



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.

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1. Introduction

Gallium (Ga) and indium (In) are chalcophilic metallic trace elements that are non-essential for life. (Potędnik 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; Potędnik 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; Maneesuwanarat 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). Poedniok 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 Ga³⁺ and In³⁺ are acidic, and upon hydrolysis form the aqueous species Ga/In(OH)²⁺, Ga/In(OH)₂⁺, Ga/In(OH)₃⁰ 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-Ga₂O₃, 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 Ga³⁺ and 38 nm⁻¹ for In³⁺ (Shannon, 1976), both elements likely bond with hard inorganic ligands such as F⁻, PO₄³⁻, and SO₄²⁻; 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; Poedniok 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 (Poedniok 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 (CaCO₃) in the following

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