et al. (2002)	
	Beech		0.016-0.22				Navrátil et al. (2002)	
	Alder		0.14-0.42				Navrátil et al. (2002)	
	Strawberry		0.2-0.3				Jeon et al. (2019)	
	Yerba mate (edible)	0.023	0.002-0.12				Motta et al. (2020)	
	<i>Calhina vulgaris</i>	0.0063			0.19		Schmidt and Dietl (1988)	

	<i>Salvia</i> species		0.0086-0.031				Tunay et al. (2020)
	Monocotyledonous plants	0.023	<DL-0.127				Zádrapová et al. (2019)
	Dicotyledonous plants	0.032	<DL-0.102				Zádrapová et al. (2019)
Other B	Strawberry	0.4					Jeon et al. (2019)
	Citrus fruit		≥0.000018				Filippini et al. (2019)
<b>Bismuth</b>							
Category	Species	Concentration	BAC	TF	Experimentally contaminated?	Reference	
Poaceae A	Wheat and barley		0.0036	0.12			Omberg et al. (2011)
	Grass		0.00042-0.001	0.00095-0.0024			Germund Tyler and Tommy Olsson (2001)
		0.049	0.01-0.21				Li and Thornton (1993)
	Lakebank sedge and grass		≤0.095		Yes		Fahey et al. (2008)
Poaceae B	Wheat	0.0003	0.0001-0.0005				Eriksson (2001)
	Barley	0.00048	0.0002-0.0009				Eriksson (2001)
	Wheat and barley		0.0014	0.045			Omberg et al. (2011)
	Corn		0.01-0.03				Jung et al. (2002)
Vegetable A	Soybean		0.02-0.13				Jung et al. (2002)
	Mushroom	2.7	1.9-9				Muñoz et al. (2005)
		1664	236-8894	1.1	0.16-5.0		Elekes and Gabriela (2010)
		1.3	≤5.9				Dursun et al. (2006)
		0.98	≤1.6	0.01			Niedzielski et al. (2017)
	Mushroom		0.04-0.08				Ivanić et al. (2019)
Vegetable B	Pepper		0.01-0.04				Jung et al. (2002)
	Spring onion		0.05-0.42				Jung et al. (2002)
Other A	Tea	0.022	0.0039-0.11				王小平 et al. (2008)
	Perilla		0.04-0.11				Jung et al. (2002)
	Umbelliferae family		0.02-0.14	0.009-0.07			Pueyo et al. (2003)
	Beech	0.0035		0.038			Tyler (2005)
	<i>Buddleia davidii</i>	2.9					Wei et al. (2011)
	<i>Potentilla acervata</i>		0.01-1.58	0.001-0.047			Yurgenson and Gorban (2020)
Other B	Jujube		0.01-0.04				Jung et al. (2002)
<b>Cerium</b>							
Category	Species	Concentration	BAC	TF	Experimentally contaminated?	Reference	
Poaceae A	Wheat		0.064-2.0	0.0018-0.032	0.0035-0.51	REE Fertilizer	Wen et al. (2001)
		0.27	0.070-0.65				Li et al. (2001)
		2.8	0.23-16				Fang et al. (2007)
		0.40	0.19-0.68				Zhang and Shan (2001)
	Barley		≤∞2	0.0037-0.010		Yes	Kotelnikova et al. (2020)

	Wheat and barley		0.48	0.048		Omberg et al. (2011)
	Rice	0.031-19		0.00049-2.54	0.012-5.0	REE Fertilizer
		0035-0.72				Li et al. (1998)
	Corn	0.034-0.63				Li et al. (1998)
	Grass	0.024-0.45				Germund Tyler and Tommy Olsson (2001)
		0.33	0.0044			Laul et al. (1979)
	<i>Sasa nipponica</i>	0.0046-0.11				Fu et al. (2001)
Poaceae B	Wheat	0.071-0.13		0.0018-0.0028	0.0021-0.094	REE Fertilizer
		0.0034	0.0019-0.0076			Eriksson (2001)
	Barley	0.0044	0.0023-0.0091			Eriksson (2001)
	Wheat and barley		0.14	0.014		Omberg et al. (2011)
	Rice	0.0046-0.049		0.00069-0.00097	0.0015-0.053	REE Fertilizer
		0.0036	0.0016-0.0056			Li et al. (1998)
		0.036	0.017-0.078	0.00047	0.00021-0.0010	Šmuc et al. (2012)
	Corn	0.0040	0.0018-0.011			Li et al. (1998)
Vegetable A	Rape	2.36	0.024			Cao et al. (2000)
	Cabbage	0.10-0.68		0.0016-0.011		REE Fertilizer
	Chinese cabbage	0.71-3.8		0.011-0.062		REE Fertilizer
	Tomato	0.469	0.205-0.757			Spalla et al. (2009)
	Pepper	1.3-2.27		0.013-0.0227	0.38-0.66	Cao et al. (2000)
	Leafy vegetables		0.0062			Sheppard et al. (2010)
	Various vegetables	0.029				Zhuang et al. (2017)
Vegetable B	Cucumber	0.041-0.045		0.00065-0.00072		REE Fertilizer
	Tomato	0.015-1.3		0.00023-0.022		REE Fertilizer
		0.00797	0.00378-0.01144			Spalla et al. (2009)
	Pepper	0.19	0.0019	0.055		Cao et al. (2000)
	Root crops		0.00067			Sheppard et al. (2010)
Other A	Tea	0.0063-0.11		0.017-0.29		Fu et al. (2001)
		0.72	0.0072			Cao et al. (2000)
		0.69	0.11-1.39			Pengbo et al. (2010)
	<i>Vicia villosa</i>	0.024-0.099		0.079-0.33		Fu et al. (2001)
	<i>Taxodium japonicum</i>	0.0089-0.075		0.10-0.87		Fu et al. (2001)
	<i>Populus sieboldii</i>	0.0176-0.55		0.17-5.3		Fu et al. (2001)
	<i>Dicranopteris dichotoma</i>	738.63-2290.33		1.8-5.4	0.50-1.5	Khan et al. (2017)
	<i>Dicranopteris linearis</i>	95.5-98.66		0.37-0.56	0.14-0.27	Khan et al. (2017)
	<i>Melastoma malabathricum</i>	118.53-187.44		1.9-3.1	2.4-3.9	Khan et al. (2017)

	<i>Cyperus difformis</i> <i>Rottb.</i>	24.96		0.16		0.42		Khan et al. (2017)
	<i>Cyperus kyllingia</i> Rottb.	410.63		2.3		25		Khan et al. (2017)
	<i>Cyperus distans</i> L.		123.6-684.47		2.2-3.8		0.58-3.2	Khan et al. (2017)
	<i>Cyperus rotundus</i> L.		339.69- 2283.67		1.3-8.5		0.25-1.7	Khan et al. (2017)
	<i>Filipendula ulmaria</i>	0.065						Tyler and Olsson (2005)
	<i>Geum rivale</i>	0.10						Tyler and Olsson (2005)
	<i>Ranunculus ficaria</i>	0.14						Tyler and Olsson (2005)
	<i>Anemone nemorosa</i>	0.30						Tyler and Olsson (2005)
	<i>Convallaria majalis</i>	0.026						Tyler and Olsson (2005)
	<i>Stellaria nemorum</i>	0.042						Tyler and Olsson (2005)
	<i>Maianthemum bifolium</i>	0.12						Tyler and Olsson (2005)
	<i>Trientalis europaea</i>	0.053						Tyler and Olsson (2005)
Other B	Fruit			<b>0.00021</b>				Sheppard et al. (2010)
<b>Gallium</b>								
<b>Category</b>	<b>Species</b>	<b>Concentration</b>		<b>BAC</b>		<b>TF</b>	<b>Experimentally contaminated?</b>	<b>Reference</b>
Poaceae A	Wheat and barley			0.0024		0.028		Omberg et al. (2011)
	Wheat		2.36-12.1				Yes	Syu et al. (2021)
	Rice		≤7.4		≤0.16		Yes	Su et al. (2018)
			≤75				Yes	Syu et al. (2017)
		6.5				0.27	Yes	Yu et al. (2015)
			5.02-71.4			0.058	Yes	Syu et al. (2020)
	Grass	0.36	0.23-0.58					Ha et al. (2011)
Poaceae B	Wheat		≤0.0014	0.001				Eriksson (2001)
	Barley	0.001	≤0.0019					Eriksson (2001)
	Wheat and barley			0.0016		0.019		Omberg et al. (2011)
	Rice		0.14-0.83				Yes	Syu et al. (2020)
Vegetable A	Mushroom	0.15	0.08-0.33					Niedzielski et al. (2017)
		2.7	1.4-6.6					Dursun et al. (2006)
	Fungi		1-2					Campos et al. (2012)
Other A	<i>Ageratum houstonianum</i>	0.89	0.68-1.28			1.7		Ha et al. (2011)
	<i>Commelina communis</i>	1.1	0.42-1.52			0.57		Ha et al. (2011)
	<i>Diplazium esculenta</i>	0.68	0.29-1.3			0.22		Ha et al. (2011)
	<i>Equisetum diffusum</i>	0.82	0.13-1.19			0.13		Ha et al. (2011)
	<i>Houttuynia cordata</i>	2.6	0.35-6.75			0.87		Ha et al. (2011)
	<i>Kyllingia nemoralis</i>	1.2	0.72-2.14			0.48		Ha et al. (2011)
	<i>Potamogeton oxyphyllus</i>	3.4	0.92-5.97			0.86		Ha et al. (2011)
	<i>Pteris vittata</i>	0.68	0.21-2.03			0.17		Ha et al. (2011)
	<i>Selaginella delicatula</i>	1.4	0.46-1.91			0.43		Ha et al. (2011)



	Beech	0.032		0.077			Tyler (2005)
	Strawberry		2.3-3.5				Jeon et al. (2019)
Other B	Strawberry	0.4					Jeon et al. (2019)
<b>Gadolinium</b>							
Category	Species	Concentration	BAC	TF	Experimentally contaminated?	Reference	
Poaceae A	Wheat	0.0033-0.22		0.0011-0.042	0.0014-0.44	REE Fertilizer	Wen et al. (2001)
		0.021	0.0065-0.047				Li et al. (2001)
	Barley	0.005-0.017					Wiche et al. (2016)
	Millet	0.011-0.031					Wiche et al. (2016)
	Rice	0.011-0.49		0.0020-0.15	0.036-2.0	REE Fertilizer	Wen et al. (2001)
		0.0071-0.050					Li et al. (1998)
	Corn	0.0033-0.052					Li et al. (1998)
		0.016					Wiche et al. (2016)
	Oat	0.056					Wiche et al. (2016)
	Grass	0.009-0.010					Wiche et al. (2016)
0.0031-0.025						Germund Tyler and Tommy Olsson (2001)	
		0.037		0.0060			Laul et al. (1979)
	<i>Sasa nipponica</i>	0.00071-0.0086					Fu et al. (2001)
Poaceae B	Wheat	0.0025-0.012		0.00079-0.0022	0.0017-0.097	REE Fertilizer	Wen et al. (2001)
		0.0002	<0.0001-0.0003				Eriksson (2001)
	Barley	0.0003	<0.0001-0.0005				Eriksson (2001)
	Rice		0.00039-0.011	0.00046-0.0021	0.0014-0.049	REE Fertilizer	Wen et al. (2001)
Vegetable A	Rape	0.16		0.035			Cao et al. (2000)
	Cabbage		0.010-0.034	0.0020-0.0065		REE Fertilizer	Wen et al. (2001)
	Chinese cabbage		0.039-0.15	0.0075-0.028		REE Fertilizer	Wen et al. (2001)
	Tomato	0.0414	0.0177-0.0668				Spalla et al. (2009)
	Pepper		0.13-0.21	0.016-0.027	0.46-0.75		Cao et al. (2000)
	Mushroom	0.023	<0.01-0.05				Niedzielski et al. (2017)
	Various vegetables	0.0020					Zhuang et al. (2017)
Vegetable B	Cucumber	0.0021-0.0026		0.00039-0.00050		REE Fertilizer	Wen et al. (2001)
	Tomato	0.00079-0.039		0.00015-0.0075		REE Fertilizer	Wen et al. (2001)
		0.00102	0.00046-0.00167				Spalla et al. (2009)
Pepper	0.015		0.0019	0.0054		Cao et al. (2000)	
Other A	Tea		0.0047-0.033	0.031-0.22			Fu et al. (2001)

		0.066-0.07		0.0082-0.011			Cao et al. (2000)
	<i>Vicia villosa</i>	0.0026-0.015		0.040-0.23			Fu et al. (2001)
	<i>Taxodium japonicum</i>	0.0017-0.0068		0.0032-0.13			Fu et al. (2001)
	<i>Populus sieboldii</i>	0.013-0.67		0.061-3.2			Fu et al. (2001)
	<i>Dicranopteris dichotoma</i>	47.49-75.08		1.1-1.8		0.30-0.48	Khan et al. (2017)
	<i>Dicranopteris linearis</i>	3.23-6.6		0.10-0.58		0.033-0.34	Khan et al. (2017)
	<i>Melastoma malabathricum</i>	25.66-139.52		1.5-8.1		1.8-9.7	Khan et al. (2017)
	<i>Cyperus difformis</i> Rottb.	36.53	1.6		3.1		Khan et al. (2017)
	<i>Cyperus kyllingia</i> Rottb.	87.3	2.6		13		Khan et al. (2017)
	<i>Cyperus distans</i> L.	58.47-74.41		0.96-2.2		1.8-2.3	Khan et al. (2017)
	<i>Cyperus rotundus</i> L.	118.2-175.8		3.9-5.7		0.52-0.77	Khan et al. (2017)
	<i>Filipendula ulmaria</i>	0.0071					Tyler and Olsson (2005)
	<i>Geum rivale</i>	0.0099					Tyler and Olsson (2005)
	<i>Ranunculus ficaria</i>	0.015					Tyler and Olsson (2005)
	<i>Anemone nemorosa</i>	0.033					Tyler and Olsson (2005)
	<i>Convallaria majalis</i>	0.0030					Tyler and Olsson (2005)
	<i>Stellaria nemorum</i>	0.0047					Tyler and Olsson (2005)
	<i>Maianthemum bifolium</i>	0.0069					Tyler and Olsson (2005)
	<i>Trientalis europaea</i>	0.0044					Tyler and Olsson (2005)
Other B	Lupin	0.004-0.063					Wiche et al. (2016)
<b>Indium</b>							
Category	Species	Concentration	BAC	TF	Experimentally contaminated?	Reference	
Poaceae A	Rice	≤4.3		≤0.075	≤0.30	Yes	Su et al. (2018)
		0.03-0.97			0.03-0.99	Yes	Syu et al. (2020)
	Rice	0.20-0.25		0.0012-0.0022			Chang et al. (2020)
	Grass	0.23	0.03-0.32		0.17		Ha et al. (2011)
		0.030	0.016-0.051	0.085	0.03-0.22		Waterlot et al. (2013)
	Wheat	0.027-1.12				0.01-1.33	Yes
Poaceae B	Wheat	0.06-0.19		0.0005-0.0017			Chang et al. (2020)
	Wheat		0.005				Eriksson (2001)
	Wheat	0.007-0.011		0.00065-0.00092			Chang et al. (2020)
	Barley		0.005				Eriksson (2001)
	lettuce	0.012-0.015		0.068-0.081			Waterlot et al. (2013)
	Rice	0.00368-0.0167				Yes	Syu et al. (2020)
	Rice	0.009-0.012		0.00083-0.00106			Chang et al. (2020)
Vegetable A	Mushroom	4.4	1.5-7.5				Niedzielski et al. (2017)

Other A	<i>Ageratum houstonianum</i>	0.87	0.51-1.54		0.82		Ha et al. (2011)
	<i>Commelina communis</i>	0.32	0.06-0.48		1.1		Ha et al. (2011)
	<i>Diplazium esculenta</i>	2.1	1.03-3.19		2.6		Ha et al. (2011)
	<i>Equisetum diffusum</i>	0.14	0.01-0.45		0.25		Ha et al. (2011)
	<i>Houttuynia cordata</i>	1.1	0.07-2.32		3.7		Ha et al. (2011)
	<i>Kyllingia nemoralis</i>	0.56	0.14-1.69		1.7		Ha et al. (2011)
	<i>Potamogeton oxyphyllus</i>	1.1	0.26-2.22		1.8		Ha et al. (2011)
	<i>Pteris vittata</i>	0.98	0.04-5.14		0.62		Ha et al. (2011)
	<i>Selaginella delicatula</i>	3.9	3.12-4.28		9.7		Ha et al. (2011)
		Beech	0.0002		0.029		
<b>Lanthanum</b>							
Category	Species	Concentration	BAC	TF	Experimentally contaminated?	Reference	
Poaceae A	Wheat		0.055-0.94	0.0022-0.031	0.0040-0.54	REE Fertilizer	Wen et al. (2001)
		0.15	0.043-0.37				Li et al. (2001)
		1.3	0.11-7.2				Fang et al. (2007)
		0.21	0.12-0.43				Zhang and Shan (2001)
	Barley		0.024-0.077				Wiche et al. (2016)
	Barley		≤∞6	0.020-0.037		Yes	Kotelnikova et al. (2020)
	Wheat and barley			0.0024	0.056		Omberg et al. (2011)
	Millet		0.033-0.98				Wiche et al. (2016)
	Rice		0.012-1.4	0.00039-0.24	0.017-0.32	REE Fertilizer	Wen et al. (2001)
			0.021-0.37				Li et al. (1998)
	Corn		0.019-0.34				Li et al. (1998)
			0.01				Wiche et al. (2016)
	Oat		0.15				Wiche et al. (2016)
	Grass		0.064-0.065				Wiche et al. (2016)
		0.021-0.22				Germund Tyler and Tommy Olsson (2001)	
		0.17	0.0047			Laul et al. (1979)	
	<i>Sasa nipponica</i>		0.0039-0.087			Fu et al. (2001)	
Poaceae B	Wheat		0.042-0.074	0.0021-0.0039	0.0025-0.10	REE Fertilizer	Wen et al. (2001)
		0.0017	0.0009-0.0043				Eriksson (2001)
	Barley	0.0026	0.0012-0.0057				Eriksson (2001)
	Wheat and barley			0.00061	0.014		Omberg et al. (2011)
	Rice		0.0040-0.048	0.00033-0.0016	0.00040-0.073	REE Fertilizer	Wen et al. (2001)
		0.0018	0.00091-0.0032				Li et al. (1998)
	0.027	0.009-0.035	0.00046	0.00023-0.00096		Šmuc et al. (2012)	

Vegetable A	Corn	0.0015	0.001-0.006			Li et al. (1998)
	Rape	11.7		0.24		Cao et al. (2000)
	Cabbage		0.065-0.83		0.0022-0.028	REE Fertilizer Wen et al. (2001)
	Chinese cabbage		0.080-3.5		0.0027-0.12	REE Fertilizer Wen et al. (2001)
	Tomato	0.322	0.131-0.792			Spalla et al. (2009)
	Pepper		0.77-1.54		0.016-0.031	0.41-0.81 Cao et al. (2000)
	Mushroom	0.047	<0.01-0.13			Niedzielski et al. (2017)
	Leafy vegetables			0.0068		Sheppard et al. (2010)
Various vegetables	0.017				Zhuang et al. (2017)	
Vegetable B	Cucumber		0.021-0.025		0.00070- 0.00084	REE Fertilizer Wen et al. (2001)
	Tomato	0.00749	0.0043-0.96		0.00014-0.032	REE Fertilizer Wen et al. (2001)
	Pepper	0.19	0.00297- 0.01569			Spalla et al. (2009)
Vege b	Root crops			0.0038	0.10	Cao et al. (2000)
	Other A		0.00075			Sheppard et al. (2010)
Other A	Tea		0.012-0.072		0.030-0.18	Fu et al. (2001)
			0.62-0.66		0.013-0.015	Cao et al. (2000)
		0.55	0.07-1.16			Pengbo et al. (2010)
	<i>Vicia villosa</i>		0.014-0.072		0.063-0.32	Fu et al. (2001)
	<i>Taxodium japonicum</i>		0.0073-0.049		0.024-0.17	Fu et al. (2001)
	<i>Populus sieboldii</i>		0.098-3.4		0.084-2.9	Fu et al. (2001)
	<i>Dicranopteris dichotoma</i>		59.39-1568		0.63-17	Khan et al. (2017)
	<i>Dicranopteris linearis</i>		48.27-101.32		0.78-2.9	0.082-0.22 Khan et al. (2017)
	<i>Melastoma malabathricum</i>		36.43-158.59		1.0-4.5	1.3-5.6 Khan et al. (2017)
	<i>Cyperus difformis</i> Rottb.	17.71		0.27		0.60 Khan et al. (2017)
	<i>Cyperus kyllingia</i> Rottb.	365.84		6.1		35 Khan et al. (2017)
	<i>Cyperus distans</i> L.		145.63-413.8		3.5-5.0	0.70-2.0 Khan et al. (2017)
	<i>Cyperus rotundus</i> L.		396.4-568.9		6.6-9.5	0.42-0.61 Khan et al. (2017)
	<i>Filipendula ulmaria</i>	0.050				Tyler and Olsson (2005)
	<i>Geum rivale</i>	0.084				Tyler and Olsson (2005)
	<i>Ranunculus ficaria</i>	0.10				Tyler and Olsson (2005)
	<i>Anemone nemorosa</i>	0.44				Tyler and Olsson (2005)
	<i>Convallaria majalis</i>	0.025				Tyler and Olsson (2005)
	<i>Stellaria nemorum</i>	0.035				Tyler and Olsson (2005)
<i>Maianthemum bifolium</i>	0.075				Tyler and Olsson (2005)	
<i>Trientalis europaea</i>	0.031				Tyler and Olsson (2005)	
Other B	Lupin		0.20-0.39			Wiche et al. (2016)
Other B	Fruit			0.00035		Sheppard et al. (2010)
<b>Neodymium</b>						

Category	Species	Concentration	BAC	TF	Experimentally contaminated?	Reference			
Poaceae A	Wheat	0.026-0.79		0.0017-0.029	0.0027-0.61	REE Fertilizer	Wen et al. (2001)		
		0.12	0.034-0.31				Li et al. (2001)		
		1.2	0.10-6.9				Fang et al. (2007)		
		0.13	0.08-0.15		0.046		Zhang and Shan (2001)		
	Barley		0.02-0.63				Wiche et al. (2016)		
	Barley		≤∞7	0.030-0.039		Yes	Kotelnikova et al. (2020)		
	Wheat and barley		0.0022	0.054			Omberg et al. (2011)		
	Millet		0.028-0.087				Wiche et al. (2016)		
	Rice		0.091-0.29				Li et al. (1998)		
			0.010-0.64	0.00037-0.22	0.014-0.50	REE Fertilizer	Wen et al. (2001)		
	Oat	0.14					Wiche et al. (2016)		
	Corn		0.016-0.25		0.20		Li et al. (1998)		
	Corn	0.081					Wiche et al. (2016)		
	Grass		≤1.79	0.022	0.006-0.05	0.063	0.018-0.14	Yes	Carpenter et al. (2015)
			0.016-0.22					Germund Tyler and Tommy Olsson (2001)	
		0.15	0.0043				Laul et al. (1979)		
Grass		0.049-0.051					Wiche et al. (2016)		
<i>Sasa nipponica</i>		0.0020-0.044	0.0053				Fu et al. (2001)		
Poaceae B	Wheat	0.0012	0.0006-0.0028				Eriksson (2001)		
			0.020-0.044	0.0012-0.0019	0.0016-0.078	REE Fertilizer	Wen et al. (2001)		
	Barley	0.0015	0.0007-0.0033				Eriksson (2001)		
	Wheat and barley			0.00053	0.013			Omberg et al. (2011)	
	Rice		0.0011-0.0030					Li et al. (1998)	
			0.0021-0.016		0.00055-0.00088	0.0016-0.11	REE Fertilizer	Wen et al. (2001)	
	0.014	0.008-0.029	0.00042	0.00021-0.00086			Šmuc et al. (2012)		
Corn	0.0010	0.00085-0.0053		0.0014			Li et al. (1998)		
Vegetable A	Rape	3.08	0.075				Cao et al. (2000)		
	Cabbage		0.092-0.23	0.0033-0.0085		REE Fertilizer	Wen et al. (2001)		
	Chinese cabbage		0.10-0.77	0.0038-0.029		REE Fertilizer	Wen et al. (2001)		
	Pepper		0.6-1.11	0.015-0.027	0.35-0.64		Cao et al. (2000)		
	Tomato	0.28	0.14-0.48					Spalla et al. (2009)	
			≤3.02	0.013	0.007-0.016	0.097	0.027-0.21	Yes	Carpenter et al. (2015)
	Mushroom	0.29	0.11-0.45					Niedzielski et al. (2017)	
4.5		2.8-7.1					Campos et al. (2009)		
Radish		≤4.21	0.021	0.02-0.022	0.15	0.095-0.25	Yes	Carpenter et al. (2015)	
Vege a	Leafy vegetables		0.0043				Sheppard et al. (2010)		
Vegetable B	Pepper	0.096	0.0023	0.055			Cao et al. (2000)		

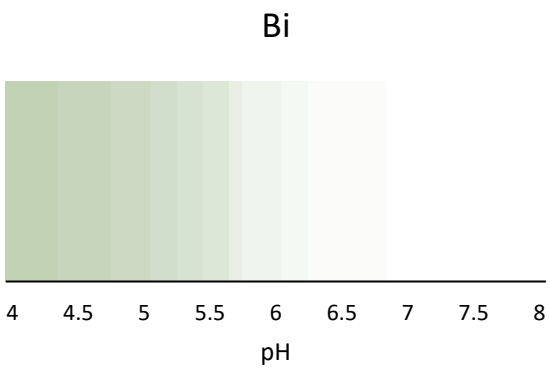
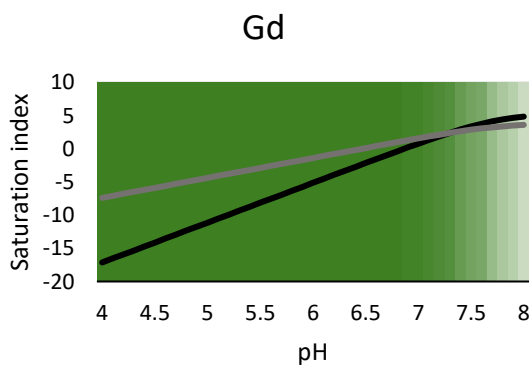
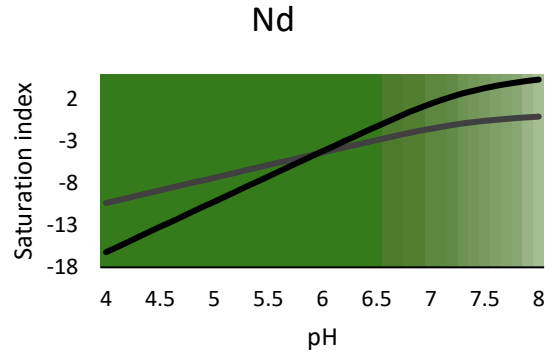
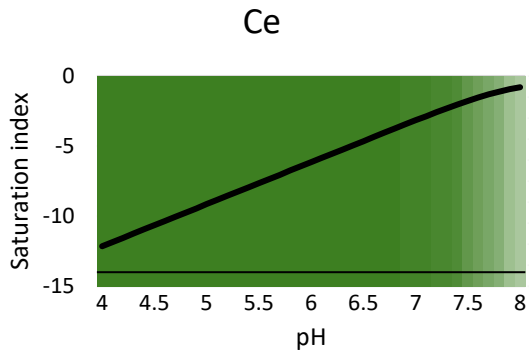
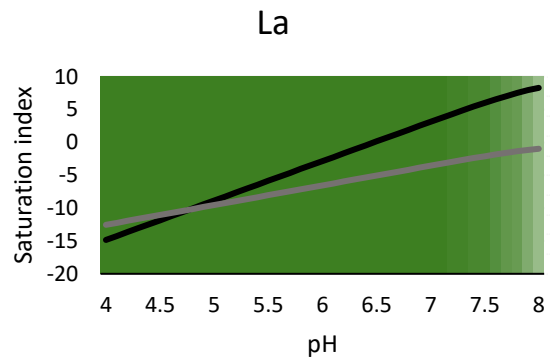
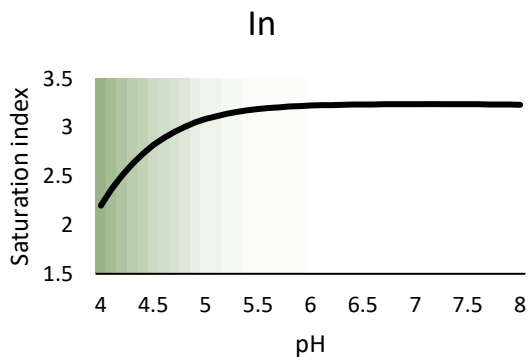
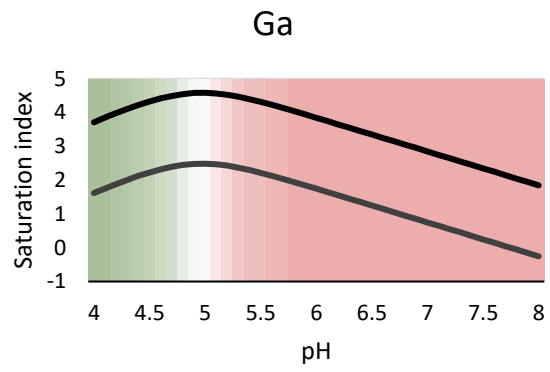
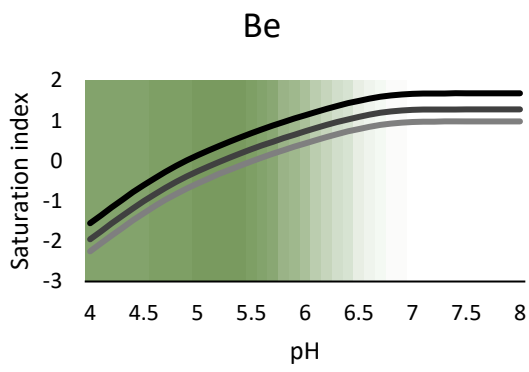
	Tomato	0.0046	0.0025-0.0071						Spalla et al. (2009)
			0.0015-0.32					0.000055-0.012	REE Fertilizer Wen et al. (2001)
	Cucumber		0.0050-0.0052					0.00018-0.00019	REE Fertilizer Wen et al. (2001)
	Root crops			0.00054					Sheppard et al. (2010)
	Various vegetables	0.011							Zhuang et al. (2017)
Other A	Tea		0.36-0.38					0.009-0.011	Cao et al. (2000)
		0.48	0.01-1.22						Pengbo et al. (2010)
			0.0087-0.066					0.0021-0.16	Fu et al. (2001)
	Coconut palm		0.48-1.0						Yes Wahid et al. (2000)
		3.2		0.076			0.33		Wahid et al. (2003)
	<i>Vicia villosa</i>		0.011-0.064					0.044-0.25	Fu et al. (2001)
	<i>Taxodium japonicum</i>		0.0061-0.031					0.034-0.17	Fu et al. (2001)
	<i>Dicranopteris dichotoma</i>		112.23-1499					1.0-13	0.16-2.2 Khan et al. (2017)
	<i>Dicranopteris linearis</i>		6.45-16.44					0.073-0.32	0.11-0.12 Khan et al. (2017)
	<i>Melastoma malabathricum</i>		33.55-49.13					0.63-0.92	1.7-2.4 Khan et al. (2017)
	<i>Cyperus difformis</i> Rottb.	13.65		0.20				0.88	Khan et al. (2017)
	<i>Cyperus kyllingia</i> Rottb.	315.81		3.7				34	Khan et al. (2017)
	<i>Cyperus distans</i> L.		82.47-231.53					1.1-1.9	0.59-1.7 Khan et al. (2017)
	<i>Cyperus rotundus</i> L.		115.33-503.7					1.4-6.1	0.52-2.3 Khan et al. (2017)
	<i>Filipendula ulmaria</i>	0.029							Tyler and Olsson (2005)
	<i>Geum rivale</i>	0.043		0.0013					Tyler and Olsson (2005)
	<i>Ranunculus ficaria</i>	0.067		0.0019					Tyler and Olsson (2005)
	<i>Anemone nemorosa</i>	0.16		0.020					Tyler and Olsson (2005)
	<i>Convallaria majalis</i>	0.011		0.0014					Tyler and Olsson (2005)
	<i>Stellaria nemorum</i>	0.017		0.0020					Tyler and Olsson (2005)
	<i>Maianthemum bifolium</i>	0.034		0.0077					Tyler and Olsson (2005)
	<i>Trientalis europaea</i>	0.020		0.0045					Tyler and Olsson (2005)
	Milkweed		≤3.0	0.017	0.007-0.029	0.12	0.042-0.25	Yes	Carpenter et al. (2015)
	Showy ticktrefoil		≤2.1	0.01	0.007-0.012	0.045	0.042-0.049	Yes	Carpenter et al. (2015)
	Vaccinium	0.10	0.073-0.13	0.042	0.005-0.10				Markert (1987)
	<i>Populus sieboldii</i>		0.053-2.6		0.075-3.76				Fu et al. (2001)
	Beech	0.061		0.042					Tyler (2005)
	Pine	0.16	0.15-0.16	0.088	0.042-0.13				Markert (1987)
	Various forest species	0.16	0.12-0.22		0.043-0.079				Markert and De Li (1991)
Other B	Orange	0.047	0.015-0.12						Cheng et al. (2015)
	Lupin		0.018-0.31	0.01					Wiche et al. (2016)
Other B	Fruit			0.00021					Sheppard et al. (2010)
<b>Tellurium</b>									

Category	Species	Concentration	BAC	TF	Experimentally contaminated?	Reference		
Poaceae A	Barley		2			Davis et al. (1978)		
	Wheat and barley		0.022	0.28		Omberg et al. (2011)		
Poaceae B	Wheat		0.001			Eriksson (2001)		
	Barley		0.001			Eriksson (2001)		
	Wheat and barley		0.013	0.16		Omberg et al. (2011)		
		0.0008	0.0003-0.0012	0.013	0.0033-0.036		Yang et al. (2014)	
	Brown rice	0.0059	0.0003-0.12	0.044	0.005-0.23		Yang et al. (2014)	
Vegetable A	Lettuce	0.0031		0.015			Yang et al. (2013)	
		0.0016		0.099			Yang et al. (2013)	
	Cabbage	0.000292	0.000131-0.000567				Filippini et al. (2019)	
	Leafy vegetables	0.0023	0.001-0.0038	0.041	0.0059-0.11		Yang et al. (2014)	
	Leafy vegetables	0.000310	≤0.000745				Filippini et al. (2019)	
	Komatsuna				0.014-0.051	Yes	Fujiwara et al. (2017)	
	Garlic	2.7	0.69-4.8		0.073	0.057-0.094	Yes	Ogra et al. (2015)
	Mushroom	2.1	0.37-5.8					Niedzielski et al. (2017)
	Mushroom	0.004488	0.001021-0.008012					Filippini et al. (2019)
	Carrot	0.0038		0.044				Yang et al. (2013)
	Japanese radish	0.0035		0.11				Yang et al. (2013)
	Vegetable B	Fruit vegetables	0.0018	0.0005-0.0027	0.026	0.005-0.061		Yang et al. (2014)
		Tomato	0.000051	0.000019-0.000136				Filippini et al. (2019)
		Garlic	0.00002					
		2.4	0.69-4.2		0.066	0.057-0.080	Yes	Ogra et al. (2015)
Onion and garlic		0.000142	0.000054-0.000621					Filippini et al. (2019)
Alliums		0.0016	0.0003-0.0025	0.034	0.0027-0.079			Yang et al. (2014)
Potato		0.00006		0.00087				Yang et al. (2013)
Potato		0.000189	0.000049-0.000955					Filippini et al. (2019)
Japanese radish		0.0012		0.037				Yang et al. (2013)
Radish					0.012-0.03	Yes		Fujiwara et al. (2017)
Tubers		0.0011	0.0001-0.0018	0.024	0.0013-0.092			Yang et al. (2014)
Root vegetables		0.0017	0.001-0.0031	0.022	0.0045-0.055			Yang et al. (2014)
Root vegetables		0.000206	≤0.000631					Filippini et al. (2019)
Various vegetables		0.00035						D'Ulivo (1997)
Other A	Indian mustard		≤39			Yes	Ogra et al. (2010)	
	Cactus	0.006					Cowgill (1988)	
	Legumes	0.0017	0.0011-0.0021	0.02	0.0057-0.044		Yang et al. (2014)	
	Various trees	0.016	0.002-0.038				Cowgill (1988)	

	Various flowering plants	0.017	0.003-0.024	Cowgill (1988)
Other B	Various flowering plants	0.017	0.002-0.03	Cowgill (1988)
	Citrus fruit	0.000138	≤0.297	Filippini et al. (2019)

<sup>a</sup>A: above-ground, shoot, leaf or stem biomass, B: grain, seed, fruit or edible organ biomass; <sup>b</sup> Detection limit (DL) is specified if the concentration is below it; <sup>c</sup>BAC = concentration in plant material (mg kg<sup>-1</sup>) / concentration in soil (mg kg<sup>-1</sup>) Bu-Olayan and Thomas (2009); <sup>d</sup>TF = concentration in above-ground organ (mg kg<sup>-1</sup>) / concentration in roots (mg kg<sup>-1</sup>) Bu-Olayan and Thomas (2009).



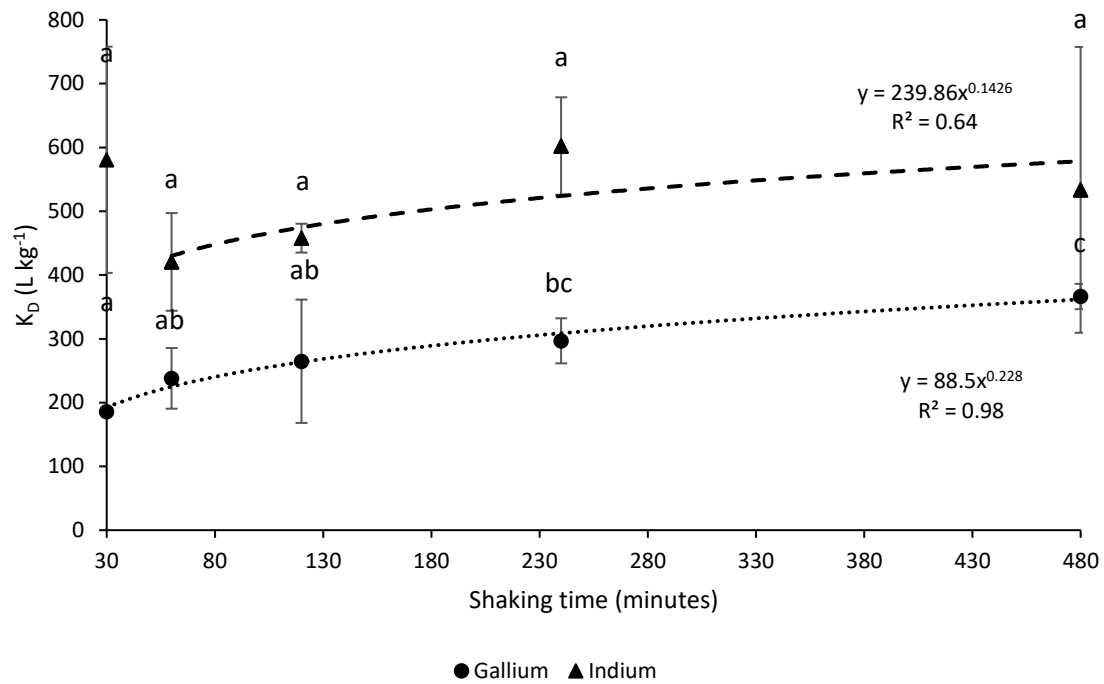


**Fig. A.1 Net aqueous charge and saturation indexes of hydroxide and carbonate precipitates for Be, Bi, Ga, In, La, Ce, Nd and Gd.**

Predicted with the conditions in Table A#.

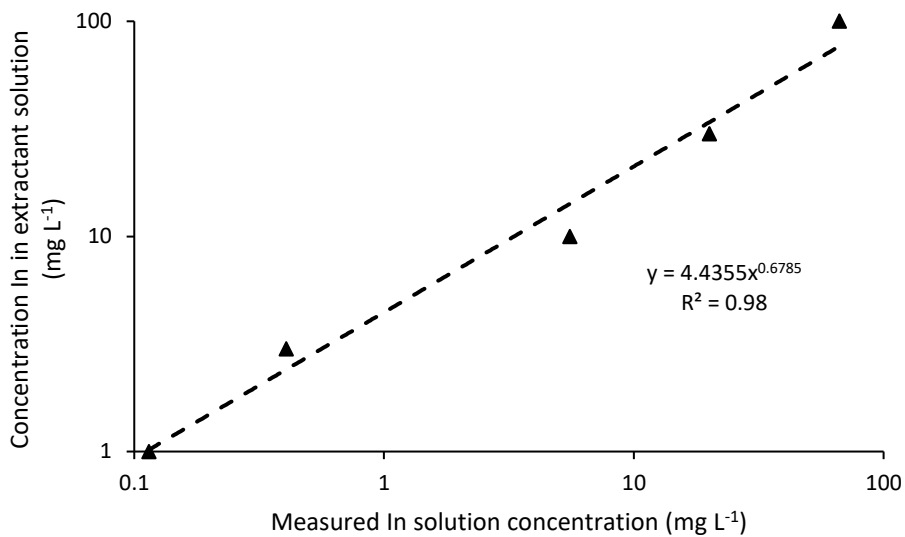
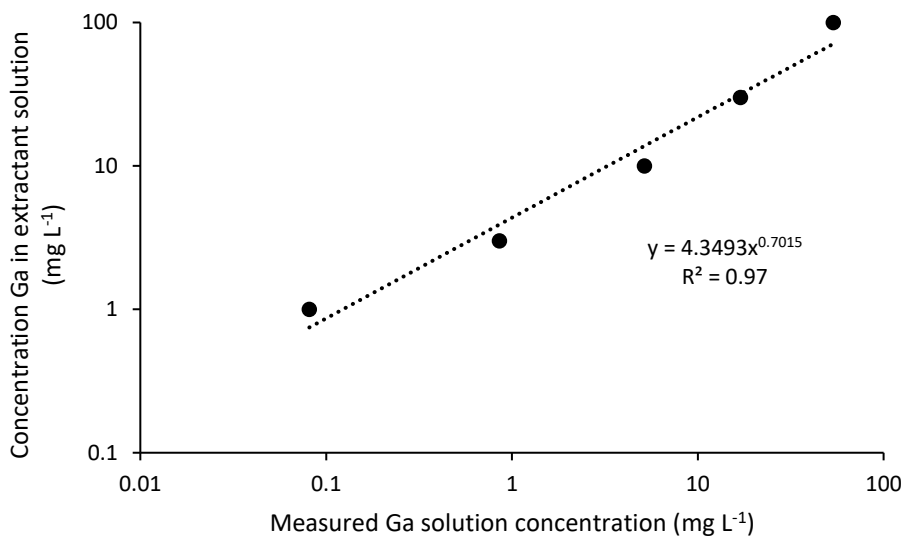
Dark green = +3, white = 0, light red = -1 charge.

## Appendix B



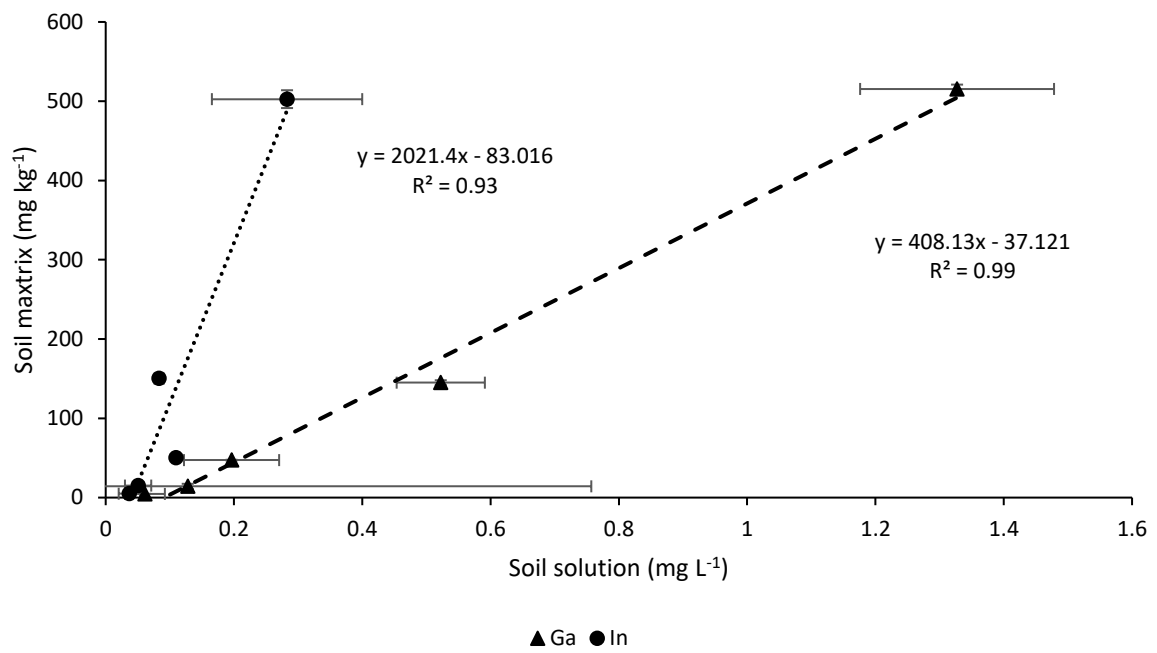
**Fig. B.1 Effect of shaking time on  $K_D$ .**

Error bars denote standard deviation of mean values; different letters denote significance;  $n = 3$ . No significant increase in In  $K_D$  after 120 minutes, and Ga  $K_D$  increased just 39% in the subsequent 300% time increment, thus considered relatively stable.



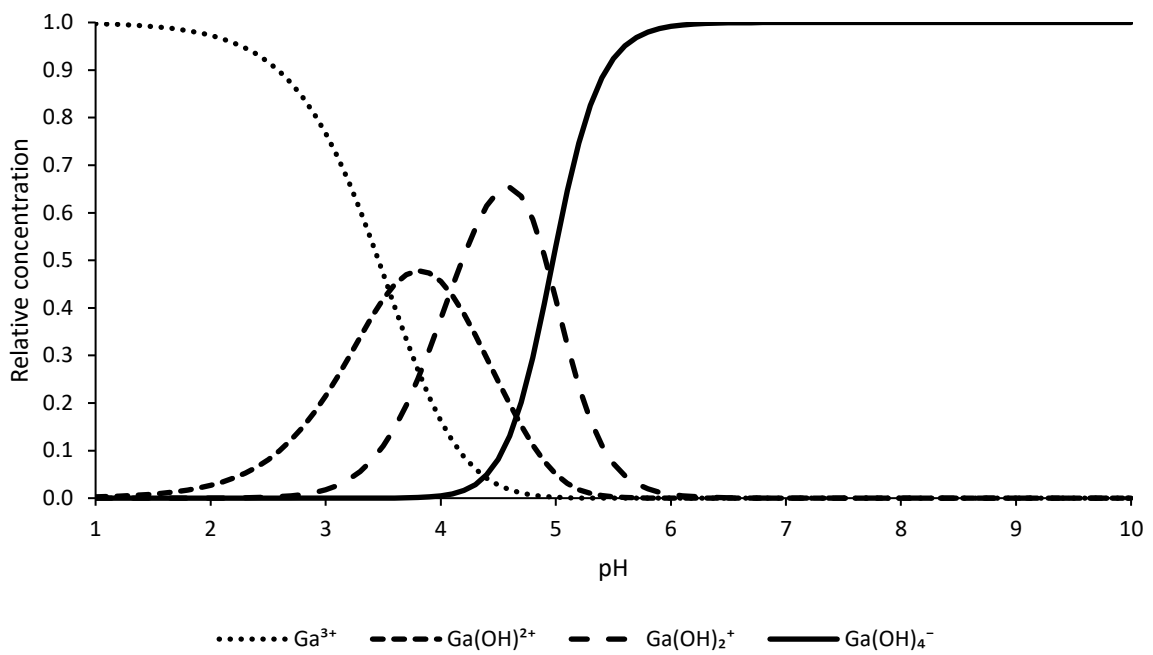
**Fig. B.2 Identification of the Ga (above) and In (below) correction factors.**

Mean values,  $n = 3$ . Correction factors were identified by trendline equations, where  $y = C_f$  and  $x =$  the measured concentration in the extractant solution.



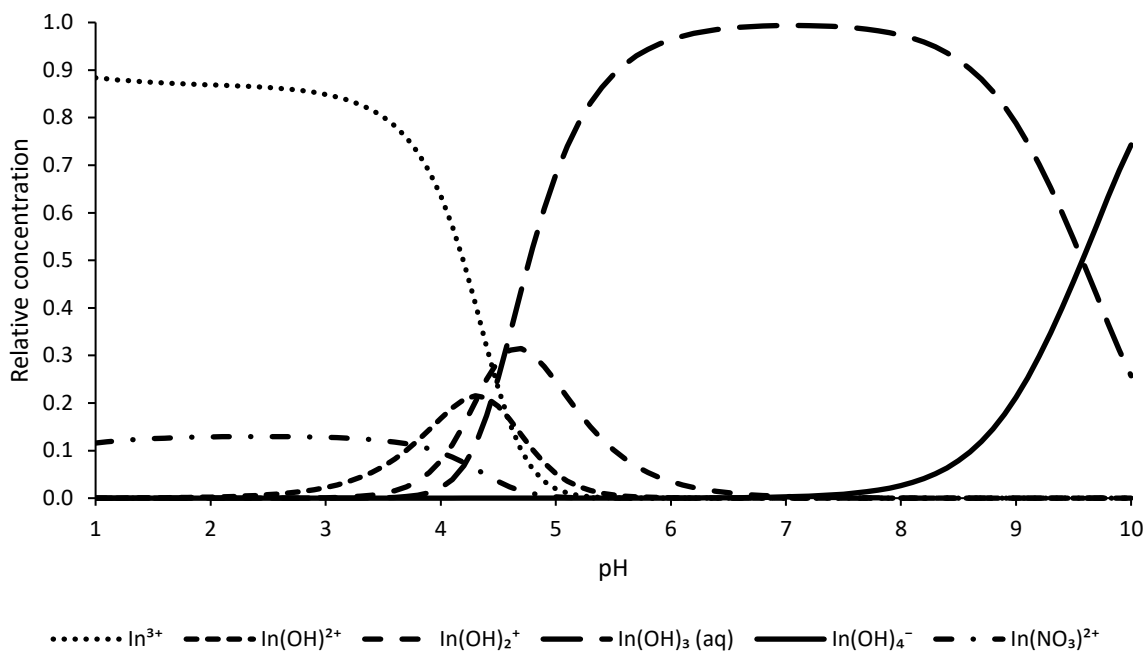
**Fig. B.3 Soil matrix concentration as a function of soil solution concentration.**

Error bars denote standard deviation of mean values;  $n = 3$ .



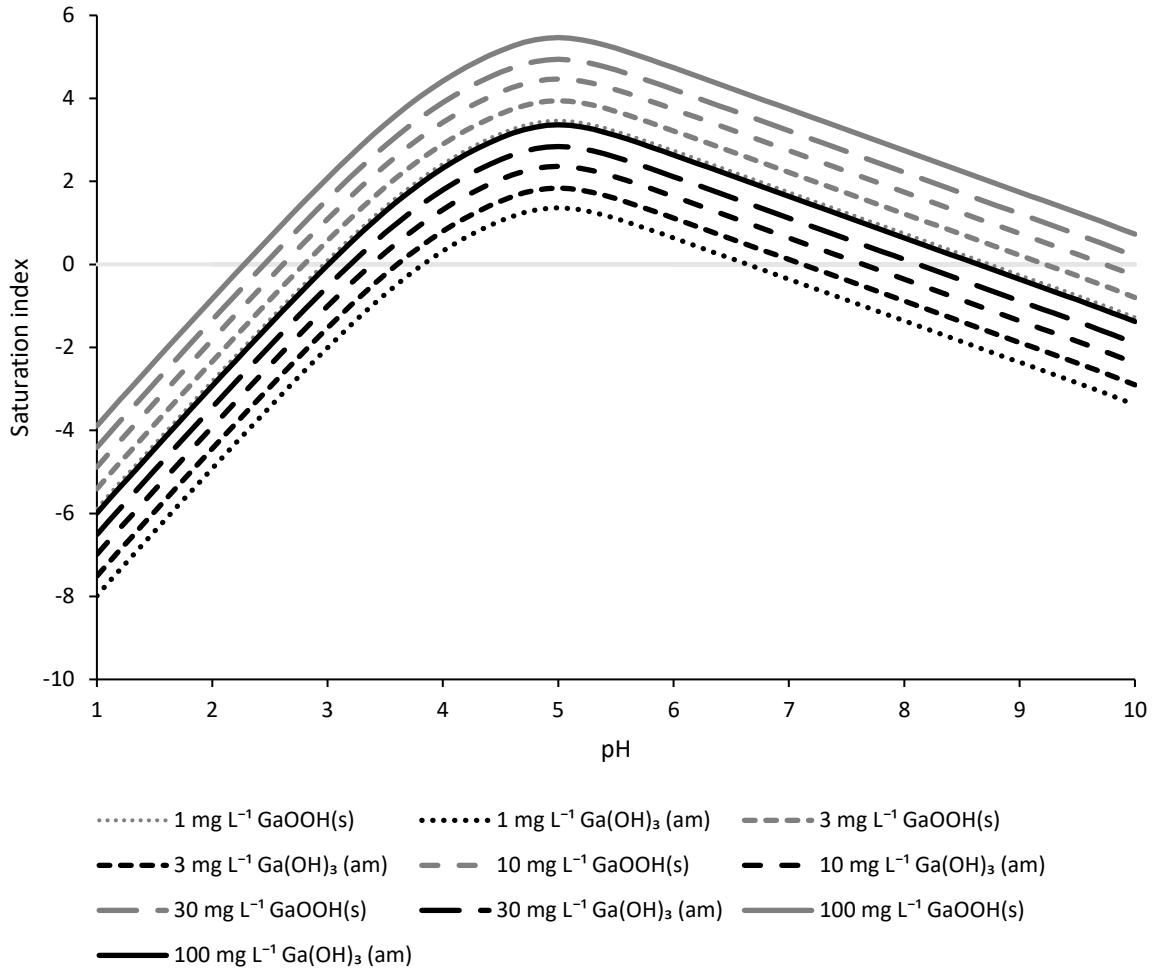
**Fig. B.4** Relative concentrations of aqueous mononuclear Ga hydroxyl species modelled from Visual MINTEQ 3.1.

Values are relative to the sum of aqueous species.



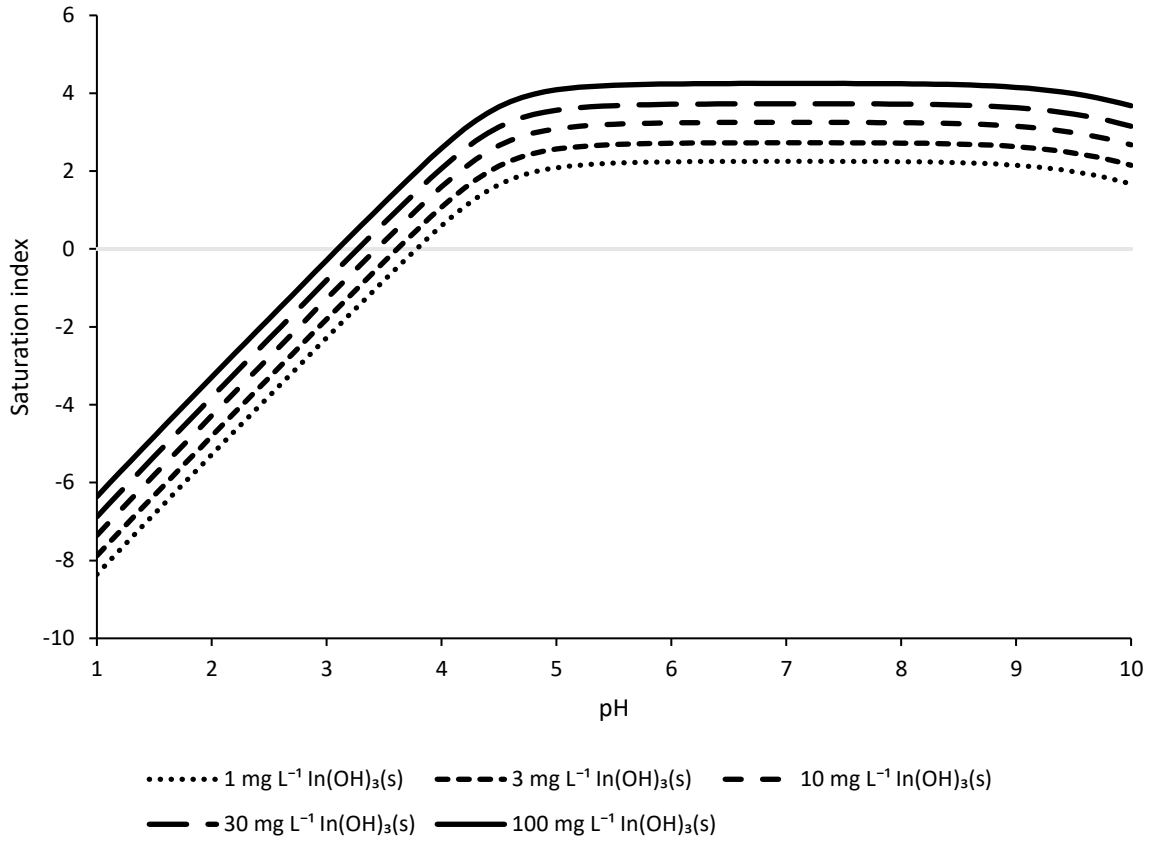
**Fig. B.5 Relative concentrations of aqueous mononuclear In species modelled from Visual MINTEQ 3.1.**

Values are relative to the sum of aqueous species.



**Fig. B.6 Saturation indexes of Ga precipitates modelled from Visual MINTEQ 3.1.**





**Fig. B.7** Relative saturation indexes of In precipitate modelled from Visual MINTEQ 3.1.

**Table B.1 Growth chamber settings.**

Day temperature	20°C ( $\pm 0.2$ )
Night temperature	12°C ( $\pm 0.2$ )
Temperature control	Ramp mode
Rate of temperature change	5 min °C <sup>-1</sup>
Day length	16 hours (6am-10pm)
Photosynthetically active radiation	800 $\mu\text{mol m}^{-2} \text{s}^{-1}$ ( $\pm 2$ ) 15.5 hours; 500 $\mu\text{mol m}^{-2} \text{s}^{-1}$ ( $\pm 2$ ) 0.5 hours
Relative humidity	70%

**Table B.2 Parameters used in Visual MINTEQ 3.1 modelling.**

<b>Initial screen parameters</b>			
Parameter	Concentration/value		
Ca <sup>2+</sup>	0.05 M		
CO <sub>2</sub>	0.00038 atm		
Temperature	20°C		
Ionic strength	To be calculated		
<b>Concentration</b>			
Ga <sup>3+</sup> (mg L <sup>-1</sup> )	In <sup>3+</sup> (mg L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (M)	
1	-	0.100043	
3	-	0.100129	
10	-	0.10043	
30	-	0.10129	
100	-	0.1043	
-	1	0.1000261	
-	3	0.1000784	
-	10	0.100261	
-	30	0.100784	
-	100	0.10261	
-	-	0.1	
<b>pH gradient simulation</b>			
Initial screen parameters			
pH	Fixed at...1		
Multi-problem/sweep tab options			
Problem type	Sweep: one parameter is varied		
Number of problems	91		
Sweep component	pH		
Start value	1.0		
Increment between values	0.1		
Add comp./species	Ga	Concentration (aqueous species)	Ga <sup>3+</sup> GaOH <sup>2+</sup> Ga(OH) <sub>2</sub> <sup>+</sup> Ga(OH) <sub>4</sub> <sup>-</sup>
		Saturation index (precipitated species)	Ga(OH) <sub>3</sub> (am) GaOOH(s)
	In	Concentration (aqueous species)	In <sup>3+</sup> InOH <sup>2+</sup> In(OH) <sub>2</sub> <sup>+</sup> In(OH) <sub>3</sub> (aq) In(OH) <sub>4</sub> <sup>-</sup> InNO <sub>3</sub> <sup>2+</sup>
		Saturation index (precipitated species)	In(OH) <sub>3</sub> (s)
<b>Concentration gradient simulation</b>			
pH	Calculated from mass balance		

**Table B.3 Comparison of mean bioaccumulation factors for Ga, In, and common TE contaminants (mg kg<sup>-1</sup> plant biomass (Robinson et al., 2009)).**

Reference	Omberg et al. (2011)	Eriksson (2001)	Tyler (2005)	Tyler (2004a)	Waterlot et al. (2013)		Li et al. (2016)
Species	Barley/wheat grain	Wheat/barley grain <sup>a</sup>	Beech leaves	Beech roots	Ryegrass shoots	Lettuce leaves	Cabbage, garlic, onion, lettuce, spinach
Contamination	Uncontaminated	Possibly agricultural	Uncontaminated	Uncontaminated	Natural, and Pb-Zn smelter		Rare metal recycling smelter
Time between contamination and sampling.	-	-	-	-	0-3 years for one plant (20-27 sites); 28-31 years since emissions significantly reduced for the other (7-27) <sup>b</sup>		0 years
Cd	0.00025	0.16	0.30	0.79	0.28	1.5	0.51
U	0.00056	0.000027	0.035	0.10	-	-	-
Cr	0.0012	0.0005	0.16	0.29	-	-	-
<b>Ga</b>	<b>0.0016</b>	<b>0.00011</b>	<b>0.077</b>	<b>0.15</b>	-	-	-
Pb	0.0020	0.00045	0.0083	0.20	0.0037	0.011	1.1
Tl	0.0023	0.0017	0.051	5.0	-	-	0.042
Cs	0.0029	0.0016	0.65	5.0	-	-	-
As	0.0031	0.0074	0.029	-	-	-	0.61
Ni	0.0037	0.012	0.18	0.32	-	-	-
Sb	0.0039	0.0024	0.048	-	-	-	0.11
Sn	0.0096	0.054	0.022	0.11	-	-	-
W	0.012	0.0045	0.058	-	-	-	-
Se	0.031	0.052	-	-	-	-	-
Cu	0.20	0.27	0.81	1.00	0.10	0.11	0.91
Zn	0.50	0.40	0.60	0.80	0.22	0.093	6.8
<b>In</b>	-	-	<b>0.029</b>	<b>0.11</b>	<b>0.081</b>	<b>0.062</b>	<b>0.0021</b>

<sup>a</sup>0.8 wheat + 0.2 barley data, though only Ga barley value used; <sup>b</sup>Douay et al. (2008).

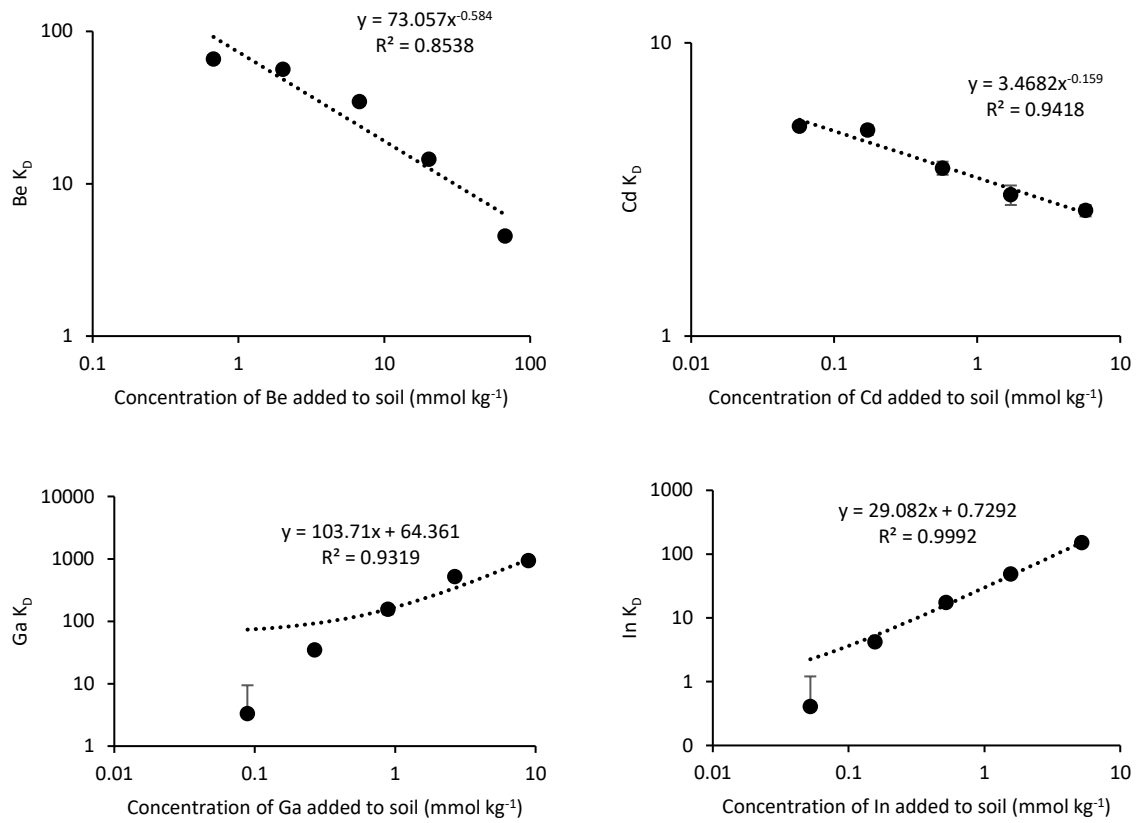
## Appendix C

**Table C.1 Details of the ETEC and Cd salts added to solution**

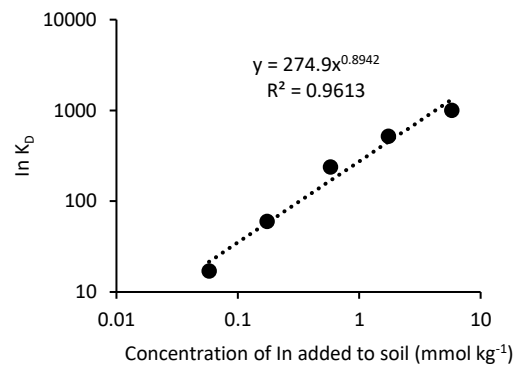
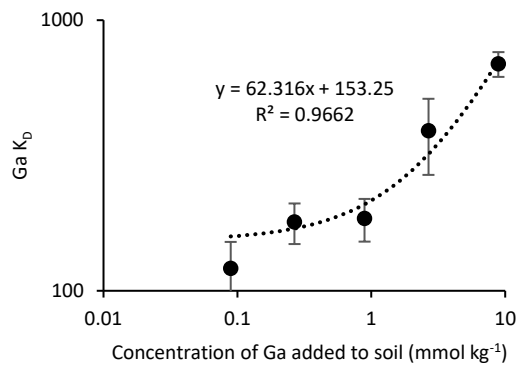
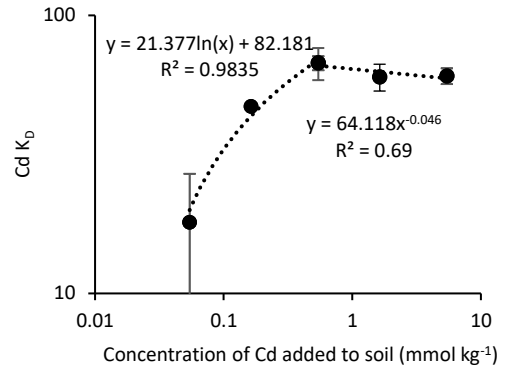
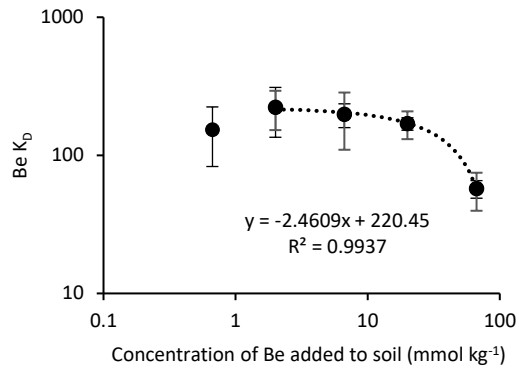
Element	Formula	Mass (g) added to make 1 L of 100 mg L <sup>-1</sup> ETEC solution
Be	BeSO <sub>4</sub> ·4H <sub>2</sub> O	1.966
Cd	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	0.2744
Ga	Ga(NO <sub>3</sub> ) <sub>3</sub>	0.3668
In	In(NO <sub>3</sub> ) <sub>3</sub>	0.2620
Te	KTeO <sub>3</sub> ·3H <sub>2</sub> O	0.2413
I	KIO <sub>3</sub>	0.1686
	KI	0.1308
La	La(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	0.3117
Ce	Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	0.3099
Nd	Nd(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	0.3039
Gd	Gd(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	0.2870
Bi	Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	0.2321

**Table C.2 Volumes of 1 M KOH added to batch sorption samples for the three soil types in the pH gradient (μL)**

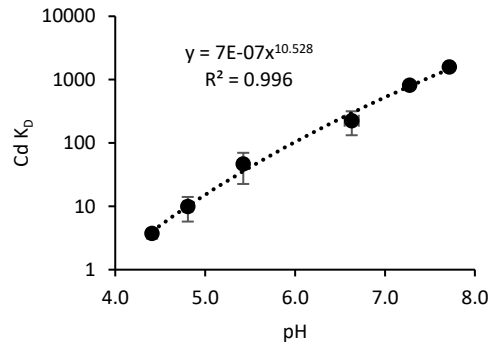
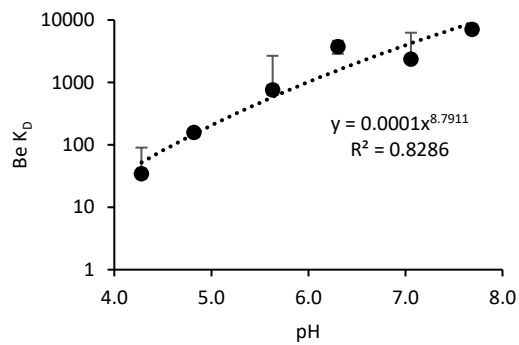
Sample type	RFMW	RFT	GOO
1	68	223	260
2	136	459	520
3	205	694	780
4	273	929	1040
5	341	1165	1300

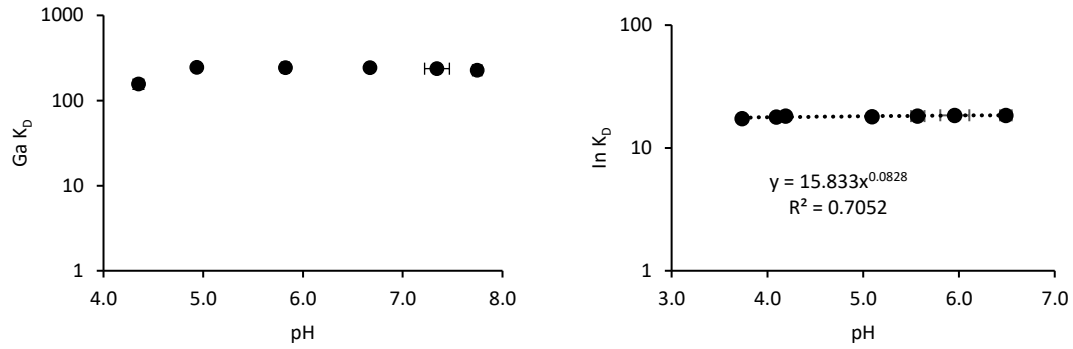


**Fig. C.1 Effect of ETEC and Cd concentration on the  $K_D$  of Be, Cd, Ga and In in the RFT when 1-100  $\text{mg L}^{-1}$  ETEC or Cd added to batch sorption experiments.**

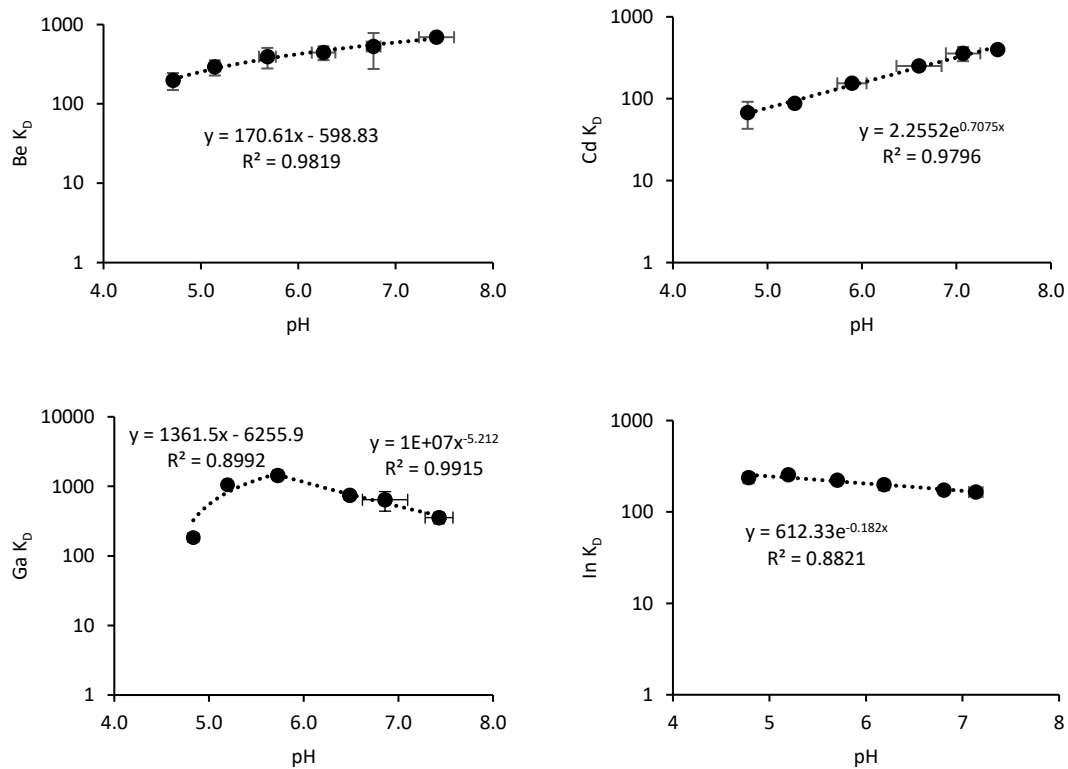


**Fig. C.2 Effect of ETEC and Cd concentration on the  $K_D$  of Be, Cd, Ga and In in GOO soil when 1-100  $\text{mg L}^{-1}$  ETEC or Cd added to batch sorption experiments.**





**Fig. C.3 Effect of pH on the  $K_D$  of Be, Cd, Ga, In, La, Ce, Nd and Gd in the RFT soil when 10 mg L<sup>-1</sup> ETEC or Cd added to batch sorption experiments.**



**Fig. C.4 Effect of pH on the  $K_D$  of Be, Cd, Ga, In, La, Ce, Nd and Gd in the GOO soil when 10 mg L<sup>-1</sup> ETEC or Cd added to batch sorption experiments.**

**Table C.3 Equation fit (sum of normalised error, Chapter 4 Equation 5) and coefficients for sorption of Be, Cd, Ga, In, La, Ce, Nd and Gd in the RFMW soil.**



Element	Langmuir		Freundlich		Linear		Logarithmic	
	Coefficients ( $k_a, q_m$ )	Fit	Coefficients ( $n, k_f$ )	Fit	Coefficient ( $m$ )	Fit	Coefficients ( $a, c$ )	Fit
Be	<b>4.5, 0.014</b>	<b>0.246</b>	<b>1.9, 0.0084</b>	<b>0.247</b>	0.0035	2.97	0.0016, 0.0082	0.369
Cd	2.5, 0.0031	0.195	<b>1.2, 0.0034</b>	<b>0.0015</b>	0.0054	0.529	7.3E-5, 0.00046	1.05
Ga	27, 0.0094	2.54	0.72, 5.9	1.73	0.26	2.45	<b>0.0011, 0.0094</b>	<b>1.07</b>
In	-0.0083, -0.55	3.58	0.092, 1.1E+21	2.96	0.0046	3.58	<b>0.0099, 0.054</b>	<b>0.909</b>
La	<b>36, 0.93</b>	<b>0.0498</b>	1.2, 8.7	0.224	19	0.923	0.024, 0.21	1.03
Ce	<b>41, 1.0</b>	<b>0.108</b>	1.2, 12	0.306	26	0.824	0.028, 0.25	0.877
Nd	<b>52, 0.95</b>	<b>0.0423</b>	1.2, 13	0.251	30	0.855	0.021, 0.19	1.11
Gd	<b>128, 0.48</b>	<b>0.00414</b>	1.1, 26	0.0281	51	0.116	0.016, 0.15	0.522

Equation of best fit for each element is bolded.

**Table C.4 Equation fit (sum of normalised error, Chapter 4 Equation 5) and coefficients for sorption of Be, Cd, Ga and In in the RFT soil.**

Element	Langmuir		Freundlich		Linear		Logarithmic	
	Coefficients ( $k_a, q_m$ )	Fit	Coefficients ( $n, k_f$ )	Fit	Coefficient ( $m$ )	Fit	Coefficients ( $a, c$ )	Fit
Be	<b>2.4, 0.024</b>	<b>0.14</b>	1.7, 0.012	0.216	0.0064	2.74	0.0018, 0.0088	0.721
Cd	1.4, 0.0032	0.105	<b>1.2, 0.0024</b>	<b>0.013</b>	0.0034	0.32	6.4e-5, 0.00037	1.02
Ga	-0.055, -0.80	2.32	<b>0.14, 1.3E+13</b>	<b>1.66</b>	0.044	2.32	-0.0026, -0.014	2.11
In	-0.028, -0.19	2.28	31, 47	4	0.0053	2.28	<b>0.042, 0.16</b>	<b>0.176</b>

Equation of best fit for each element is bolded.

**Table C.5 Equation fit (sum of normalised error, Chapter 4 Equation 5) and coefficients for sorption of Be, Cd, Ga and In in the GOO soil.**

Element	Langmuir		Freundlich		Linear		Logarithmic	
	Coefficients ( $k_a, q_m$ )	Fit	Coefficients ( $n, k_f$ )	Fit	Coefficient ( $m$ )	Fit	Coefficients (a, c)	Fit
Be	<b>2.0, 0.086</b>	<b>0.15</b>	1.2, 0.067	0.47	0.17	0.598	0.0024, 0.014	1.33
Cd	8.9, 0.0025	2.06	<b>0.73, 0.16</b>	<b>0.88</b>	0.025	1.69	<b>0.00077, 0.0043</b>	<b>0.875</b>
Ga	-0.21, -0.79	1.06	<b>0.72, 2.4</b>	<b>0.39</b>	0.16	1.06	0.00017, 0.0014	1.53
In	-0.027, -0.80	3.18	4.7, 175105586	1.7	0.022	3.18	<b>0.0032, 0.020</b>	<b>0.373</b>

Equation of best fit for each element is bolded.

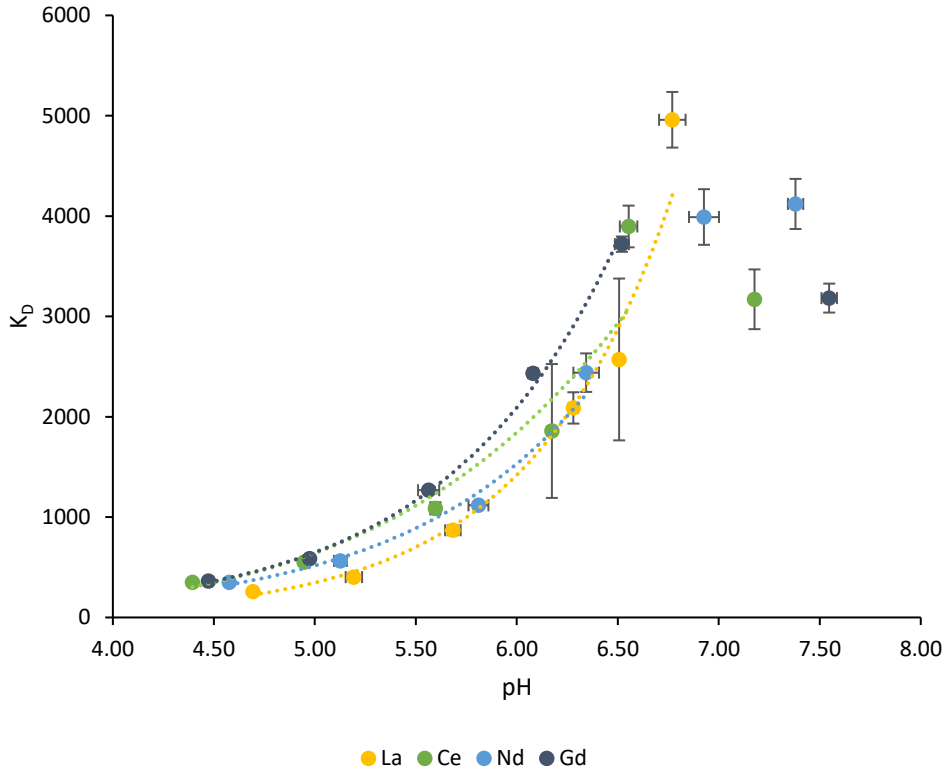


Fig. C.5 Effect of pH on the  $K_D$  of La, Ce, Nd and Gd in the GOO soil when  $10 \text{ mg L}^{-1}$  ETEC or Cd added to batch sorption experiments.

Table C.6 pH of the solution in the batch sorption concentration gradient.

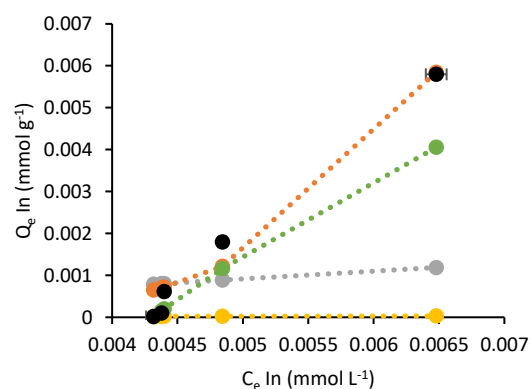
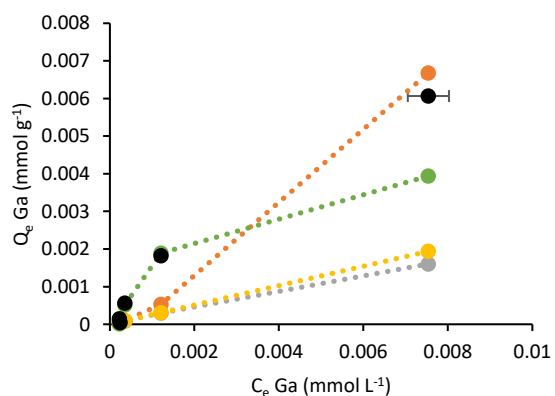
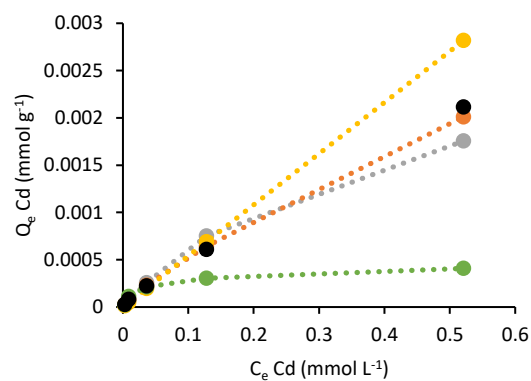
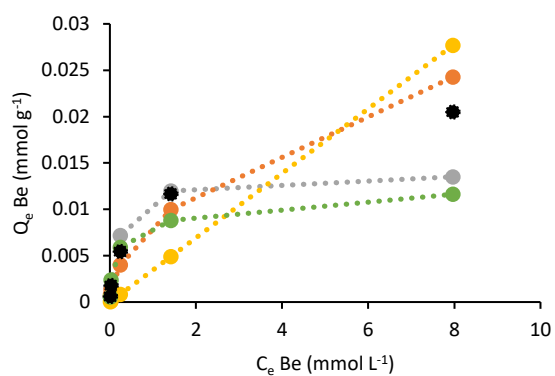
RFMW					
Element	1 mg L <sup>-1</sup>	3 mg L <sup>-1</sup>	10 mg L <sup>-1</sup>	30 mg L <sup>-1</sup>	100 mg L <sup>-1</sup>
Be	4.8 (0.0067)	4.7 (0.0067)	4.5 (0.0033)	4.2 (0.0033)	3.8 (0.0033)
Cd	4.7 (0.0088)	4.7 (0.0033)	4.7 (0.0033)	4.7 (0.0033)	4.6 (0.0067)
Ga	4.7 (0.0033)	4.7 (0.0033)	4.6 (0.0033)	4.5 (0)	4.1 (0.0033)
In	4.6 (0.022)	4.7 (0.0058)	4.6 (0)	4.6 (0.0067)	4.4 (0.0033)
I	4.8 (0.0067)	4.8 (0.0058)	4.8 (0.0033)	4.8 (0.0033)	4.7 (0.021)
La	4.9 (0.023)	4.9 (0.0088)	4.8 (0.0088)	4.7 (0.012)	4.6 (0.0033)
Ce	4.5 (0.015)	4.4 (0.0033)	4.4 (0.0058)	4.4 (0.0067)	4.3 (0.0033)
Nd	4.8 (0.01)	4.7 (0.0067)	4.7 (0.0067)	4.7 (0.01)	4.5 (0.0088)
Gd	4.9 (0.021)	4.8 (0.0067)	4.8 (0.0067)	4.6 (0.033)	4.4 (0.015)
RFT					
Element	1 mg L <sup>-1</sup>	3 mg L <sup>-1</sup>	10 mg L <sup>-1</sup>	30 mg L <sup>-1</sup>	100 mg L <sup>-1</sup>
Be	4.4 (0.0067)	4.3 (0.0033)	4.3 (0.025)	4.1 (0.013)	4.0 (0.01)
Cd	4.5 (0.031)	4.5 (0.0088)	4.4 (0.0058)	4.4 (0.0033)	4.4 (0.012)
Ga	4.4 (0.0067)	4.4 (0.0058)	4.4 (0.015)	4.3 (0.0067)	4.2 (0.0067)
In	3.8 (0.0058)	3.8 (0.0067)	3.7 (0.0088)	3.7 (0.0033)	3.6 (0.0058)
I	4.6 (0.0033)	4.6 (0.0033)	4.6 (0.0067)	4.6 (0.0058)	4.6 (0.0033)
GOO					
Element	1 mg L <sup>-1</sup>	3 mg L <sup>-1</sup>	10 mg L <sup>-1</sup>	30 mg L <sup>-1</sup>	100 mg L <sup>-1</sup>
Be	4.8 (0.0088)	4.8 (0.0033)	4.7 (0.0033)	4.6 (0.0033)	4.2 (0.0033)
Cd	4.7 (0.17)	4.8 (0.0033)	4.8 (0.0058)	4.8 (0.0033)	4.8 (0.0033)
Ga	4.9 (0.0033)	4.9 (0.0058)	4.8 (0.0033)	4.8 (0)	4.7 (0.0033)
In	4.8 (0.01)	4.8 (0.0058)	4.8 (0)	4.8 (0.0033)	4.8 (0.0033)

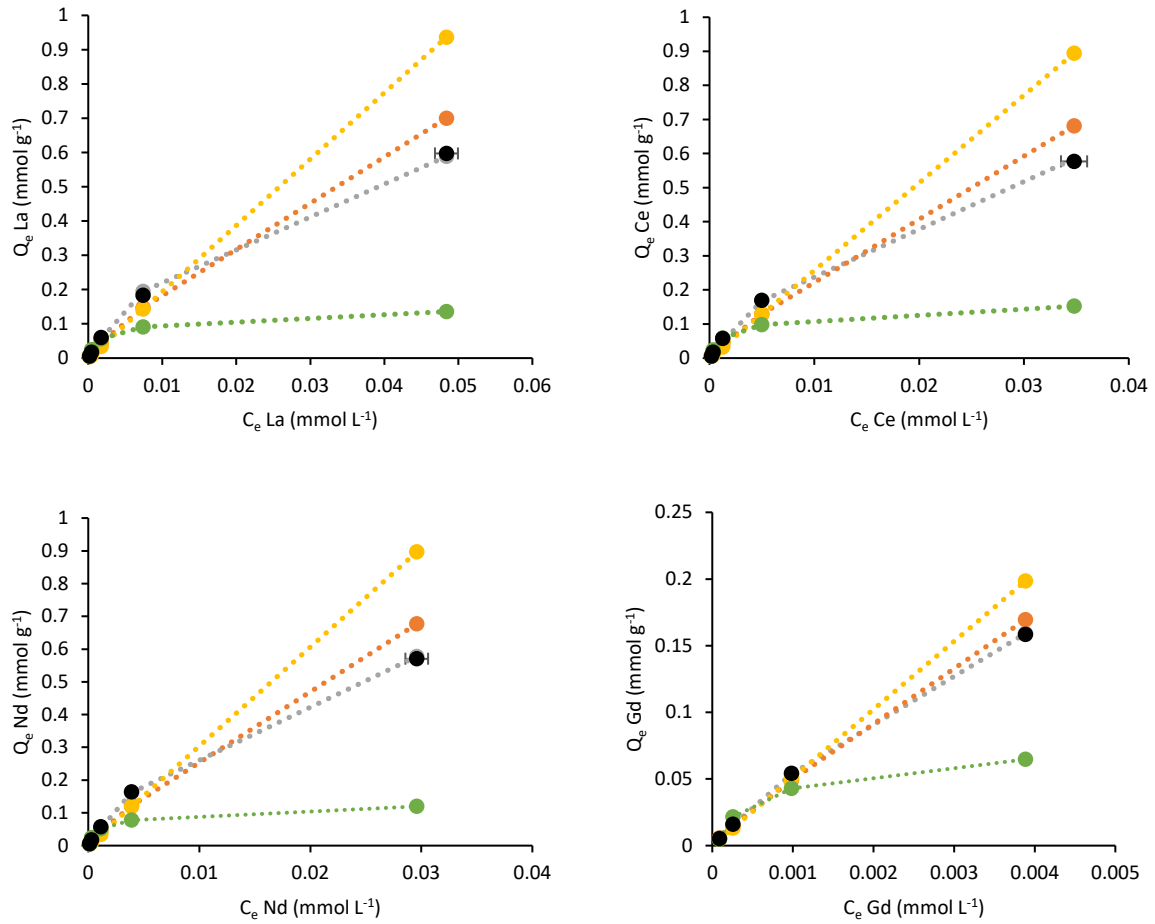
I	4.9 (0.0067)	4.9 (0.0033)	4.9 (0)	4.9 (0.0033)	4.9 (0.0033)
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**Table C.7 Selected chemical properties of Be, Cd, Ga, In, La, Ce, Nd and Gd.**

Element and ionic charge	Ionic radii <sup>a</sup>	Ionic potential <sup>b</sup> of single ion	Molar concentration in 10 mg L <sup>-1</sup> solution (μmol L <sup>-1</sup> )
Be <sup>2+</sup>	0.45	Be <sup>2+</sup> 4.44	1110
Cd <sup>2+</sup>	0.95	Cd <sup>2+</sup> 2.11	89
Ga <sup>3+</sup>	0.620	Ga <sup>3+</sup> 4.84	143
In <sup>3+</sup>	0.800	In <sup>3+</sup> 3.75	87
La <sup>3+</sup>	1.032	La <sup>3+</sup> 2.91	72
Ce <sup>3+</sup>	1.01	Ce <sup>3+</sup> 2.97	71
Nd <sup>3+</sup>	0.983	Nd <sup>3+</sup> 3.05	69
Gd <sup>3+</sup>	0.938	Gd <sup>3+</sup> 3.20	64

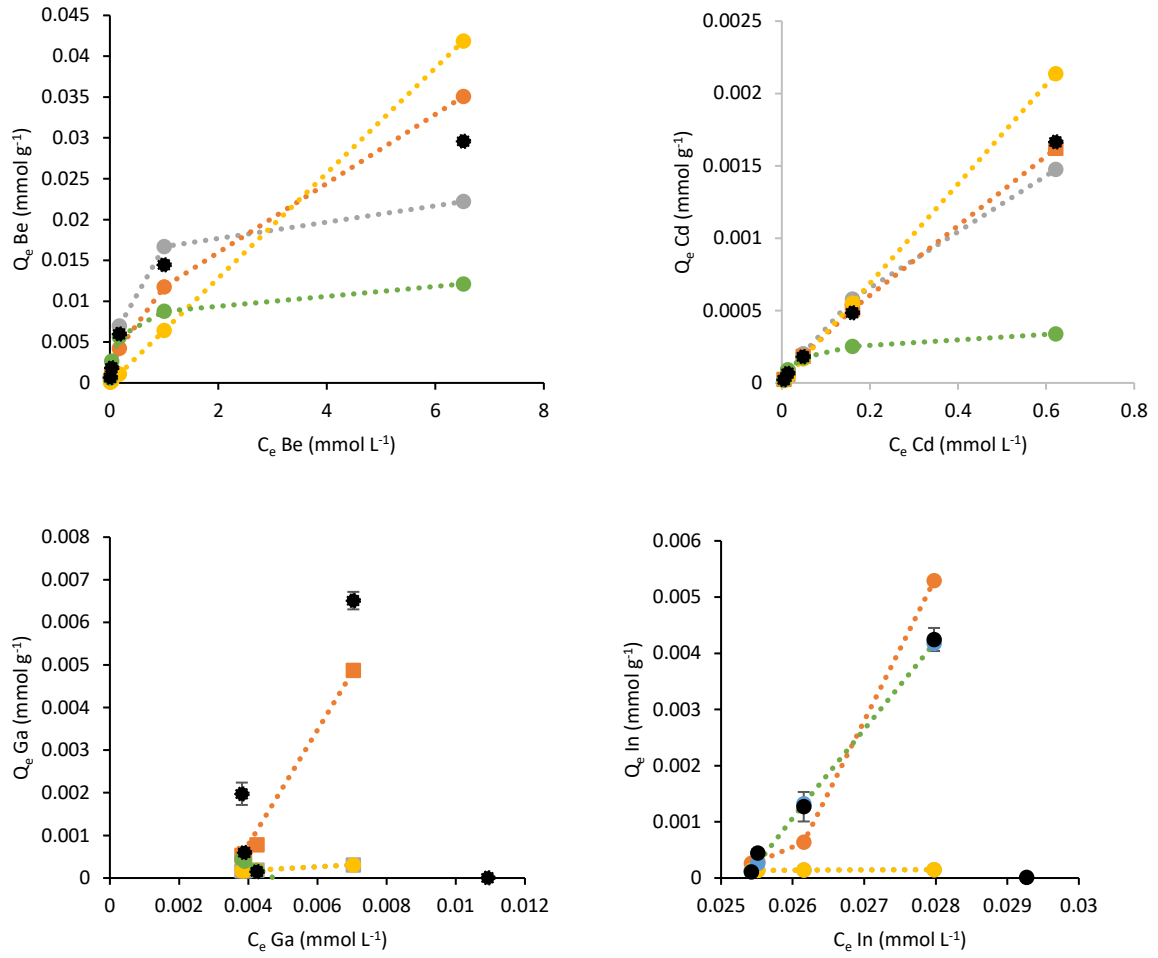
<sup>a</sup>VI coordination (Shannon, 1976), <sup>b</sup>Charge/ionic radius (Å) (Tyler, 2004).





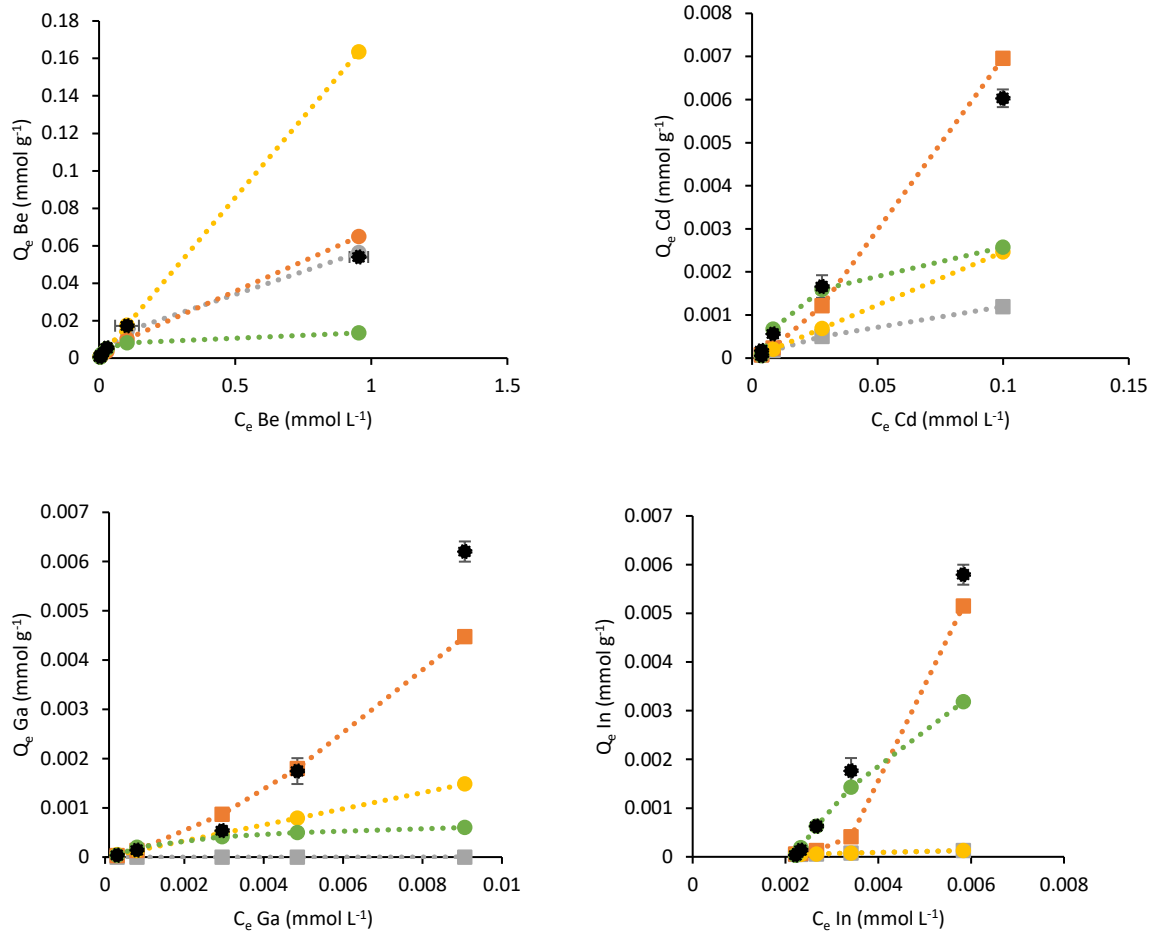
**Fig. C.6 Fit of the Logarithmic, Freundlich, linear and logarithmic trendlines for Be, Cd, Ga, In, La, Ce, Nd, and Gd in the RFMW soil.**

Langmuir, Freundlich, linear, logarithmic



**Fig. C.7** Fit of the Logarithmic, Freundlich, linear and logarithmic trendlines for Be, Cd, Ga, and In in the RFT soil.

Langmuir, Freundlich, linear, logarithmic



**Fig. C.8** Fit of the Logarithmic, Freundlich, linear and logarithmic trendlines for Be, Cd, Ga, and In in the GOO soil.

Langmuir, Freundlich, linear, logarithmic

**Table C.8** Detection limits of the ETECs in samples ( $\text{mg L}^{-1}$ )

Element	Detection limit
Be	0.0023
Cd	0.0024
Ga	0.00048
In	0.0011
La	0.010
Ce	0.031
Nd	0.00010
Gd	0.00054

**Table C.9 Effect of soil type on the  $K_D$  of Be, Cd, Ga, and In. Soil types listed vertically from low to high  $K_D$ .**

Element	Concentration of ETEC added to soil ( $\text{mg L}^{-1}$ )			pH of the soil solution		
	1	10	100	5	6	7
Be	RFT 66	RFMW 23	RFMW 2.6	RFMW 64	RFMW 315	GOO 595
	RFMW 71	RFT 35	RFT 4.5	RFT 140	GOO 425	RFMW 1210
	GOO 154	GOO 197	GOO 57	GOO 254	RFT 693	RFT 2687
Cd	RFT 5.2	RFT 3.7	RFT 2.7	RFMW 8.1	RFMW 32	RFMW 129
	RFMW 10	RFMW 6.1	RFMW 4.1	RFT 16	RFT 109	GOO 319
	GOO 18	GOO 67	GOO 61	GOO 78	GOO 157	RFT 552
Ga	RFT 3.3	RFT 157	RFT 934	RFT 247	RFT 241	RFT 236
	GOO 121	GOO 185	GOO 690	GOO 552	GOO 880	GOO 394
	RFMW 180	RFMW 1591	RFMW 807	RFMW 2026	RFMW 2716	RFMW 821
In	RFT 0.41	RFT 17	RFT 152	RFT 18	RFT 18	RFT 19
	RFMW 3.9	RFMW 140	RFMW 895	RFMW 150	RFMW 158	RFMW 165
	GOO 17	GOO 237	GOO 994	GOO 246	GOO 205	GOO 171

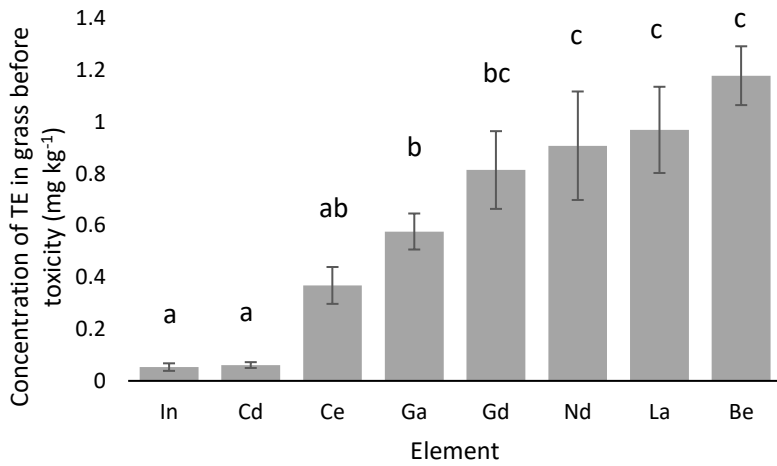
## Appendix D

**Table D.1 Common uses, year consumption and natural plant concentrations of the ETECs Be, Ga, In, La, Ce, Nd and Gd.**

Element	Plant concentrations (mg kg <sup>-1</sup> )		Uptake in plants spiked with ETECs (mg kg <sup>-1</sup> , μmol kg <sup>-1</sup> )	
	Background	Elevated (without visible toxicity)	Before toxicity	With toxicity
Be	<ul style="list-style-type: none"> <li>• Lettuce: 0.06 (Wang et al., 2021)</li> <li>• Grass: 0.0051 (Tyler &amp; Olsson, 2001)</li> <li>• Wheat grain: &lt;0.0005 (Eriksson, 2001)</li> </ul>	<ul style="list-style-type: none"> <li>• Potato foliage: 30 (Bohn &amp; Seekamp, 1979)</li> <li>• Collards foliage: 10 (Kaplan et al., 1990)</li> <li>• Oat foliage: 2 (Bohn &amp; Seekamp, 1979)</li> </ul>	0.1-10.1, 11-1121 (Kaplan et al., 1990; Williams & Le Riche, 1968)	0.4-32, 44-3551 (Sajwan et al., 1996; Williams & Le Riche, 1968)
Ga	<ul style="list-style-type: none"> <li>• Strawberry: 0.4 (Jeon et al., 2019)</li> <li>• Beech leaf: 0.032 Tyler, 2005)</li> <li>• Wheat grain: 0.0014 (Eriksson, 2001)</li> </ul>	<ul style="list-style-type: none"> <li>• Rice foliage: 75 (Syu et al., 2017)</li> <li>• Wheat foliage: 12.1 (Syu et al., 2021)</li> <li>• Mushroom: 6.6 (Dursun et al., 2006)</li> </ul>	2-74, 29-1061 (Syu et al., 2017; Wheeler & Power, 1995)	5-16, 72-229 (Su et al., 2018; Syu et al., 2021)
In	<ul style="list-style-type: none"> <li>• Wheat grain: 0.11 (Chang et al., 2020)</li> <li>• Grass: 0.051 (Waterlot et al., 2013)</li> <li>• Beech leaf: 0.0002 (Tyler, 2005)</li> </ul>	<ul style="list-style-type: none"> <li>• Mushroom: 7.5 (Niedzielski et al., 2017)</li> <li>• Pteris vittata: 5.14 (Ha et al., 2011)</li> <li>• Rice foliage: 4.3 (Su et al., 2018)</li> </ul>	1.1-4.2, 9.6-37 (Su et al., 2018; Syu et al., 2021)	2.5-6.6, 22-57 (Su et al., 2018; Syu et al., 2021)
La	<ul style="list-style-type: none"> <li>• Grass: 0.17 (Laul et al., 1979)</li> <li>• Tea: 0.072 (Fu et al., 2001)</li> <li>• Various vegetables: 0.017 (Zhuang et al., 2017)</li> </ul>	<ul style="list-style-type: none"> <li>• <i>Cyperus rotundus</i> L.: 568.9 (Khan et al., 2017)</li> <li>• Barley foliage: 6 (Kotelnikova et al., 2020)</li> <li>• <i>Populus sieboldii</i>: 3.4 (Fu et al., 2001)</li> </ul>	0.44-6.5, 3.2-47 (Hao et al., 2021; Hu et al., 2002)	0.95-120, 6.8-864 (Hao et al., 2021; Rezaee et al., 2018)
Ce	<ul style="list-style-type: none"> <li>• Grass: 0.33 (Laul et al., 1979)</li> <li>• Pepper: 0.19 (Cao et al., 2000)</li> <li>• Corn: 0.011 (Li et al., 1998)</li> </ul>	<ul style="list-style-type: none"> <li>• <i>Dicranopteris dichotoma</i>: 2290.33 (Khan et al., 2017)</li> <li>• Rice foliage: 19 (Wen et al., 2001)</li> <li>• Chinese cabbage: 3.8 (Wen et al., 2001)</li> </ul>	6.7, 48 (Hu et al., 2002)	16, 114 (Hu et al., 2002)
Nd	<ul style="list-style-type: none"> <li>• Grass: 0.051 (Wiche &amp; Heilmeyer, 2016)</li> <li>• Rice: 0.029 (Šmuc et al., 2012)</li> <li>• Tomato: 0.0071 (Spalla et al., 2009)</li> </ul>	<ul style="list-style-type: none"> <li>• <i>Melastoma malabathricum</i>: 49.13 (Khan et al., 2017)</li> <li>• Mushroom: 7.1 (Campos et al., 2009)</li> <li>• Barley foliage: 7 (Kotelnikova et al., 2020)</li> </ul>	1.79-13, 12-90 (Carpenter et al., 2015)	6.69-221, 46-1532 (Carpenter et al., 2015; Rezaee et al., 2018)
Gd	<ul style="list-style-type: none"> <li>• Grass: 0.025 (Tyler &amp; Olsson, 2001)</li> <li>• Pepper: 0.015 (Cao et al., 2000)</li> <li>• Barley grain: 0.0003 (Eriksson, 2001)</li> </ul>	<ul style="list-style-type: none"> <li>• <i>Cyperus rotundus</i> L.: 175.8 (Khan et al., 2017)</li> <li>• <i>Dicranopteris dichotoma</i>: 75.08 (Khan et al., 2017)</li> <li>• Rice foliage: 0.49 (Wen et al., 2001)</li> </ul>	-	-

The 'background' column consists of examples of the concentrations of ETECs typically found in various plant species in environments without contamination, and the 'elevated' column has examples of unusually high uptake of the ETECs in plants without toxicity.



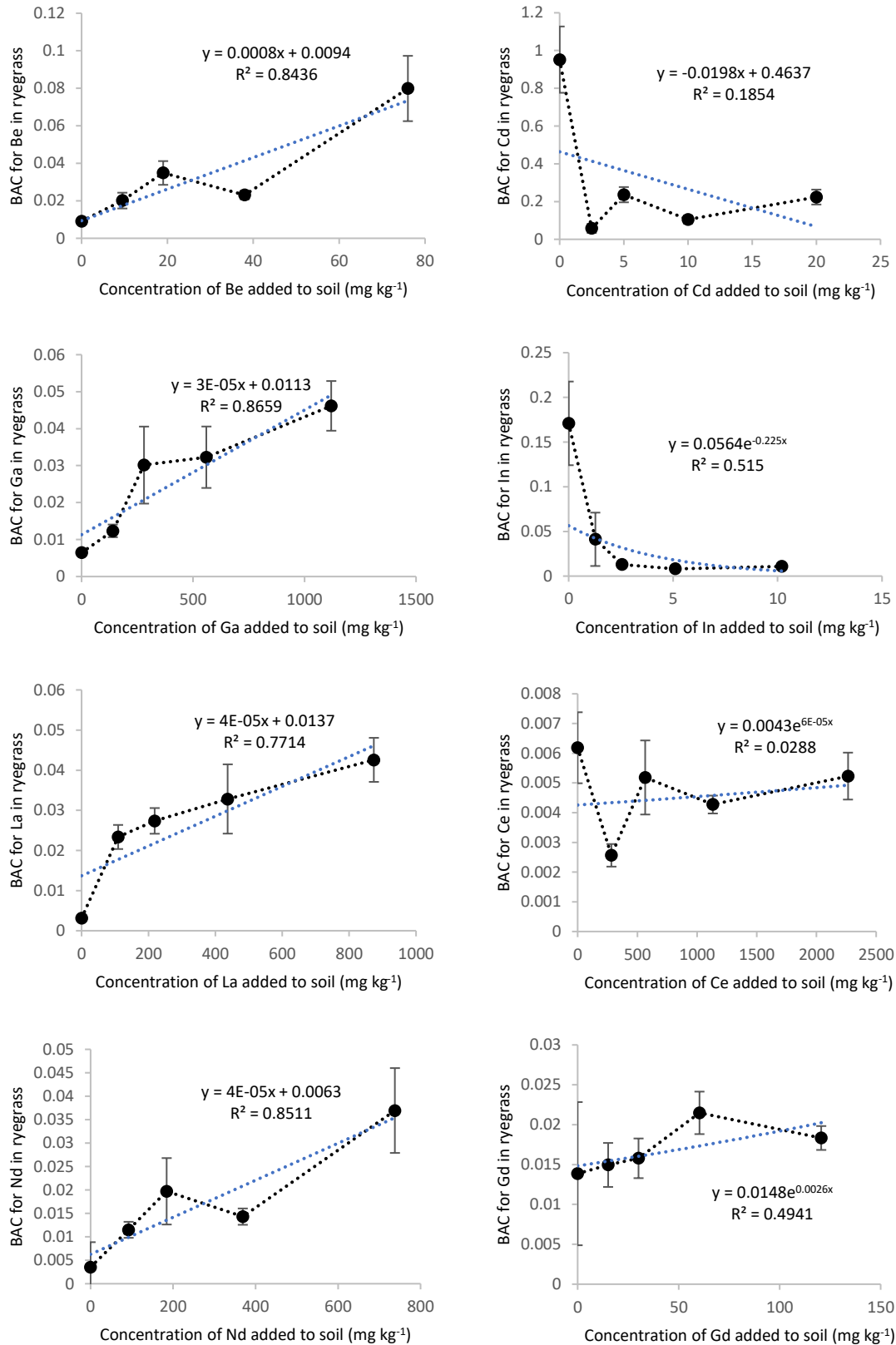


**Fig. D.1 Maximum concentration of TEs in perennial ryegrass before toxicity.**

The letters denote significant differences through LSD.

**Table D.2 Mass and molar mass of the ETECs and Cd in perennial ryegrass growing in the control soil, in vertical order from low to high**

Mass (mg kg <sup>-1</sup> )	Molar mass (μmol kg <sup>-1</sup> )
In 0.053	In 0.46
Cd 0.061	Cd 0.54
Be 0.12	Ce 2.6
Ce 0.37	Gd 3.5
Gd 0.55	Nd 6.3
Ga 0.58	La 7.0
Nd 0.91	Ga 8.3
La 0.97	Be 13



**Fig. D.2** Effect of the concentration of the ETECs and Cd added to soil on the bioaccumulation coefficients of the ETECs and Cd in perennial ryegrass

**Table D.3 Mean concentrations of the ETECs and Al in green versus black tea**

<b>Element</b>	<b>Green tea (mg kg<sup>-1</sup>)</b>	<b>Black tea (mg kg<sup>-1</sup>)</b>	<b>Concentration of ETEC or Al in black tea compared to green (%)</b>
Al	2224	1200	54
Be	0.23	0.052	22
Ga	0.67	0.49	73
In	0.15	0.15	101
La	3.3	2.1	63
Ce	0.91	0.70	77
Nd	2.5	1.5	62
Gd	0.48	0.34	70

## Appendix E

Table E.1 Locations of sampling sites (decimal degrees).

Site <sup>a</sup>	Longitude	Latitude
N01	175.278014	-40.401778
N02	175.151052	-39.768389
N03	175.156416	-39.458531
N04	174.997049	-38.484856
N05	174.051039	-36.147308
N06	173.619256	-35.424183
N07	172.901202	-34.586622
N08	174.449332	-35.983378
N09	175.521017	-37.202081
N10	175.521409	-37.202964
N11	175.428014	-36.883747
N12	175.793123	-37.06545
N13	176.347823	-38.2767
N14	175.367486	-40.355886
S01	173.955483	-41.475458
S02	173.697609	-41.619039
S03	173.746916	-41.364956
S04	173.767856	-41.331947
S05	173.358552	-41.202097
S06	173.26625	-41.302183
S07	173.007011	-41.293728
S08	172.997172	-41.070689
S09	172.980487	-41.185281
S10	172.890202	-41.008106
S11	172.889973	-40.967261
S12	172.892649	-40.9434
S13	172.822838	-41.007878
S14	172.795901	-40.91595
S15	172.807978	-40.864669
S16	172.781474	-40.841103
S17	172.632151	-40.735186
S18	172.617688	-40.726531
S19	172.621914	-40.555056
S20	173.086487	-41.387508
S21	172.813257	-41.388408
S22	172.590705	-41.793847
S23	172.331099	-41.849569
S24	172.251542°	-41.850211
S25	171.899811	-41.912211
S26	171.480067	-41.761297
S27	172.105229	-41.377078
S28	172.13908	-41.253586
S29	172.121008	-41.212906
S30	171.971147	-41.527919
S31	171.971429	-41.537917

S32	171.247772	-42.454789
S33	171.565094	-42.338475
S34	171.718451	-42.167772
S35	171.717581	-42.169475
S36	171.857022	-42.089028
S37	172.180214	-42.357139
S38	172.181858	-42.3586
S39	171.366966	-42.761456
S40	171.462468	-42.723272
S41	171.068767	-42.709742
S42	171.015896	-42.845492
S43	170.816213	-42.890886
S44	170.380171	-43.262861
S45	170.186722	-43.367778
S46	169.974106	-43.454708
S47	169.479212	-43.7094
S48	169.196756	-44.274156
S49	169.184305	-44.659719
S50	169.193083	-45.022442
S51	168.79267	-44.993017
S52	168.714865	-45.339167
S53	168.676367	-45.479744
S54	167.759741	-45.441072
S55	167.923252	-45.339744

<sup>a</sup>N: North Island, S: South Island.

## Appendix F

**Table F.1 Concentration ranges of the ETECs and Cd added to soil in the batch sorption experiments versus the plant pot trials**

Element	Concentration of TE added to soil (mmol kg <sup>-1</sup> )	
	Batch sorption experiments	Plant pot trials
Be	0.67-67	1.1-8.4
Cd	0.053-5.3	0.022-0.18
Ga	0.086-8.6	2.0-16
In	0.052-5.2	0.011-0.089
La	0.043-4.3	0.79-6.3
Ce	0.43-4.3	2.0-16
Nd	0.042-4.2	0.64-5.1
Gd	0.038-3.8	0.096-0.77

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