

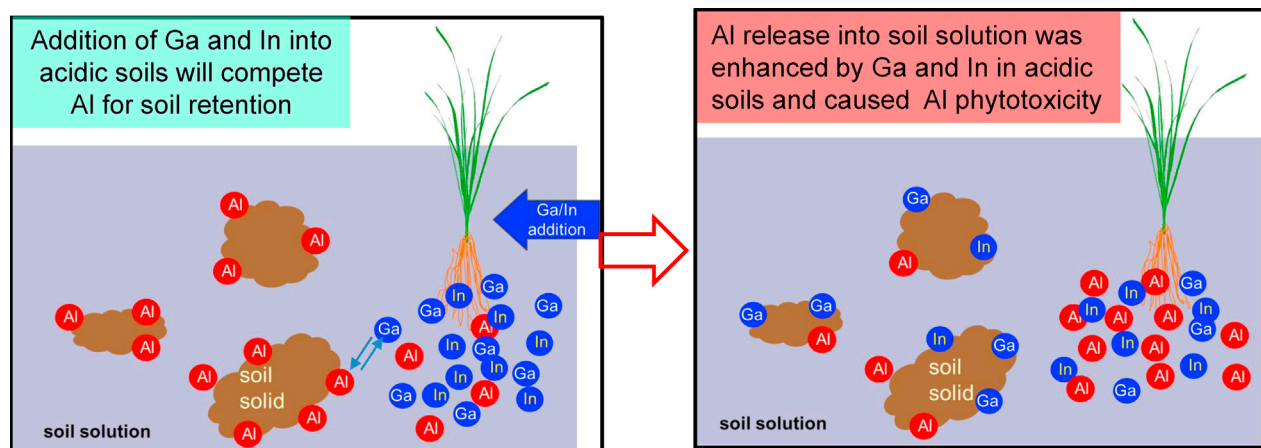


Research Paper

Growth inhibition of rice (*Oryza sativa* L.) seedlings in Ga- and In-contaminated acidic soils is respectively caused by Al and Al + In toxicity

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GRAPHICAL ABSTRACT



HIGHLIGHTS

- Growth inhibition of rice plant in Ga-spiked acidic soils is due to Al toxicity.
- Growth inhibition of rice plant in In-spiked acidic soils is due to Al + In toxicity.
- Growth inhibition of rice plant by Ga and In in neutral/alkaline soils is negligible.

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ABSTRACT

Limited information exists on the effects of emerging contaminants gallium (Ga) and indium (In) on rice plant growth. This study investigated the effects on growth and uptake of Ga and In by rice plants grown in soils with different properties. Pot experiment was conducted and the rice seedlings were grown in two soils of different pH (Pc and Cf) spiked with various Ga and In concentrations. The results showed concentrations of Ga, In, and Al in soil pore water increased with Ga- or In-spiking in acidic Pc soils, significantly decreasing growth indices. According to the dose-response curve, we observed that the EC₅₀ value for Ga and In treatments were 271 and 390 mg kg⁻¹ in Pc soils, respectively. The context of previous hydroponic studies suggests that growth inhibition of rice seedlings in Ga-spiked Pc soils is

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Rice seedlings

mainly due to Al toxicity resulting from enhanced Al release through competitive adsorption of Ga, rather than from Ga toxicity. In-spiked Pc soils, both In and Al toxicity resulted in growth inhibition, while no such effect was found in Cf soils due to the low availability of Ga, In and Al under neutral pH conditions.

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1. Introduction

Gallium (Ga) and indium (In) compounds are being extensively utilized in semiconductor manufacturing and the electro-optical industry [1,2]. The present vigorous development of high-tech industries raises the concern that large amounts of wastewater derived from associated manufacturing processes may easily become a potential source of environmental contamination. Once industrial effluents containing Ga and In are discharged into rivers or through irrigating systems, their presence may influence the growth and productivity of crops. Humans may also be exposed to Ga and In via the food chain, which could pose severe health risks. Studies have suggested that Ga and In metalloids are generally toxic to laboratory animals and may potentially cause testicular toxicity and increase tumor occurrence [3]. Chepesiuk [4] also found that exposure to gallium arsenide (GaAs) and indium arsenide (InAs) can result in both acute and chronic toxicity to the lungs, kidneys, and reproductive organs. Considering that groundwater concentrations of Ga and In in science-focused industrial parks are significantly higher than those of non-industrial areas in Taiwan [5], a wider understanding is needed to further assess the potential impact of Ga and In-containing wastewater on the environment.

Ga and In are amphoteric elements placed in the IIIA group in the periodic table. Their species depend on the pH and oxidation state of the environment. The valence of both elements is generally +3, while oxidation states of +1 or +2 can also exist dependent on environmental conditions [1]. At room temperature, soluble species such as Ga^{3+} , $\text{Ga}(\text{OH})_2^+$, $\text{Ga}(\text{OH})_2^{2+}$, In^{3+} , $\text{In}(\text{OH})_2^+$, and $\text{In}(\text{OH})_2^{2+}$ are predominant under acidic conditions, while In can be transformed into the insoluble $\text{In}(\text{OH})_3$ at pH 5–9 [1,6]. The chemical characteristics of Ga and In are similar to those of Aluminum (Al), and several studies have reported on Al dynamics in soils and on related toxicity to rice plants [7–9]. However, little information about the effects of Ga and In on the growth of rice plants grown in Ga/In-contaminated soils exists to date.

Rice (*Oryza sativa* L.) is the staple food for over 90% of the population in Asia [10]. This universal food item may represent a potential route by which human beings are exposed to Ga and In, especially in areas near high-tech industrial parks. Our previous study showed that exposing rice seedlings to Ga and In in hydroponic experiments had different effects on the growth of rice plants. A significant increase in growth indices was observed with increasing Ga concentration in culture solutions ($<10 \text{ mg Ga L}^{-1}$), which suggests that Ga may accelerate the growth of rice seedlings. In contrast, under In exposure, nutrient deficiency and growth inhibition occurred when In concentrations were higher than 0.04 mg L^{-1} [11]; the toxicity mechanism was similar to that of Al toxicity [12]. In addition, Kopittke et al. [13] also found that adding soluble Ga and In to cowpeas in solution culture caused cell rupture within 2 h and reduced the elongation of cowpea roots. Yu et al. [14] found that Ga retarded the relative growth rate, transpiration rate, and water-use efficiency of rice seedlings after 2 days of exposure to increasing Ga concentrations in solution culture. Due to the complexity of paddy soils, factors like pH, redox potential, cation exchange capacity (CEC), and organic matter content all affect the fate of Ga and In in soils. Consequently, the effects of Ga and In on rice seedlings in hydroponic experiments might differ from those in soil cultiva-

tion. Existing literature on the dynamics of Ga and In elements in various soil systems is relatively scarce. Therefore, the objective of this study was to investigate the effects of Ga and In on the growth of rice seedlings and to assess the fate of these elements in various soil systems.

2. Materials and methods

2.1. Soil sampling and properties

Surface soils (0–30 cm) were randomly collected from the Pinchen series, Taoyuan (northern Taiwan), and the Chengchung series, Tainan (southern Taiwan). Soil samples were air-dried, sieved to a particle size below 2 mm, homogenized, and preserved in plastic vessels. Basic properties were determined as follows. Soil pH was measured at a 1:1 ratio of soil to water [15]. The hydrometer method [16] was used to determine soil texture. Cation exchange capacity (CEC) was determined using the NH_4OAC method [17]. Organic matter content was determined by the Walkley–Black wet digestion method [18]. Crystalline and amorphous iron and aluminum contents were extracted with dithionite-citrate-bicarbonate (DCB) and ammonium oxalate, respectively [19,20]. Plant available-aluminum (Al) in soils was determined by the 0.02 M calcium chloride (CaCl_2) extraction method [21]. The basic physical and chemical properties of the two tested soils are presented in Table 1. The Pinchen soil (Pc) had low pH, CEC, and O.M, which are notable features of acidic soils (pH = 4.1). In contrast, the Cf soil had high pH (pH = 7.4) and CEC. The textures of the Pc and Cf soils were clay and silty clay loam, respectively. Both amorphous Al content and Fe oxide were lower in Cf soils than in Pc soils. Native Ga concentrations in Pc and Cf were 22 and 11 mg kg^{-1} , respectively; In concentrations were below the detection limit.

2.2. Ga and In treatment

The two tested soils were prepared by artificially spiking with GaCl_3 (99.999%, ultra dry; Alfa Aesar) and InCl_3 (99.999%, anhydrous; Alfa Aesar), respectively. Concentrations of both treatments were 0, 50, 100, 200, and 400 mg kg^{-1} . Each treatment was prepared in three replicates.

2.3. Pot experiments

The Taikeng 9 cultivar of paddy rice (*Oryza sativa* L.) was used in this study due to its high quality and because it is commonly planted in Taiwan. Rice seeds were sterilized by soaking in a solution containing 30% hydrogen peroxide and 1% sodium hydrochloride for 30 min, then rinsed with distilled water several times to make sure the residual solution was completely washed away. For pre-germination, seeds were placed on moist tissue paper in Petri dishes at 37°C for 4 days. After germination, rice seedlings were transferred into unspiked soils and grown for 14 days. Four well-grown seedlings were selected and transplanted together into each one pot filled with 500 g of the Ga or In-spiked soils for 50 days of cultivation. Each treatment was conducted in three replicates. Water levels of pots were maintained at about 5 cm above the soil

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