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The mobility and plant uptake of gallium and indium, two emerging contaminants associated with electronic waste and other sources

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HIGHLIGHTS

- Gallium and indium are more strongly bound to soil than other common trace element contaminants.
- Gallium and indium are poorly translocated into the aerial portions of *Lolium perenne*.
- Gallium and indium are likely to accumulate in soil.
- Soil ingestion is the most likely exposure pathway for humans and animals.

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ABSTRACT

Gallium (Ga) and indium (In) are increasingly susceptible to soil contamination via disposal of electronic equipment. Chemically similar to aluminium (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^{-1}) showed strong retention of both elements to the soil matrix, with mean distribution coefficient (K_D) values of 408 and 2021 L kg^{-1} for Ga and In respectively. 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$(OH)^{2+}$ and Ga/In$(OH)_2^+$ transitioned to Ga/In$(OH)_4^-$. Movement into the aboveground portions of perennial ryegrass (*Lolium perenne* L.) was low, with bioaccumulation factors of 0.0037 for Ga and 0.0002 for In; foliar concentrations peaked at 11.6 mg kg^{-1} and 0.015 mg kg^{-1} respectively. The mobility of Ga and In in the soil - plant system is low compared to other common trace element contaminants such as cadmium, copper, and zinc. Therefore, Ga and In are likely to accumulate in soils and soil ingestion, either directly, via inhaled dust, or dust attached to food, 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.

1. Introduction

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

Both elements are used extensively in electronic equipment. Gallium arsenide (GaAs) and gallium nitride (GaN) semiconductors are used in wireless and optoelectronic applications (Butcher and Brown, 2014). Indium-tin oxide (ITO) is used as a coating on liquid crystal displays, plasma displays and touch screens (Schwarz-Schampera, 2014). From 1995 to 2015, Ga production increased from 62 to 469 tonnes and In 239–769 tonnes (U.S. Geological Survey, 2017a; b). Both elements could enter the environment through the manufacture or disposal of electronic equipment (Robinson, 2009; Maneesuwannarat et al., 2016). Environmental contamination associated with e-waste is less of an issue in developed countries compared to developing countries (Robinson, 2009). Oguchi et al. (2011) reported that Ga is

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increasingly used in electronic equipment, which indicates that it will be present in e-waste. Similarly, Chen et al. (2015) reported that industrial sludge associated with electronic manufacturing contained 40–42 mg kg^{-1} In. Up to 4.6 mg kg^{-1} In was present in soil surrounding recycling sites in Indian slums (Ha et al., 2009), and up to 2.8 mg kg^{-1} 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 (Schwarz-Schampera, 2014; Lu et al., 2017). Ha et al. (2011) and Boughriet et al. (2007) measured up to 97 and 75 mg kg^{-1} In, respectively, in soil surrounding a Pb-Zn mine and a smelter. Others reported lower concentrations of 1.6 mg kg^{-1} (Waterlot et al., 2013), 1.4 mg kg^{-1} (Li et al., 2016), 0.55 mg kg^{-1} (Sterckeman et al., 2002) and 0.37 mg kg^{-1} (Aide, 2009). Połedniok et al. (2012) reported soil Ga concentrations at five sites near mines or metal processing plants ranging 93–441 mg kg^{-1} Ga and nearby agricultural soils contained 39–219 mg kg^{-1} 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^{-1} Ga in coal from China and the Former Soviet Union, while Font et al. (2007) and Fang and Gesser (1996) reported found fly ash concentrations of 37.5–320 mg kg^{-1} 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^{-1} Ga, and studies in Sweden reported biosolids concentrations of 1–41 mg kg^{-1} (Eriksson, 2001; Ahlberg et al., 2006).

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 through a variety of exposure pathways (White and Hemond, 2012). While there are data for acute and chronic human and animal exposure to In and Ga (Homma et al., 2003; Kjølholt et al., 2003; Ivanoff et al., 2012; Ayadi et al., 2014), there are currently no food and drinking water safety limits.

While the speciation of Ga and In may vary according to their use, when released into the environment they are likely to revert to the +3 oxidation state and their behaviour in soil is likely dominated by the stability of their respective aqueous trivalent species, ion hydrolysis and hydroxide precipitation (Wood and Samson, 2006). The octahedral hydrated cations Ga^{3+} and In^{3+} are acidic, and upon hydrolysis form the aqueous species $Ga/In(OH)^{2+}$, $Ga/In(OH)_2^+$, $Ga/In(OH)_3^0$ and $Ga/In(OH)_4^-$, 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 and Mukherjee, 2007). The hydroxide forms $Ga(OH)_4^-$ and $In(OH)_3$ are the dominant species in most agricultural soils, with pHs of 5.5–7.0 (McLaren and Cameron, 1996; Wood and Samson, 2006; Desutter and Godsey, 2010). 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. The solubility of α-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 $In(OH)_3$ (Wood and Samson, 2006). Transformation of $Ga/In(OH)_3$ to α-GaOOH, β-Ga_2O_3, In analogues and other mineral forms occurs from aging, heat and/or pressure (Pokrovski et al., 1997; Bernstein, 1998). Due to their high ionic potentials of 48 nm^{-1} for Ga^{3+} and 38 nm^{-1} for In^{3+} (Shannon, 1976), both elements likely bond with hard inorganic ligands such as F^-, PO_4^{3-}, and SO_4^{2-}; softer In also bonds strongly with Cl^- (Wood and Samson, 2006). Both elements are frequently complexed by organic acids, such as citric, malic and acetic, released in soil by root exudation (Jaitz et al., 2011; Boros et al., 2014; Chang et al., 2017). Although their aqueous oxidation state is always +3 (Wood and 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 and 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 (Hou et al., 2005; Boughriet et al., 2007; Waterlot et al., 2013) and just 55–85% of Ga was sorbed in (Połedniok et al., 2012). However (Sheppard et al., 2007), reported that K_D values (solid/solution concentration coefficients) of Ga and In in Canadian soils were 11,000 and 2800 respectively.

There is limited information on plant uptake of Ga and In. Gallium concentrations of <0.001 mg kg^{-1} were reported in wheat and barley grains (Eriksson, 2001) in five Swedish arable soils containing <9 mg kg^{-1} Ga. A selection of edible mushrooms contained 1.4–6.6 mg kg^{-1} Ga (Dursun et al., 2006). *Leersia hexandra* and *Houttuynia cordata* in Vietnam contained 0.36–2.57 mg kg^{-1} Ga (Ha et al., 2011). Higher concentrations have been obtained under hydroponic conditions with 2 mg kg^{-1} and 74 mg kg^{-1} found in wheat and rice (Wheeler and Power, 1995; Syu et al., 2017). Indium concentrations were <0.005 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 0.001–0.005 mg kg^{-1} In (Li et al., 2016), while Vietnamese vegetables contained 0.14–3.89 mg kg^{-1} (Ha et al., 2011), with up to 151 mg kg^{-1} in rice growing near a metal recycling centre with unquantified, but probably elevated, soil Ga concentrations. Most Ga and In accumulate in the roots with shoot: root ratios of 0.028 and 0.11 Ga in barley and wheat (Wheeler and Power, 1995; Omberg et al., 2011), 0.082–0.22 Ga in *Arabidopsis thaliana* (Chang et al., 2017), and <0.32 of both elements in rice (Yu et al., 2015; Syu et al., 2017). Gallium and In may behave similarly to Al, which is retained in the 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., the most common pastoral species in many pasturelands); and aqueous speciation modelling was completed with Visual MINTEQ 3.1.

2. Materials and methods

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 (Valentinuzzi et al., 2015; Al Mamun et al., 2016) and are presented in Table 1. The pH of the soil was adjusted approximately 4 years before this work by mixing the soil thoroughly with laboratory grade lime ($CaCO_3$) in the following

Table 1
Physical and chemical properties of Pukekohe soil, from [a]Landcare Research (2018) and Valentinuzzi et al. (2015). Values in brackets represent the standard error of the mean (n = 3).

[a]Texture profile	Loam/silty loam over clay
[a]Topsoil clay	22–34%
[a]Drainage class	Imperfectly/moderately well drained
[a]Profile available water (0–30 cm)	High (51–66 mm)
pH (H_2O)	5.95 (0.04)
CEC (me $100g^{-1}$)	22
Base saturation (%)	70
C (%)	2.1
N (%)	0.23
Olsen P (me 100 g^{-1})	290
N available (kg ha^{-1})	50
Total P (mg kg^{-1})	3414 (26)
Total S (mg kg^{-1})	491 (6)
Total Ca (mg kg^{-1})	4147 (117)
Total Mg (mg kg^{-1})	2400 (95)
Total K (mg kg^{-1})	1951 (59)
Total Cd (mg kg^{-1})	1.5 (0.0)
Total Cu (mg kg^{-1})	65 (0)
Total Mn (mg kg^{-1})	1266 (12)
Total Zn (mg kg^{-1})	173 (1)
Total Fe (mg kg^{-1})	44606 (96)
Total Pb (mg kg^{-1})	61 (1)
Ga $Ca(NO_3)_2$-extractable (mg kg^{-1})	<0.005
In $Ca(NO_3)_2$-extractable (mg kg^{-1})	<0.003
Cd $Ca(NO_3)_2$-extractable (mg kg^{-1})	0.015 (0.002)
Cu $Ca(NO_3)_2$-extractable (mg kg^{-1})	0.13 (0.02)
Mn $Ca(NO_3)_2$-extractable (mg kg^{-1})	40 (4)
Zn $Ca(NO_3)_2$-extractable (mg kg^{-1})	0.37 (0.06)
Fe $Ca(NO_3)_2$-extractable (mg kg^{-1})	1.65 (0.20)

proportions: 0.3, 0.6, 1.3 or 10 wt%, resulting in soil pH (1:2.5 mass soil: vol. H_2O) values of 5.5, 6.0, 6.8, 7.0 and 7.1 respectively (Valentinuzzi et al., 2015).

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 (±0.1) of soil was equilibrated with a.

0.05 M $Ca(NO_3)_2$ solution that had been spiked with a known amount of Ga or In by mixing in an end-over-end shaker. Agitation times of 30–480 min revealed that retention was relatively stable after 120 min (Fig. S1); subsequent experiments used this equilibration time. The extraction mixture was centrifuged at 1880 g for 10 min, 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.

The effect of concentration on the amount removed from the solution phase was measured using soil-affected change in solubility from 0.05 M $Ca(NO_3)_2$ solutions spiked with 1, 3, 10, 30, 100 or 1000 mg L^{-1} Ga or In. The effect of pH was determined by equilibrating with the series of limed soils, using 10 mg L^{-1} Ga/In spiked 0.05 M $Ca(NO_3)_2$. The extractant pH in un-spiked extracts of the entire lime series was measured after 120 min agitation, using a Mettler Toledo pH meter.

2.3. Plant uptake trial

Perennial ryegrass (*Lolium perenne* L.) was grown in pots (diameter ca. 6.5 cm, height ca. 8 cm) containing 250 g of the Pukekohe granular soil spiked with 0, 15, 31, 63, 125, 250, 500, 1000 or 2000 mg kg^{-1} Ga, or 0, 1.5, 3, 6, 13, 25, 50, 100 or 200 mg kg^{-1} In. The 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. Pots were placed in a growth chamber (settings on Table S1) on the 31st of July 2017, in a randomised-block design. There were a total of 68 pots. Before planting (50 seeds per pot), the spiked soils were put through a wet-dry cycle and placed in a growth chamber. Planting occurred on the 7th of August 2017. Saucers were filled with water daily. Four weeks after germination, 40 mL of 10,000 mg L^{-1} urea ($CO(NH_2)_2$) was applied to each pot. After six weeks of growth (on the 18th of September 2017), ryegrass was harvested 1.5 cm above the soil surface, rinsed with deionized water, placed in a drying oven at 60 °C until a constant weight was obtained, and ground using a Cyclotec 1093 sample mill (FOSS Analytical A/S, Hillerød, Denmark). The dry biomass was recorded.

2.4. Sample preparation and analysis

Plant samples underwent microwave digestion (CEM MARS Xpress, CEM Corporation, Matthews, 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_3, 2 mL 30% H_2O_2. 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^{-1} 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^{-1} (Sheppard et al., 2009) using Equation (1) and Equation (2).

$$C_s = \frac{\left(C_i - C_f\right)V}{m} \tag{1}$$

$$K_D = C_s \big/ C_f \tag{2}$$

where, C_s is the concentration of Ga/In retained by the soil matrix (mg kg^{-1}), C_i is the initial concentration in the extractant solution (mg L^{-1}), C_f is the concentration in the filtered solution (mg L^{-1}), V is the volume of the filtered solution (L), and m is the mass of soil used (kg). Correction factors were applied to C_f (Fig. S2).

Summary statistics were calculated in MS Excel; post hoc one-way ANOVA (analysis of variance) LSD (least significance differences) tests were calculated in RStudio (https://www.rstudio.com), significance at $p \le 0.05$.

2.5. Speciation modelling

The distribution between the different species of Ga and In in the extractant solutions were modelled using Visual MINTEQ 3.1 (Gustafsson, 2013) to estimate the effect that the changes in solution pH following equilibration alone could have on the metal species' distribution. The extractant solutions were simulated with each of the concentrations of Ga and In to estimate possible differences in aqueous hydroxide speciation and precipitation across a range of pHs. The model input parameters are given in Table S2.

3. Results

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 trend-lines of soil plotted against solution concentrations, were 408 (21) L kg^{-1} and 2021 (64) L kg^{-1} for Ga and In, respectively, (with standard errors) (Fig. S3). However, the degree of sorption (adsorption and precipitation) significantly increased ($p < 0.05$) when K_D was plotted against the concentration added to soil (Table 2). The K_D of Ga rose logarithmically from 88 to 392 L kg^{-1} with 1–100 mg L^{-1} in the extracting solution. In jumped sharply from 458 to 1812 L kg^{-1} between 10 and 30 mg L^{-1}.

Retention of Ga and In by the soil matrix decreased as the pH of the soil solution increased, across the range tested (Fig. 1). The K_D of Ga significantly decreased from 689 L kg^{-1} at pH 5.5, to 265 L kg^{-1} at 7.1. Indium decreased from 1266 to 458 L kg^{-1} respectively, with particularly significant drops in the lowest 0.5 and highest 0.3 in the range tested. Although both trend-lines were similar in shape, the K_D of In was consistently 73–153% higher than Ga.

3.2. Species present in the system

The equilibrium modelling predicted that $Ga(OH)_4^-$ and $In(OH)_3$ were the dominant species at pHs measured in the extraction solutions, accounting for >89.9% of all aqueous Ga and In (Table 3). As the pH rose from 5.5 to 7.1, anionic forms of both elements were expected to increase in dominance – $Ga(OH)_4^-$ 92.4–99.9%, and $In(OH)_4^-$0.008–0.338%. 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, the saturation index of Ga peaked at pH 5, thus decreased in the range tested (Fig. S6), and In increased to peak at 6.8–7.3 (Fig. S7). Saturation indexes increased with concentration. Partitioning of the metals between the different species across the pH range 1–14 is shown in the Supporting Information (Figs. S4 and S5).

Modelling of the spiked extraction solutions showed differences in the species distribution, depending on the spiked concentration. Cation dominance increased with concentration, with 60.4% Ga^{3+} and 71.9% In^{3+} in the 100 mg L^{-1} spike solutions, versus <0.1% in the 1 mg L^{-1} spike. Above 3 mg L^{-1} Ga and 30 mg L^{-1} In saturation indexes decreased due to pH having a larger effect than concentration on the net values; the $Ga(OH)_3$ (am) saturation index decreased from 1.27 to 0.78, despite a rise of 1.58–3.11 from 3 to 100 mg L^{-1}.

3.3. 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. 2). Uptake of Ga peaked at 11.6 mg kg^{-1} with 2000 mg kg^{-1} added to soil, with the trend indicating further uptake is possible, while In plateaued at 0.02 with 100 mg kg^{-1} in soil, significantly higher than at 25 and 50 mg^{-1}. 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 ($R^2 = 0.99$). There was no significant effects of either Ga or In on the biomass of the *L. perenne* (data not shown). The average dry biomass per pot was 2.27 g.

Table 2
Effect of the concentration of Ga and In added to soil on K_D.

Solution concentration (mg L^{-1})	Soil concentration (mg kg^{-1})	K_D Ga (L kg^{-1})	K_D In (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 denote the standard deviation of the mean; different letters denote significance; $n = 3$. Soil concentration calculated from mass added to sample.

4. Discussion

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; however, it is useful to acknowledge its limitations as a static measure. Other factors, such as colloidal transport, could also affect movement of the metals in soils (McLaren and Cameron, 1996), however measuring these was outside the scope of this work.

The K_D values in this study for Ga, with a mean K_D of 408 L kg^{-1}, were significantly lower than the values of 11,000 and 13,000 L kg^{-1} reported for Canadian soils (Sheppard et al., 2007, 2009). These differences are likely due to analytical methods since there was no aging of the Ga and In in our batch experiments, thus it is likely that a greater proportion of the total Ga and In here was still in the labile pool. Precipitated $Ga(OH)_3$ ages to less soluble α-GaOOH, with geomorphological transformation to β-Ga_2O_3 and other minerals possible (Pokrovski et al., 1997; Bernstein, 1998). 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).

Gallium and In are relatively immobile compared to other common trace element contaminants in soil. Sheppard et al. (2007) ranked Ga and In as the 3rd and 7th 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 and Olsson, 2002).

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 and Samson, 2006);) and thus readily precipitate at most commonly found soil pHs. 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. Minteq-predicted precipitation trends suggested that Ga and In precipitation as hydroxide species was most likely at around pH 5(Figs. S6 and S7). Gallium precipitation becomes less likely at > pH 5, due to the formation of $Ga(OH)_4^-$, while the corresponding In species only forms at above pH 8. 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,

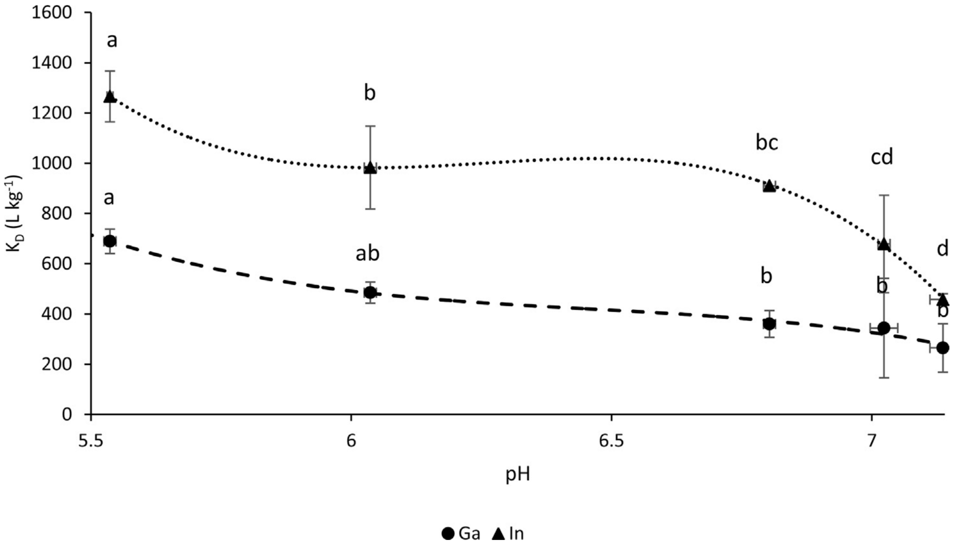

Fig. 1. Effect of extractant solution pH on K_D of Ga and In. Error bars denote standard deviation of mean values; different letters denote significance; $n = 3$ except Ga pH 6.04 $n = 2$, In pH 7.02 $n = 5$, In pH 6.80 $n = 1$.

Table 3

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

Lime applied (wt%)	pH	Aqueous species (%)[a]						Saturation index[b]	
		Ga/In^{3+}	Ga/In(OH)$^{2+}$	Ga/In(OH)$_2^+$	In(OH)$_3$ (aq)	Ga/In(OH)$_4^-$	In(NO$_3$)$^{2+}$	Ga/In(OH)$_3$ (am/s)	GaOOH(s)
Ga									
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
In									
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	–

[a] Percentage of the total concentration of aqueous Ga/In.

[b] Saturation index (SI) > 0 denotes oversaturation and further precipitation; SI < 0 dissolution.

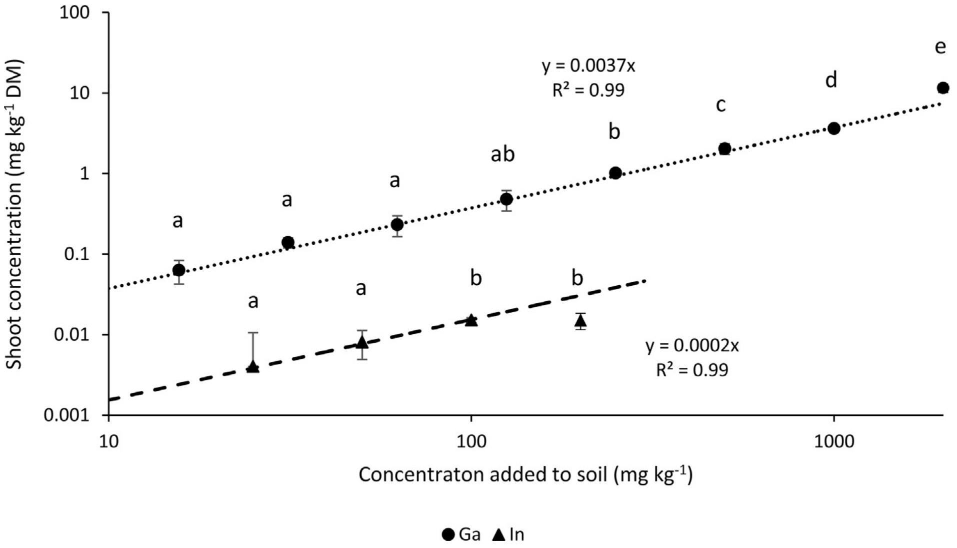

Fig. 2. Effect of the concentration of Ga and In added to soil on ryegrass shoot concentrations. Error bars denote standard deviation of mean values; different letters denote significance; $n = 4$.

in the oxide/reducible fraction.

The decrease in K_D with pH may be attributed to the formation of poorly-adsorbing dissolved anionic metal (oxyhydr)oxide species, 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 me 100 g^{-1}, considered medium within New Zealand (Blakemore et al., 1981). When the K_D of In dropped from 910 to 458 L kg^{-1} at pH 6.80 to 7.1, the proportion of $In(OH)_2^+$ was predicted to decrease from 0.568 to 0.285%, and $In(OH)_4^-$ increased from 0.169 to 0.338% (Table 3). In the first significant drop (1266–983 L kg^{-1}, at pH 5.5–6.0), total cationic In was predicted to have decreased from 11% to 4%. Lower precipitation cannot be attributed to either scenario; the relative saturation index is likely to have remained constantly high across this pH range. In the significant decrease in Ga K_D of 689–360 L kg^{-1} 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 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 (Figs. S4 and S5, Wood and Samson (2006)) and believed to be a determinant factor, a linear trendline was not forced through the data (Fig. 1). Data from Bi and Westerhoff (2016) supports this theory. Sorption of Ga to SiO_2 and Al_2O_3 was much lower at pH 9.5 than 4.5 and 7; Al_2O_3 had a greater affinity for the cations, and the strongly negative SiO_2 (point of zero charge ~2) repelled $Ga(OH)_4^-$. 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^{-1} to 0.015 μg L^{-1} as the pH rose from 5.37 to 7.25 in work by Tyler and Olsson (2001). Similarly, in Su et al. (2018) pore water concentrations were approximately 514 μg L^{-1} Ga and 474 μg L^{-1} In in the pH 4.1 soil, versus 230 μg L^{-1} Ga and 0.38 μg L^{-1} In at pH 7.4, in 400 mg kg^{-1} spiked soil zero days after planting. The lower 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 me 100 g^{-1}, respectively, and pH values were beyond the range tested (the polynomial trend-line in Fig. 1 cannot be accurately extrapolated). Logarithmic increases in K_D by Watmough (2008), from 10,000 L kg^{-1} at pH 4 to almost 100,000 L kg^{-1} 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 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^{-1}; 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 $Ga/In(OH)_3$ increased, rising further above the low solubility threshold. Saturation indexes greater than zero (Figs. S6 and S7) indicated oversaturation thus precipitation proportional to the mass entering the system. Two previous studies observed similar

Table 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^{-1})	pH	Aqueous species (%)						Saturation index (at pH 5.5)	
		Ga/In^{3+}	$Ga/In(OH)^{2+}$	$Ga/In(OH)_2^+$	$In(OH)_3$ (aq)	$Ga/In(OH)_4^-$	$In(NO_3)^{2+}$	$Ga/In(OH)_3$ (am)	GaOOH(s)
Ga									
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)
In									
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)	–
Unspiked 0.05 M $Ca(NO_3)_2$ solution									
0	5.6	–	–	–	–	–	–	–	–

patterns; aqueous In was 0.02–0.04 μg L^{-1} in contaminated Vietnamese soils, with total soil In concentration around 100 mg kg^{-1} (Ha et al., 2011). Połedniok (2008) measured a 0.5 mg kg^{-1} difference in extractable Ga despite the industrial soil containing 93 mg kg^{-1} versus 38 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 $Ga(NO_3)_3$ and $In(NO_3)_3$ undergo extensive hydrolysis that can greatly reduce the pH (Table 4). In the extractant solutions, reductions in pH of 1.8 and 2.3 were predicted with 100 mg L^{-1} In and Ga respectively. Because the pH of the spiked extracts after equilibration was not measured, the actual reductions are unknown, however, it is likely that the buffering capacity of the soil is likely to have resisted the pH change. This capacity is expected to be medium-high for the Pukekohe soil with a medium CEC and high base saturation (Blakemore et al., 1981).

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. 1, Table 2, Fig. S1). In Tyler and Olsson (2002) K_D values were 14,211 and 967 L kg^{-1} for Ga and In respectively, but concentrations in the uncontaminated soils were much higher for Ga, at 5.4 mg kg^{-1} Ga and 0.029 mg kg^{-1} In. Data assumed close to background levels (3–70 mg kg^{-1} Ga, 0.01–0.5 mg kg^{-1} In (Kabata-Pendias and Mukherjee, 2007)) were used in Sheppard et al. (2007), with distribution coefficients of 11,000 L kg^{-1} Ga and 2800 L kg^{-1} In.

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 considered in the modelling. 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 me 100 g^{-1}, of which 70% was occupied by the basic cations Ca^{2+}, Mg^{2+}, K^+ and Na^+.

4.2. Mobility of Ga and In in the plant system

Perennial ryegrass was capable of adsorbing 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. 2), but the amount taken up increased with contamination ($p > 0.05$). Concentrations applied (15–2000 mg kg^{-1} Ga, 1.5–200 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 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. Although the K_D was not measured in that work, the slightly lower CEC (16.2 and 18.0 versus 22 me 100 g^{-1}) and higher pH (7.3–7.5 versus 5.5) in their contaminated soils may have contributed to lower values and, hence greater bioavailability. Extremely high concentrations in hydroponic rice, up to 74 mg kg^{-1} Ga and 151 mg kg^{-1} In may have been possible due to the absence of soil (Syu et al., 2017); soil experimentation only yielded 10 mg kg^{-1} Ga and 8.3 mg kg^{-1} In (Su et al., 2018). The plateau of 0.015 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 mg L^{-1} solution In caused significant reductions in root and shoot biomass for rice seedlings, though both increased with 15 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 and 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, 2004, 2005).

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 S3). Gallium had the second and fourth lowest bioaccumulation factors 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, 2004) in the acidic organic horizon in both studies. In Su et al. (2018) rice plant bioaccumulation factors 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. Omberg et al. (2011) found a correlation of $r = -0.45$ between K_D and bioaccumulation factors across many elements and plant organs, and the bioaccumulation factors 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 5). In addition, bioaccumulation factors 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.

4.3. Potential for movement into the food chain

Although little Ga and In taken up by ryegrass, the impact on animal health cannot be currently predicted. Data and findings from Waterlot et al. (2013) showed that ≤0.37% of added Ga and ≤0.05 mg kg^{-1} 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^{-1} 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 μM solubility) (Bernstein, 1998; Wood and Samson, 2006). Across a range of natural water bodies, just ≤0.03 μg L^{-1} Ga and 0.1 ng kg^{-1} In has been reported

Table 5
Comparison of Ga and In K_D values in literature.

Element	K_D (L kg^{-1})	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^{-1} Ga		
	689	Maximum, pH 5.5		
	219,779	Minimum, pH 5.4	Single site, 0–10 cm, grass/deciduous trees, Sweden, uncontaminated	Tyler and Olsson (2001), [a]
	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), [b]
	11,000	Mean	Many sites, Canada, uncontaminated/not recently	Sheppard et al. (2007)
	210	Minimum		
	200,000	Maximum		
	2000	pH 3.8	Many similar sites, sandy to sandy-loam, mature forest, 0–5 cm, Canada, uncontaminated	Watmough (2008), [c]
	100,000	pH 7		
	1300	Peat (*Spagnum*), fen, *Pinus* forest	Individual sites, 0–30 cm, Sweden, uncontaminated	Sheppard et al. (2009)
	2600	Clayey silty till, fen, mixed forest		
	5900	Sandy till, oak forest		
	7800	Peat, former fen, spruce forest		
	7800	Clay gyttja, open fen		
	9400	Clay gyttja, fen, alder forest		
	14,000	Clayey silty till, arable		
	5500	Mean		
	13,000	Mean	Many sites, Canada, uncontaminated/not recently	Sheppard et al. (2009)
	880	5th percentile		
	110,000	95th percentile		
In	2021	Mean	Single site, loam/silty loam, vegetable growing, 0–25 cm, New Zealand, experimentally contaminated	Current study
	163	Minimum, 1 mg L^{-1} In		
	3187	Maximum, 30 mg L^{-1} In		
	967	Mean	Many sites, pH 4.29, sandy-silty, beech deciduous forest, 0–7.5 cm, Sweden, uncontaminated	Tyler and Olsson (2002), [b]
	2800	Mean	Many sites, Canada, uncontaminated/not recently	Sheppard et al. (2007)
	180	Minimum		
	11,000	Maximum		

[a] Calculated from graphical solution data and the total solution concentration.
[b] calculated from table data.
[c] collected from graph.

(Kabata-Pendias and Mukherjee, 2007). Soil retention is effective at restricting movement into waterbodies; ≤40% In leached 35 cm in 18 months, with only 5–38% moving below the top 2 cm in several soil types (Hou et al., 2005). Stream water contained 1–79 pmol L^{-1} Ga versus 4.6–33 mg kg^{-1} in associated Californian topsoil (Shiller and 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 mg kg^{-1} Ga or 20 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 and Mirick, 2006)), 29 mg Ga or 2.9 mg In sheep (9.5% of diet DM (Freer et al., 2012; Ford and Beyer, 2014)), and 340 mg Ga or 34 mg In for dairy cattle (9% of diet (Dairy NZ; Ford and Beyer, 2014)).

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, there 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.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2018.06.111.

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