



## Mobility and retention of indium and gallium in saturated porous media

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### ABSTRACT

Transport of indium and gallium is reported in laboratory column experiments using quartz sand as a model porous medium representative of a groundwater system. With increased use of indium and gallium in recent years, mainly in the semiconductor industry, concerns arise regarding their environmental effects. The transport and retention behavior of these two metals were quantified via batch and column experiments, and numerical modeling. The effect of natural organic matter on indium and gallium mobility was studied by addition of humic acid (HA). Measured breakthrough curves from column experiments demonstrated different binding capacities between indium and gallium, stronger for indium, with the presence of HA affecting retention dynamics. For indium, the binding capacity on quartz decreases significantly in the presence of HA, leading to enhanced mobility. In contrast, gallium exhibits slightly higher retention and lower mobility in the presence of HA. In all cases, the binding capacity of gallium to quartz is much weaker than that of indium. These results are consistent with the assumption that indium and gallium form different types of complexes with organic ligands, with gallium complexes appearing more stable than indium complexes. Quantitative modeling confirmed that metal retention is controlled by complex stability.

### 1. Introduction

Indium and gallium are metals of low abundance in the Earth's crust, with typical concentrations of 0.11–0.25 mg/L indium and 15–19 mg/L gallium [1,2]. These two chemical elements were of only minor technical relevance in the past. Anthropogenic release was mainly via pollution-intensive processes such as mining and burning of fossil energy carriers in which indium and gallium were present as trace metals [3]. Correspondingly, there has been only moderate interest in these elements from the environmental sciences community.

However, over the last two decades, both indium and gallium have played a key role in the modern semiconductor industry. They are central to integrated circuits and photoelectric devices in products of mass production, such as smartphones, tablet computers, and digital cameras [4,5]. The predominant Ga compounds in semiconductors are GaAs and GaN [6,7] while the most common use (> 50%) of indium is as indium tin oxide (ITO), a transparent, heat reflective and electrically conductive coating used on screens in electrical equipment [7–9]. Both elements are extremely useful in these applications due to their relatively high electron mobility and charge transfer efficiency [10] thus they are often near irreplaceable. Consequently, there has been a sudden and dramatic increase in the demand for indium and gallium in the last decade (Fig. S1).

Increased industrial use often leads to increased environmental concentrations [3] and development of new potential environmental sources such as e-waste [11] and biosolids [12]. For example, Tokumaru et al. [11] reported an extremely high degree of indium contamination in e-waste recycling soil with an enrichment factor > 40 compared to control site soil. Similarly, Poledniok [13] reported systematic higher concentrations of Ga in soil from an industrial area in Poland compared to agricultural soil from the same region. With respect to groundwater, Chen [4] reported that wells in an industrial area in Taiwan had a mean Ga concentration of 19.34 µg/L, compared to 0.05 and 0.02 µg/L in groundwater from two non-industrialized zones, and concentrations of 9.25 µg/L vs. 0.04 and 0.01 µg/L, respectively, for In. These findings raise serious concern, given that gallium and especially indium have negative impacts on living organisms, like reduction in root length and weight for *Arabidopsis thaliana* and rice [3,14–16]. In addition to natural ecosystems, toxicity to various organisms was reported [17–20] and human health might also be affected if indium and/or gallium reach groundwater systems that provide drinking water [14]. In a different context, gallium has been applied to diagnose tumors in medical tests as gallium citrate complexes [21] and can thus be released from hospital wastewater plants.

Currently, the environmental speciation and the ecotoxicity of indium and gallium are not well constrained. However, these elements

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are widely accepted to be predominantly trivalent, and hydrolyze in solution (to  $\text{Ga/In(OH)}^{2+}$ ,  $\text{Ga/In(OH)}_2^+$ ,  $\text{Ga/In(OH)}_3^\circ$  and  $\text{Ga/In(OH)}_4^-$ ). Moreover, these elements complex to hard inorganic ligands when available, and precipitate readily in pure water [1]; both elements also complex with organic molecules rich in hydroxyl and carboxy groups [15]. Analogy to other metals suggests that toxicity may be exhibited when concentrations in the environment change abruptly [3].

The transport behavior of indium and gallium in groundwater systems remains poorly understood; to date it has in essence not been reported in the literature. Moreover, although the sorption behavior of indium and gallium has been studied, to some extent, for technical sorbents utilized for recovery (e.g., from aluminum and zinc ores [22–25]), research on their interaction with typical minerals of soil systems is only in its infancy [10,26].

The objectives of this study were to provide insights into the retention and transport behavior of indium and gallium organic complexes in porous media that are representative of some groundwater environments. Trisodium citrate was used as a complexation agent that stabilizes indium and gallium in solution; it is a naturally prevalent molecule representative of short-chain organic acids present in soil. Study of this system is a crucial step towards fuller understanding of the environmental fate of these elements. Quartz sand was chosen as a simple model porous medium. Sorption equilibrium tests were first performed and interpreted in terms of Langmuir and Freundlich sorption isotherms. Transport behavior in saturated quartz sand columns was then studied, with examination also of the effect of humic acid (HA) – representative of natural organic matter – on indium and gallium mobility. Because of the hydrolysis of indium(III) and gallium(III) in a pH range typical of sand and soils, indium(III) and gallium(III)-organic acid complexes are not expected to be significant [1]. However, indium(III) and gallium(III) are known to form relatively strong polynuclear complexes with  $\alpha$ -hydroxyl acids in acidic media [27]. Moreover, HAs are known to form complexes with metal ions [28–30] and they can thus influence significantly the binding and transport behavior of metal ions in aqueous environments [30–32]. It is further noted that citrate is an extremely soluble low molecular weight organic acid [33], whereas humic acid has a much higher molecular weight, is far less soluble (particularly under acidic conditions), and is frequently found in colloidal material [34]. Hence, their roles in these experiments are almost mutually exclusive. Finally, quantitative numerical modeling of the experiments confirmed the factors controlling the retention of indium and gallium.

## 2. Materials and methods

### 2.1. Materials

Indium(III) chloride ( $\text{InCl}_3$  98%), gallium(III) nitrate hydrate anhydrous basis ( $\text{Ga(NO}_3)_3 \cdot \text{H}_2\text{O}$  99.9%), trisodium citrate dihydrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ ), sodium bromide ( $\text{NaBr} \geq 99.5\%$ ), hydrochloric acid ( $\text{HCl} \geq 37\%$ ), nitric acid ( $\text{HNO}_3$  70%), and humic acid (HA) sodium salt were purchased from Sigma-Aldrich (for more information on the HA, see Section 3 in the SI). Medium size sand (UNIMIN, USA) was used in all experiments (for more information on the sand, see Section 3 in the SI). Cobalt (10 mg/L stock solution) was purchased from Inorganic Ventures and used as an internal standard in analytical measurements. All solutions were prepared using double deionized water (DDW, 18.2 M $\Omega$  cm).

### 2.2. Stock solution

Indium and gallium complexes with added trisodium citrate dihydrate, hereafter referred as citrate, were found to produce stable complexes in aqueous solutions. Citrate is a typical component of soil organic matter and often used as a model molecule, for small natural organic ligands, that are prevalent in the subsurface environment and

interact with various metals [35]. All working solutions that are described hereafter were prepared from stock solutions of 10 mg/L indium or gallium, including citrate, and referred to hereafter as indium or gallium solution. A molar ratio of 1:4.5 metal to citrate was shown to yield stable complexes in aqueous solution and was thus applied in all cases. For solutions that contain HA, the above working (stock) solutions were mixed with 10 mg/L HA.

### 2.3. Sorption isotherms

Sorption equilibrium experiments were performed to quantify the mass of indium and gallium that adsorbs to sand under equilibrium conditions. Full details of these experiment protocols, and the results and interpretation, are described in the Supporting Information (SI).

### 2.4. Column experiments

Transport behavior of indium and gallium was studied by vertical sand column experiments. The experiments were carried out in duplicates with solution concentrations of 1 mg/L metal and a molar ratio of 1:4.5 metal to citrate, or subsequently also including 10 mg/L of HA (which is considered a common environmental level). In addition, each stock solution contained 500  $\mu\text{g/L}$  bromide ( $\text{NaBr}$ ) which served as a nonreactive tracer. All relevant figures depict the ratio of inlet concentration to measured outlet concentration  $C/C_0$  vs. pore volume (PV; 1 PV = total volume of fluid in the column).

Two polycarbonate columns with lengths of 18.2 cm and 19 cm, and inner diameter of 3 cm were used. Each packed column underwent a 24 h saturation phase, which involved saturation with DDW, from the bottom of the column, via a peristaltic pump to displace air in the pores. The DDW reservoir was then substituted by a reservoir solution with the respective metal complexes, and fraction collection at the column outlet began. After running the experiment for 90–130 pore volumes, the reservoir was switched back again to DDW. For the entire experiment, the pump delivery rate was 1.1 mL/min.

The pH of each collected sample was measured online with an electrode placed at the outlet of each column. The pH was stable and comparable within less than 0.25 pH units for all experiments as shown in Figs. S3–S5.

### 2.5. Concentration analyses

All samples were analyzed via ICP-MS (Agilent 7700 s) for indium, gallium and bromide concentrations. Before measurement, each sample was filtered through a 0.45  $\mu\text{m}$  PVDF (polyvinylidene fluoride) membrane and then diluted with nitric acid, resulting in a total acid content of 2%.

### 2.6. Modeling

The transport of indium and gallium complexes was quantified using the software package Hydrus 1D [36], which can model transport and retention of multiple solutes in water-saturated porous media. An inverse mode was applied to fit sorption parameters to experimental breakthrough curves (BTCs), using a nonlinear least squares optimization routine, to evaluate the relevance of various nonequilibrium kinetic sorption models. Fits of tracer BTCs to the advection-dispersion equation, associated with each indium or gallium transport experiment, were used to obtain the dispersivity. Water content and bulk density were calculated from gravimetric measurements and the geometry of the column. For these simulations, steady state, uniform flow through a saturated column was assumed. The effect of more complicated flow behavior, such as mobile and immobile water, was neglected in this study. Full details of the models are described in the SI.

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