



Review of indium, gallium, and germanium as emerging contaminants: occurrence, speciation and evaluation of the potential environmental impact

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Abstract: The increasing demand for indium, gallium, and germanium driven by high-tech industries has spurred extensive research into their environmental interaction, despite their rarity in the Earth's crust. Understanding the chemical forms and mechanisms of occurrence of these elements – from production through – and their interactions with the environment is crucial for future environmental impact assessments. The aim of this paper is to highlight: (i) the compounds and applications of indium, gallium, and germanium in high-tech manufacturing, (ii) the complexes of these elements, their reactivity, and stability under specific conditions, (iii) possibilities for recovering and recycling these elements from end-of-life (EOL) products through leaching and extraction, (iv) their toxicity and health impacts, and (v) pollution indices affected by background concentrations of these elements in soils or sediments. Despite their low natural abundance and low recycling input rates (IRI), the lack of comprehensive toxicity data poses a significant challenge in assessing the potential ecological risk index (RI). Moreover, insufficient background data on the concentration of these elements in various environmental samples underscores the need for further research and investigation in the future.

Introduction

Due to the growing demand for indium (In), gallium (Ga), and germanium (Ge), which are considered technological critical elements (TCE), much research is being conducted to explore their environmental impact despite their limited presence on the earth's crust (Cobelo-García et al. 2015). In addition, investors are increasingly drawn to renewable energy industries, which are more favorable risk-return profile, particularly since the Russian-Ukrainian conflict began (Mohammed et al. 2023). Moreover, aligning with COP26 summit perspectives and attaining the net-zero goal by 2050 is crucial (Frenzel et al. 2017). The increasing shift toward a sustainable economy raises the need for photovoltaic (PV) panels, thus boosting the demand for constituent elements of this technology, such as indium, silicon, gallium, tellurium and germanium (EC JRC, 2016). The inclusion of TCE in modern technology products is causing notable alterations in the natural environmental cycle at the Earth's surface. It is important to delve deeper into the effects of TCE on biogeochemical cycles and the potential threats they pose to both human and biological health (Jabłońska-Czapla et al. 2022, Jin et al. 2016, Karbowska et al. 2022). Gallium and indium are post-transition metal elements

that belong to group 13 (boron group), while germanium is a metalloid from group 14 (carbon group). Elements in group 13 show oxidation numbers of +1 and +3, whereas elements in group 14 differ substantially, including non-metals like carbon, metalloids like germanium and silicon, and post-transition metals. The oxidation number for germanium can be +2 and +4 (Petrucci et al. 2017).

It is worth noting that one of the obstacles facing the speciation of indium, gallium, germanium, and other TCEs is the low concentration levels near the limit of detection (LOD). Hence, more sophisticated hyphenated techniques, such as High-Performance Liquid Chromatography coupled to Mass Detection (HPLC–MS), are required (Wojcieszek et al. 2018). The aim of this paper is to draw attention to (i) indium, gallium, and germanium compounds and their applications in the high-tech manufacturing industry, such as indium tin oxide (ITO), germanium(IV) oxide (GeO₂), and gallium arsenide (GaAs); (ii) the reactivity and stability of indium, gallium, and germanium complexes under specific conditions; (iii) the recovery and recyclability of these elements from end-of-life (EOL) products through extraction techniques using different types of acids; (iv) the toxicity and health impacts of In, Ga and Ge; and (v) the evaluation of the potential environmental

impact of these elements and the obstacles that are hindering their assessment process. At the same time, the strengths and weaknesses will be discussed for each level in order to identify current potential gaps and develop adequate knowledge, along with suggestions for possible research in the future.

Sources and high-tech applications of indium, gallium, and germanium

The concentration of In, Ga and Ge, known as less studied technology critical elements (LSTCE), in various elements of the environment are presented in several publications (Bu-Olayan and Thomas 2020, Dang et al. 2021, Jabłońska-Czapla and Grygoyć 2021, Kouhail et al. 2020, Kouhail et al. 2022, Romero-Freire et al. 2019). Figure 1 displays a hypothetical path for In, Ga, and Ge. Like most other rare earth elements (REEs), these elements exist mainly as by-products of some ores and minerals. In addition, their presence has recently become more prevalent in ecosystems due to anthropogenic disturbances induced by metallurgical production. For instance, exposure to mining activities and weathering promotes the erosion of In, Ga, and Ge via water and wind (Lui et al. 2021). Clearly, leakage and loss of these elements in the ecosystem can occur during slag processing (Ettler et al. 2022), electronics manufacturing, and recycling of waste electrical and electronic equipment (WEEE) (Charles et al. 2020, Jabłońska-Czapla et al. 2023).

In a review of the indium cycle conducted by White and Hemond (2012), the largest input of indium to the environment comes from the mining industry rather than semiconductors and electronic manufacturing. However, this might change in the future when the WEEE reaches its end of life (EOL). Furthermore, Ladenberger et al. (2015) indicated that indium

in the European agricultural and grazing soils (0.0176 mg/kg and 0.0177 mg/kg, respectively) is closely connected to the bedrock's geology, particularly the mineralization of Zn and Sn. Shiller (1998) investigated Ga in the Atlantic Ocean (10-40 pmol/kg) and concluded that the main source of Ga was aeolian. On the other hand, Shotyky et al. (2016) reported Ga in colloidal forms (10-100 ng/l) in the Athabasca River, which passes through bitumen mines in northern Alberta, Canada. According to Négrel et al. (2016), most Ge distribution in European agricultural soils is controlled by mineralization and geology, while the anthropogenic influence is related to the local factors, such as smelters and coal power plants. Additionally, Cheng et al. (2020) observed a rising concentration of Ge (1.45 mg/kg) near the Sheng-Li coal base in China and found that Ge accounts for 7.6% of the total potential pollution sources caused by coal mining.

To promote the circulation of In, Ga, and Ge in a circular economy, we need to minimize losses and maximize the recovery rate. This approach can reduce the environmental impact, help achieve sustainability goals, and decrease the need for mining exploration of these elements. Figure 2 illustrates the global production trends for In, Ga, and Ge since 1973. Notably, the production of In has surged significantly, with Ga experiencing a notable increase as well, albeit to a lesser extent. Conversely, Ge demonstrates comparatively modest growth in production over the same period. Although many industries are flourishing around the world and in Europe, the mining industries for critical raw materials (CRMs) extraction are generally limited, with some exceptions. However, CRMs are not evenly distributed across the world; their availability varies according to the industrial manufacturing and refining levels in different countries. For example, China is one of the biggest suppliers of almost all CRMs and other crucial raw materials

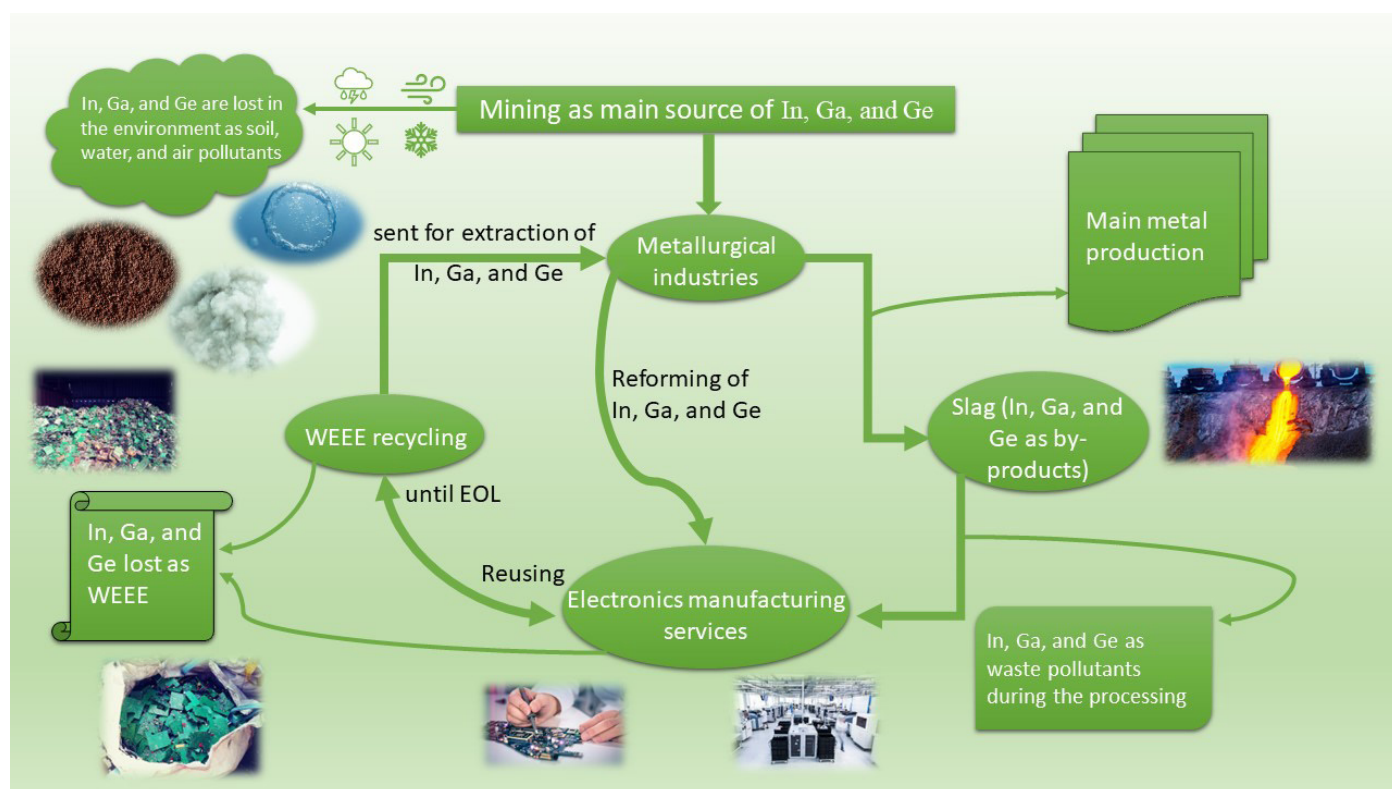


Figure 1. The life cycle of Ga, Ge, In from mining to EOL.

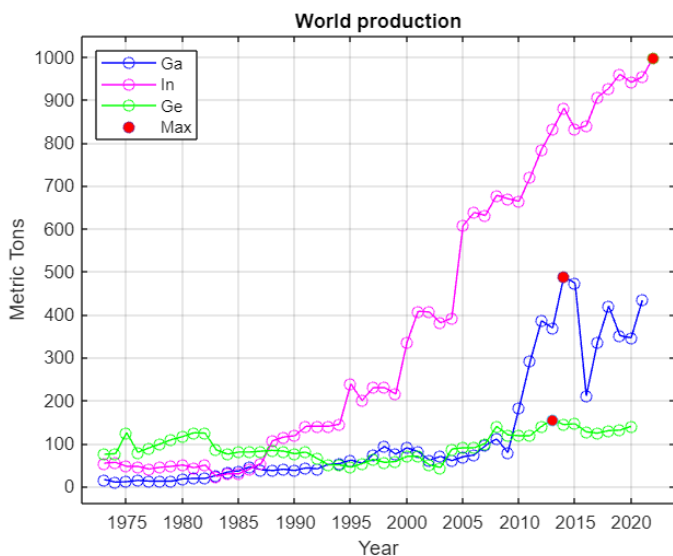


Figure 2. The world production of In, Ga, and Ge (USGS, 2014a; USGS, 2014b; USGS, 2014c).

in the world and one of the major suppliers to the European Union (EU). Therefore, any disturbance (e.g., bottleneck effect or Covid-19) that disrupts the supply chain can have a devastating impact on the relevant high-tech industries that heavily rely on CRMs (Bobba et al. 2018). It is true that In, Ga, Ge, and other TCEs play crucial roles in semiconductor manufacturing, but their contributions vary widely from one device to another, even within the same category. For example, the presence of TCEs in PV panels can vary significantly based on the type of model, whether it is organic photovoltaic (OPV), CdTe PV, or copper indium gallium diselenide (CIGS) (European Commission 2023). This significant variation in the role of these elements could result in a matrix effect due to different concentrations of these elements in the ecosystem, attributed to the diverse range of electronic waste.

Indium

The world production of In has increased exponentially since 1973, with an almost 18-fold rise as shown in Figure 2. The most notable leap in production was observed between 2004 and 2005. The most adopted form of indium in the European Union (EU) is indium tin oxide (ITO). ITO is a ternary composition of indium, tin, and oxygen, consisting specifically of 90% of indium(III) oxide and 10% of tin(IV) oxide by weight. ITO is crucial for making flat panel devices (FPDs) and has many other applications, such as in alloys and solders, thermal interface materials, light-emitting diodes (LEDs), batteries, and laser diodes (LDs). Thin films of ITO are crucial for PV panels because they are considered transparent conducting oxides (TCOs) that meet two major criteria: they are highly transparent to allow light to pass through them with minimal reflection and absorption, and they have excellent electrical conductivity, which makes them widely adopted as semiconductors. Consequently, TCOs are increasingly being used in CdTe PV cell panels. Furthermore, copper indium gallium selenide (CIGS) or $(\text{CuIn}_{1-x}\text{GaSe}_2)$, sometimes without gallium, is used as a light absorber in PV panels. Other forms and compounds of indium also have applications in semiconductors and other industries. For example, indium gallium nitride and

indium phosphide are used in semiconductor manufacturing, while indium antimonide and indium gallium arsenide are more involved in the manufacturing of infrared devices (European Commission 2020). Recently, In_2O_3 was discovered as a highly selective and stable catalyst for the production of green methanol from CO_2 (Frei et al. 2019). Appreciable efforts have been made in Japan and the Republic of Korea to recycle the most prevalent indium from ITO scraps; however, quantitative data about the refined recycled indium are not available. Indium is primarily extracted from the ore mineral sphalerite, which is commonly found in zinc deposits. The indium concentration in these deposits varies widely. Despite indium being present in small quantities in other base-metal sulphides, such as chalcopyrite, most of these deposits are not economically viable for indium extraction (Butcher and Brown 2014). Indium is also one of the critical elements released from furnace wastes (Andrzejewska-Górecka et al. 2019).

Gallium

The global production of gallium has grown by almost 27 times since 1973, with a significant rise after 2009, despite fluctuations, as shown in Figure 2. The most dominant consumption of gallium is in the form of gallium arsenide (GaAs) and gallium nitride (GaN), which account for 94% of the production share, alongside other minor compounds such as gallium antimonide (GaSb) and gallium phosphide (GaP). GaAs is considered a substrate material in manufacturing semiconductors, as well as in forming ternary compounds like InGaAs and AlGaAs. Moreover, the semiconductors made from GaAs are used in many electronic industries, including integrated circuits (ICs), optoelectronic devices, infrared emitting diodes (IREDs), LEDs, LDs, wireless telecommunications, PV cells, and high-end military applications. Not only does GaN have similar applications to GaAs, but it also offers high-temperature resistance in high-power transistors. Notably, GaSb is used in manufacturing thermo-photovoltaic systems and is increasingly substituting GaN due to its preparation simplicity and feasibility. Coal contains an average of 7 ppm Ga and oil 0.015 ppm of gallium. In some coals, the gallium content reaches up to 500 ppm. Gallium is obtained as a byproduct from zinc ore residues or bauxite due to its low concentration in the ores. However, the efficiency of production is quite low, with fewer than 10% recovered from its ores (Butcher and Brown 2014, Rongguo et al. 2016, USGS 2022).

Germanium

Since 1973, the world production of germanium has seen steady growth. Admittedly, the production has slightly ramped up, particularly after 2004, as illustrated in Figure 2. Germanium shares many chemical features with silicon and forms similar oxide complexes in the environment, such as SiO_2 and GeO_2 , which are the most stable compounds. However, they differ in terms of abundance and interactivity. Silicon is one of the backbone elements of the Earth's crust, while germanium is considered one of the critical raw materials (CRM). On the other hand, germanium is more chemically reactive than silicon. The most versatile and applicable uses of germanium in EU industries are infrared optics, optical fibers, and satellite solar cells. There are also three forms of germanium that interfere

differently with manufacturing industries: germanium powder, germanium(IV) oxide (GeO_2), and germanium tetrachloride or germanium(IV) chloride (GeCl_4) (European Commission 2020).

The obtainable reserves of germanium are coupled with certain zinc and lead-zinc-copper sulphide ores as a by-product. Notably, a significant amount of germanium is held in the ashes emitted from the combustion of certain kinds of coal. Most germanium applications in solar cells are more common in space satellite solar panels and military purposes due to their high cost and efficiency (25% and more). In addition, germanium is involved in many other industries globally, specifically in polymerization catalysts and semiconductors for various electronic components such as LEDs, screens display, and wireless telecommunications devices that use silicon-germanium transistors (European Commission 2020, USGS 2022).

Recovering and recycling of indium, gallium, and germanium

Critical raw material (CRM) resources are not evenly distributed across the world. In fact, some countries, like China, monopolize the majority of CRM production. Besides the lack of local productivity of CRMs around the globe, recycling performance is also inadequate. For instance, the EOL recycling input rates (RIR) were meager, with a few exceptions like cobalt (35%) and tungsten (42%), while precious metals and platinum group metals generally have high RIR. Admittedly, low RIR values are observed in rare earth elements and other metals, where Ga, In, and Nb have less than 1% of RIR, while Ge, Nd, Pd, and Rh have RIR between 1-10%. The low percentage of RIR can be attributed to the low concentrations and spatial distribution of these elements in recycled EOL materials. Additionally, the complexity of the product components elevates the cost of extraction and isolation of these elements (Bobba et al. 2018, Gunn 2014).

Charles et al. (2020) conducted a study to enhance the selective recovery of CRMs from WEEE components such as printed circuit boards (PCBs) and LCD screens. The study aimed to improve CRM recovery by targeting the spatial distribution of these materials in various samples of WEEE components, which likely have the highest concentration of CRMs, to increase the efficiency of the recovery process. Consequently, Ga was frequently found in transistors and LEDs, such as InGaN or GaN (blue LEDs) and GaP (green LEDs), and In was found in the LCD screens.

Many attempts to extract indium, which exists in ITO form, from LCD screens have been performed. Chinnam et al. (2020) investigated indium leaching from LCDs' square-shaped glass slices (4 cm²) and ground glass using different concentrations of aqua regia acid. Two basic agitation techniques were implemented: conventional shaking and sonication, for extracting indium. The amount of leached indium increased with the concentration of acid used, causing more harmful effects on the environment due to these acids. Notably, using a 10% aqua regia concentration, the maximum amount of leached indium (~900 mg/kg at 48 h) from the ground front glass (53µg diameters) was detected by ICP-OES after applying the conventional shaking. The process was time and energy-consuming, however, using 10% or 5% aqua regia

concentrations coupled with only 15 min of sonication agitation released 650 mg/kg of indium from the ground front glass particles, indicating higher efficiency in acid concentration and energy usage in the leaching process of indium.

The hydrometallurgical extraction of gallium (Ga) and germanium (Ge) was investigated from slag samples, where both elements were primarily concentrated in slag glass at 91–95% and 96–97%, respectively. Using different acids (H_2SO_4 0.5 M, HNO_3 1 M, HCl 1 M), the slags were milled and subjected to different temperatures and durations. It was found that sulfuric acid had the highest extraction efficiency for Ga (100%) and Ge (98%) using non-milled granulated slag at 25 °C for at least 6 h. However, no significant differences were observed in particle size, temperature, and duration parameters (Ettler et al. 2022). Due to the high possibility of retrieving valuable amounts of TCEs and the heightened threat of TCE concentration in WEEE, much research has been launched in this area. Table 1 shows some of the results of In, Ga, and Ge concentrations in various electronic products using different extraction and digestion methods. In summary, there are three main points to consider in Table 1. Firstly, depending on the electronic components and acidic solvents used, significant variations in In, Ga, and Ge recoveries were observed. For instance, In tends to be more concentrated in LCD, while Ga is found in higher concentrations in LEDs, and Ge in optical fibers. Secondly, differences were observed in similar types of electronic equipment, such as In concentration in LCD smartphones, LCD laptops, and back and front LCD glass. Thirdly, even with the same electronic equipment, some differences might be attributed to the source of module manufacturing, for example, differences in Ga concentrations in LEDs in surface-mounted devices (SMD) (Chen et al. 2020a, Chen et al. 2020b, Chinnam et al. 2020, Iqbal et al. 2022, Virolainen et al. 2020).

In a study conducted on electronic components such as solar lamps, solar cells, LED TV screens, LCD screens, photoresistors, photodiodes, and phototransistors, Willner et al. (2021) found that most of the TCEs elements are concentrated in small-sieved fractions between 0.2–0.1 mm and less than 0.1 mm. In contrast, metals such as Ba, Co, Cu, Mn, Ni, Sr, and Zn were found to be distributed variably between the sieved fractions of WEEE (Willner et al. 2021). Therefore, the complexity, variation, and distribution of In, Ga, and Ge in WEEE pose a major challenge in recycling them efficiently in an automated process and hamper the evaluation of their potential environmental impact.

In recent years, despite numerous efforts, the global recycling rates for In, Ga, and Ge are still relatively low and sometimes non-existent, unlike other precious metals that have higher global recycling rates (over 50%) (Gunn 2014). Figure 3 presents the recycled rates for these elements in the EU in recent years (Eurostat 2023). The recycling rate in the EU for In and Ge increased notably to reach 1% and 2%, respectively, in 2022, while no recycling rates for Ga were observed. Hence, remarkable efforts must be made to bridge the gap between consumption and recycling rates. This will reduce reliance on source-producing countries and help achieve EU sustainability goals. The increase in indium recycling rates and the recovery process of the world supply chain could be one of the reasons why indium was removed from the critical raw material list in

Table 1. The In, Ga, and Ge extracted counted from WEEE materials.

Element	Electronic component	Solvent	Recovered value	Unit of the recovered element	References	
In	LEDs	aqua regia and hydrofluoric acid (3:1:1 HCl: HNO ₃ : HF ratio)	2.07	%	(Chen et al. 2020b)	
		H ₂ SO ₄	1.81			
		HCl	2			
		HNO ₃	1.8			
		C ₂ H ₂ O ₄	1.65			
		NaOH	1.69			
		anhydrous ethanol and ultrapure water	0.021	mg/g	(Zhan et al. 2020)	
		LED in surface mounted device (SMD)	3 M HCl and 30% H ₂ O ₂	64.9 ± 20.2 98 ± 4	mg/kg %	(Zheng et al. 2024)
		LCD (front glass)	aqua regia (10% or 5%)	850	mg/kg	(Chinnam et al. 2020)
		LCD (back glass)	aqua regia (10% or 5%)	600	mg/kg	(Virolainen et al. 2020)
		LCD	HNO ₃	227-296	mg/kg	(Virolainen et al. 2020)
		LCD laptop	HNO ₃ (1:50)	202 ± 4.8	µg/g	(Iqbal et al. 2022)
		LCD smartphones	HNO ₃ (1:50)	186 ± 7.4		
	Solar panel	HNO ₃ (1:50)	3.82 ± 0.5	%	(Lv et al. 2019)	
	Solar panel CIGS	H ₂ SO ₄ (1:10)	19			
	Solar panel CIGS (specifically in the thin film layer)	HNO ₃ , H ₂ SO ₄ and HCl	0.1	%	(Theocharis et al. 2021)	
	Solar panel CIGS	HNO ₃	779 ± 4	mg/kg	(Savvilitidou & Gidaracos 2020)	
Ga	LEDs	aqua regia and hydrofluoric acid (3:1:1 HCl: HNO ₃ : HF ratio)	70.32	%	(Chen et al. 2020b)	
		H ₂ SO ₄	40.66			
		HCl	67.21			
		HNO ₃	55.43			
		C ₂ H ₂ O ₄	51.77			
		NaOH	58.66			
		anhydrous ethanol and ultrapure water	0.041	mg/g	(Zhan et al. 2020)	
			aqua regia (1:50)	0.084-0.381	%	(Cenci et al. 2020)
		Red LEDs in cars	HNO ₃ (1:46)	1.35	g/kg	(Annoni et al. 2020)
		LED in SMD	HCl, C ₂ H ₂ O ₄ , C ₆ H ₈ O ₇ , and C ₄ H ₆ O ₅	22.65	mg/kg	(Zhou et al. 2019)
			3 M HCl and 30% H ₂ O ₂	290.4 ± 21.2 97 ± 6	mg/kg %	(Zheng et al. 2024)
		LCD smartphones	HNO ₃ (1:50)	23.6 ± 2.5	µg/g	(Iqbal et al. 2022)
		LCD laptop	HNO ₃ (1:50)	41.4 ± 4.1		
	Solar panel	HNO ₃ (1:50)	3.27 ± 0.3			
	Solar panel CIGS	H ₂ SO ₄ (1:10)	9.26	%	(Lv et al. 2019)	
	Solar panel CIGS (specifically in the thin film layer)	HNO ₃ , H ₂ SO ₄ and HCl	0.1	%	(Theocharis et al. 2021)	
	Optical fibre	NaOH (98%) and H ₂ SO ₄ (98%)	0.1	%	(Chen et al. 2020a)	
		H ₂ SO ₄ (98%) and HF (49%)	0.11	%	(Chen et al. 2017)	
		HNO ₃ (1:50)	1858 ± 12	µg/g	(Iqbal et al. 2022)	
	Solar panel	HNO ₃ (1:50)	3.27 ± 4.4			
	LCD smartphones	HNO ₃ (1:50)	1.85 ± 0.04			
		LCD laptop	HNO ₃ (1:50)	3.42 ± 0.8	mg/kg	(Willner et al. 2021)
		Solar panel	HNO ₃ , HCl, HBF ₄ , HF H ₂ O ₂ , and their mixtures	0.131		
		TV LEDs	HNO ₃ , HCl, HBF ₄ , HF H ₂ O ₂ , and their mixtures	0.062		
		Solar lamps	HNO ₃ , HCl, HBF ₄ , HF H ₂ O ₂ , and their mixtures	0.060		
		LCD screen	HNO ₃ , HCl, HBF ₄ , HF H ₂ O ₂ , and their mixtures	0.062		
		Photoresistors	HNO ₃ , HCl, HBF ₄ , HF H ₂ O ₂ , and their mixtures	2.590		
		Phototransistors	HNO ₃ , HCl, HBF ₄ , HF H ₂ O ₂ , and their mixtures	0.231		

Contribution of recycled materials to raw materials demand in the EU

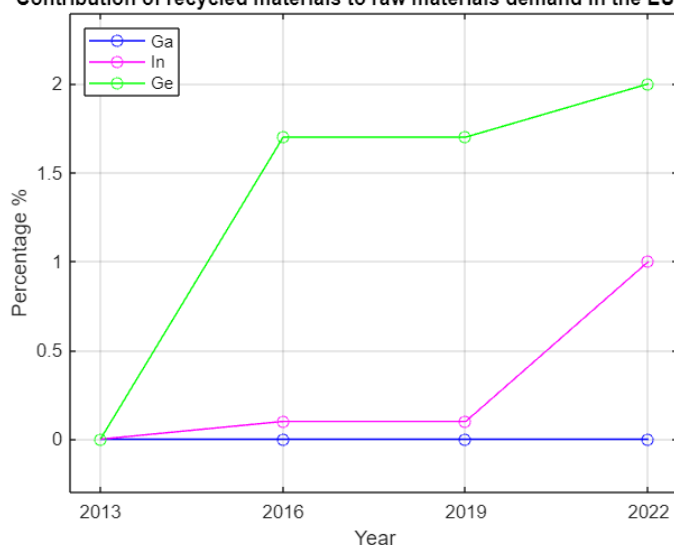


Figure 3. The trends of retrieved and recycled concentrations In, Ga, and Ge in the EU in the recent years (Eurostat, 2023).

the 2023 report, in addition to the boost in local production, which exceeded the consumption rate. Nevertheless, the importance of indium and its potential role in high-tech manufacturing cannot be ignored (Grohol and Veeh 2023).

Speciation of the indium, gallium, and germanium

Germanium, indium, and gallium exhibit varying reactions and speciation due to their placement in different groups in the periodic table. While indium and gallium belong to group 13, germanium belongs to group 14. As a result, research studies have approached germanium differently compared to indium and gallium.

Indium

Some studies on indium speciation have employed various analytical techniques. For example, Quinolinol (HQ) was used as a chelate complex with In(III) and Ga(III) before injecting it into HPLC with a methanol-water eluent (Ohashi et al. 1991). The retention time of the In complex increases with the pH rising above 2.5, stabilizing at the level of pH 4.0. This can be attributed to the increased formation of $\text{In}(\text{HQ})_3$. In contrast, the retention time of the Ga-HQ complex was less affected by pH changes.

Ionic liquids can also play a valuable role in indium speciation. In this context, mixtures of 1-alkyl-3-methylimidazolium chloride with In(III) or Ga(III) chloride in various ratios were prepared (Hardacre et al. 2010). It was assumed that chloroindate(III) ionic liquids form $[\text{InCl}_6]^{3-}$, $[\text{InCl}_5]^{2-}$, and $[\text{InCl}_4]^-$ anions in the Lewis basic state, and tetrachloroindate(III) anion in the neutral state. Only $[\text{InCl}_4]^-$ was found in the Lewis acidic, while chlorogallate(III) exhibited behavior similar to chloroaluminates(III), however, insoluble indium(III) chloride was observed in the suspension.

In another study (Deferm et al. 2017), indium(III) chloride complexes were extracted from aqueous HCl solutions of varying concentrations using ionic liquids (Cyphos® IL 101

and Aliquat® 336). It was found that indium(III) in the aqueous HCl (0–12 M) solutions forms octahedral mixed complexes with the formula $[\text{In}(\text{H}_2\text{O})_{6-n}\text{Cl}_n]^{3-n}$ ($0 \leq n \leq 6$), where n value varies with HCl concentrations. Specifically, $[\text{In}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ (0–1 M HCl), $[\text{In}(\text{H}_2\text{O})_3\text{Cl}_3]$ (1–6 M HCl), $[\text{In}(\text{H}_2\text{O})_2\text{Cl}_4]^-$ (6–10 M HCl), and $[\text{In}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ (10–12 M HCl). In the ionic liquids, indium(III) exists as a tetrahedral $[\text{InCl}_4]^-$ complex, independent of HCl concentration. The $\text{In}(\text{H}_2\text{O})_3\text{Cl}_3$ complex can be extracted by the ionic liquid phase due to its low hydration level, which explains why the highest distribution ratio of indium(III) was at an HCl concentration of 5 M. A separate investigation with a different approach (Maeno et al. 2020) found that indium hydride species formed on chabazite (CHA) zeolite support structures as part of the catalysis process for the non-oxidative dehydrogenation of ethane to form ethylene and H_2 . Specifically, $[\text{InH}_2]^+$ ions are formed by adding H_2 , contained in ethane, to In-exchanged CHA zeolite (In-CHA) at high temperatures.

According to Wood and Samson (2006), in an aqueous environment, the behavior of In can vary greatly due to the potential formation of hydroxide, chloride, fluoride, or bisulfide complexes, depending on the conditions. In particular, In(III) can form relatively stable chloride and bisulfide complexes. However, in the absence of other competing ligands, In(III) reacts with hydroxide to form $\text{In}(\text{OH})_3$ and $[\text{In}(\text{OH})_4]^-$ species. It is anticipated that the $[\text{In}(\text{OH})_4]^-$ complex would dominate in lower pH and higher temperature conditions. Several studies have reported the detection of $\text{In}(\text{OH})_3$ and $\text{In}(\text{PO})_4$ in soil and plant roots (e.g. *Oryza sativa* L., *Triticum aestivum* L., and *Arabidopsis thaliana*).

These compounds can reduce the availability of phosphate to plants. Additionally, In is often associated with iron hydroxides, and the transformation mechanisms of In speciation in soil, water, and plants are influenced by various factors, such as soil texture, pH, organic matter, and cation exchange capacity (Chang et al. 2020a, Chang et al. 2020b, Chang et al. 2023, Cheah et al. 2022, Syu et al. 2020, 2021). Research by Ringerling et al. (2019) aimed to understand the mobility and retention of gallium and indium and their possible complex formations in porous media (quartz sand) with organic acids (citric and humic acids) to simulate the physicochemical conditions of soil. The study found that indium showed a greater tendency to be retained by quartz sand, whereas, in the presence of humic acid, indium was significantly more stable in the mobile solution. In contrast, gallium showed higher mobility and lower retardation and retention in all cases compared to indium, with no significant effect of humic acid presence or absence on gallium. The differences in the retardation, retention, and mobility of gallium and indium can be attributed to the competition between forming complexes with organic ligands and inorganic ligands (OH) and the stability of these complexes.

Gallium

Poledniok (2008) analyzed Ga(III) species in agricultural (Podlasie region) and industrial (Upper Silesia region) soils using sequential extraction procedures developed by Tessier et al. (1979). The study found that most Ga(III) is concentrated in the organic fraction in industrial soils ($F1=24.7$, $F3=29.2$, $F4=35.4$, and $F5=6.9$ mg/kg), while the Ga concentration in

agricultural soil was substantially lower. Notably, the absence of a second fraction (F2) is due to gallium's inability to form carbonate species in such soils. The presence of organic matter plays a crucial role in suppressing hydrolysis, solubility, and speciation of Ga.

Chen et al. (2022) investigated Ga speciation in soils used for growing rice and found a decline in the availability of Ga in soils due to a decrease in its solubility. This decrease is caused by a shift in the dominant Ga species from Ga associated with Fe(III) hydroxides to Ga(OH)₃ precipitates. Additionally, the BCR sequential extraction showed a decrease in the F2 fraction and an increase in the F4 fraction over time when rice is grown. The highest concentrations of Ga were found in the pore waters of acidic soils with coarse texture and relatively low cation exchange capacity.

The acidic clay soil had lower Ga concentrations, followed by the alkaline clay soil, suggesting that Ga is more readily available in acidic soils. Hagvall et al. (2014) studied this relationship across a wide range of Ga concentrations (101–84,076 mg/kg) and pH values (3–8). They found that although Ga(III) primarily bonded with carboxylic groups, only a fraction of the total carboxyl sites were active in binding. The forms of Ga(III) varied depending on the reaction conditions. For example, at the lowest concentration (101–125 mg/kg, and pH 4.9–5.1), many carbon atoms bonded with Ga(III), forming a complex similar to the shape of Ga(III)-EDTA (ethylenediaminetetraacetic acid). At low Ga concentrations (1675–16,649 mg/kg), most of the organic complexes formed in the ring structure of 1 to 3 chelates throughout the pH range, significantly suppressing the hydrolysis and polymerization of Ga(III) by the organic matter. Finally, at high concentrations (67,673–84,076 mg/kg, and pH 3.0–7.0), mononuclear organic Ga(III) complexes, Ga(III) hydroxide, and free Ga(III) were observed, indicating hydrolysis processes.

Wood and Samson (2006) reviewed the aqueous speciation of Ga. They found that Ga⁺³ ions could coordinate with water molecules to form an octahedral complex. In addition, Ga tends to form relatively stable complexes with hydroxide, fluoride, sulphate, and phosphate, while forming weaker complexes with chloride and bisulfide ligands. Although α -GaOOH(s) and GeO₂ are soluble at high temperatures (300 °C and above), pure α -GaOOH(s) is soluble at relatively low temperature (25 °C). On the other hand, GaPO₄(s) tends to be more soluble in the aqueous medium (Benézéth et al. 1997, Diakonov et al. 1997). At elevated temperatures, the solubility of GaPO₄(s) increases. Tananaev and Chudinova (1964) estimated the solubility product at 25°C to be log K_{s0} = -21. Similarly, the solubility product of InPO₄, estimated by Deichman et al. (1968), indicates that GaPO₄(s) and InPO₄(s) behave similarly in the aqueous environment.

Jensen et al. (2018) conducted a sorption experiment for Ga and In in high-fertility silt loam soil and found that both elements exhibit strong retention in soil, leading to their accumulation. Remarkably, due to the formation of insoluble hydroxide forms, such as GaOOH_(s), [Ga/In(OH)]²⁺, and [Ga/In(OH)₂]⁺, the distribution coefficients for Ga and In (408 and 2021 L/kg respectively) have a proportional relationship with their concentration. However, an increase in pH triggers the transformation of insoluble hydroxides to [Ga/In(OH)₄]⁻, resulting in a reduction of the distribution coefficient values.

Germanium

Germanium has very similar chemical behavior to silicon. However, unlike germanium, which is deemed to be scarce, silicon is considered one of the most abundant elements on earth as a result it has been subjected to numerous extensive studies that would be truly valuable in understanding the potential chemical behavior of germanium (Petrucci et al. 2017). Notably, there is a trend to investigate germanium biogeochemistry cycling by comparing it to silicon in soil (Wiche et al. 2018). Germanium, much like silicon, can form tetrahedral structures with oxygen, resulting in germanates, which can serve as potential substitutes for silicate. Both elements are capable of forming germanic acid (Ge(OH)₄) and silicic acid (Si(OH)₄) in soil solutions as inorganic chemical species. However, the chemical behavior of germanium is notably distinct due to its siderophilic, chalcophilic, lithophilic, and organophilic properties under natural conditions (Bernstein 1985, Pokrovski and Schott 1998a, Pokrovski and Schott 1998b).

Germanium can be present in various forms within soil minerals, including silicates, hydroxy-sulphates, hydroxides, oxides, and sulphides (Höll et al. 2007). The source of the germanium in soil is closely linked to the soil parent material and the extent of physical, chemical, and biological weathering of the bedrock (Wiche et al. 2018). During the weathering process, germanium and silicon are released from primary minerals at different rates, initiating competition among Fe(III)-oxyhydroxide, aluminosilicate, and organic matter in the soil to incorporate these elements into their chemical structures. This process is influenced by the soil's physicochemical properties, as well as climatological and biological factors. Thus, Ge is more likely to be found as part of secondary mineral components, particularly clay minerals, rather than as highly reactive free quaternary cations of germanium (Bernstein and Waychunas 1987, Kurtz et al. 2002, Lugolobi et al. 2010, Pokrovski and Schott 1998a, Pokrovski and Schott 1998b, Pokrovsky et al. 2006, Scribner et al. 2006, Wiche et al. 2018).

There is still limited understanding regarding the speciation of germanium in soil, particularly its interactions with organic matter, which acts as organic ligands in its complexes. The pH level is crucial in the formation of Ge-complexes and influences their reactivity with organic acids such as oxalic acid, tartaric acid, citric acid, humic acid, and fulvic acid (Pokrovski and Schott 1998b, Wiche et al. 2018). A study examined germanium concentrations in moist grassland, mesic grassland, and arable land using sequential extraction sample preparation procedures to partition germanium into 5 fractions (Wiche et al. 2017). The results indicated that moist grassland had the highest total concentration of germanium, which can be attributed to the high organic matter content in this type of land. These findings suggest that organic matter provides the organic ligands necessary for forming Ge-complexes, which are more readily absorbed by plants.

Research on inorganic and organic forms of germanium, such as monomethyl and dimethyl germanium (MMGe and DMGe), has been conducted in various water environments (Filella and Matoušek 2022, García-Figueroa et al. 2021, Jabłońska-Czapla and Grygoyé 2021). Using hydride generation and cryotrapping with ICP-MS/MS analytical technique, it was found that inorganic Ge had a higher concentration than

organic Ge in Lake Geneva and rivers. However, in seawater, MMGe was the dominant species, followed by DMGe with inorganic Ge being the least concentrated. Further analysis of germanium speciation in Theisen sludge samples from copper smelting, using liquid chromatography-ICP-MS, revealed that inorganic Ge was the dominant form compared to organic Ge. Adding tartrate as a complexing agent to the samples and eluent enabled effective chromatographic separation of the Ge species (Lehmann et al. 2019). Additionally, halogens can interact with germanium(II) or (IV) to form di- or tetra-halides of germanate compounds and their corresponding complexes such as GeCl_4 , GeCl_2 , GeF_4 , GeF_2 , GeI_4 , GeI_2 , GeBr_4 , GeBr_2 , $[\text{GeCl}_5]^-$, $[\text{GeF}_3]^-$, $[\text{GeF}_5]^-$, and $[\text{GeF}_6]^{2-}$. These compounds and complexes vary depending on the isolation procedures and their stability, which is influenced by specific physicochemical conditions (Levason et al. 2011).

In addition to forming various halides, germanium can undergo hydrolysis or interact with solvents, resulting in more complex species during processes such as liquid-liquid extraction. Notable examples include $\text{GeF}_4(\text{OH})_1$ and $\text{GeF}_5(\text{OH})_1$ species (Benoit and Place 1963), $\text{GeF}_5(\text{H}_2\text{O})$ and $\text{Ge}(\text{OH})\text{F}_4(\text{H}_2\text{O})$ species (Ryss and Kulish 1964), $[\text{Ge}(\text{OH})\text{F}_2]^+$, $[\text{Ge}(\text{OH})\text{F}_4]^-$ and $[\text{HGeF}_6]^-$ species (Ciavatta et al. 1990), and finally $[\text{Ge}(\text{OH})_x\text{Cl}_{5-x}]^-$ or $[\text{Ge}(\text{OH})_x\text{Cl}_{5-x}]^{2-}$ species, where $x=3$ or 4. The pH level is crucial in determining the formation and stability of these species (Everest and Harrison 1957; Filella and May 2023).

A study investigating the speciation of germanium in soil suspected of being polluted by WEEE found that Ge(IV) was the dominant form of germanium, with monomethyl and dimethyl germanium (MMGe and DMGe) only found occasionally (Jabłońska-Czapla et al. 2023). Additionally, the study suggested a potential correlation between magnetic susceptibility and germanium concentration, which is an interesting finding.

Possible methods to assess the potential environmental impact

Since the second half of the last century, many studies have been devoted to evaluating the potential environmental impact as the concept of environmental science started to emerge. Consequently, various geochemical indicators were developed to provide information about corresponding pollutants or elements in the environment. However, the methods of evaluating sediments and soils can be classified into three main categories: geochemical evaluation, ecotoxicological evaluation, and bioindicators. The first evaluation method relies on the background or pre-industrial value of the evaluated element in soil or sediment samples in order to calculate individual pollution indices such as geoaccumulation index (I_{geo}) (Muller 1979), enrichment factor (EF) (Zoller et al. 1974), pollution loading index (PLI) (Liu et al., 2021), and pollution index (PI) (Chen et al. 2005). These indices are the basic components for calculating complex pollution indices, which provide a more comprehensive picture of the geochemical evaluation.

In the literature, many examples can be found of the application of these indices in estimating heavy metal pollution (Łyszczarz et al. 2020). However, there is an issue

with calculating pollution indices for TCEs due to difficulties in determining the background values, because environmental studies to date have not taken these pollutants into account. Additionally, technical issues such as the low availability of certified reference materials and the low concentration of these elements contribute to the limited and humble knowledge of the pre-industrial background of the TCEs in the environment (Amiel et al. 2021, Rudnick and Gao 2013).

The second evaluation method, unlike the geochemical evaluation, takes into account the potential toxicity impact on living organisms in general and benthic organisms in particular. Finally, the evaluation using bioindicators mainly relies on special plants that have the ability to absorb elements from various sources (Nawrot et al. 2021). Determining the bioavailability of elements for plants is one of the critical factors that must be considered when assessing the toxicity of the suspected contaminants. This is especially important since photosynthetic producers are at the beginning of the food chain and play a key role in determining biological magnification aspects in the ecosystem. One of the methods for estimating bioavailability is using EDTA, a complexing agent for capturing targeted elements in the soil medium (Kicińska 2019, Kicińska and Wikar 2020, Liu et al. 2021, Lo and Yang 1999). However, there are few implementations of this method with respect to Ge, and many questions regarding In and Ga complexes with EDTA in environmental samples remain unresolved.

Table 2 presents some pollution indices for In, Ga, and Ge in soil and sediment samples from different regions worldwide. It seems that the pollution levels in most indices, such as I_{geo} and PLI, are either low or moderate (Bačić et al. 2022, Klein et al. 2021b, Yu et al. 2023). Although the enrichment factor (EF) appears to give a more conservative assessment, most of the samples analyzed indicate no enrichment or only slight enrichment. The only exception is Ga, which is measured in marine sediments in Cabo de la Huerta, Spain, and shows significant enrichment (Boluda-Botella et al. 2023).

Sequential chemical extraction is a highly effective technique for fractionating the analyte sample to study the solubility and exchange rate between solid and solution phases. This analysis can help determine the potential mobility of the analyte in the environment, depending on its concentrations in each of the five fractions (Adamiec et al. 2023). Despite recent growing attention, limited research has been conducted on the environmental mobility of emerging elements such as In, Ga, and Ge using sequential extraction techniques (Chang et al. 2020a, Chang et al. 2023, Kurtz et al. 2002, Poedniok 2008, Wenzel et al. 2001, Wiche et al. 2017). Finally, the shoot-to-soil (or sometimes shoot-to-root) concentration ratio (coefficient) is widely used to determine the uptake of elements by plants. It classifies plants as excluders (ratio < 1), indicators (ratio \approx 1), or accumulators (ratio > 1) (Syu et al. 2021, Wiche et al. 2018, Wójcik et al. 2016).

Nevertheless, studies on the geochemistry of trace critical elements (TCEs) in soils and sediments have been substantially surpassed by the extensive focus on analyzing typical heavy metal (HM) pollutants. This can be attributed to two main reasons. First, most TCEs exist in low concentrations in soil and water samples, making them difficult to detect, which is reflected by limited available data regarding reference and preindustrial concentrations of TCEs in particular

Table 2. Different contamination indices for In, Ga, and Ge from various locations around the globe.

Element	Location	Land type	Value	Indices type	References	
In	industrial parks, Taiwan	soil profile (horizon A)	(0.1 to 3.23)	EF	(Liu et al. 2021)	
		soil profile (horizon B)	(0.09 to 1.85)			
		all soil profile	<0	PLI		
			<0.6			
	North sea (north side), Germany	sediments	8.70%	EDTA-extracted	EF	(Klein et al. 2022b)
			(0.6 to 2.3)	(0.8 to 1.6)		
			Upper Rhine River, Germany	-0.30	(Klein et al. 2022a)	
Middle Rhine River, Germany			0.23			
Lower Rhine River, Germany			0.40			
Tributaries of Rhine River, Germany			0.60			
Ga	Sanjiang Plain, China	wetland soils	(-1.15 to 0.87)	I_{geo}	(Yu et al. 2023)	
		farmland soils	(0.48 to 0.73)			
	Cabo de la Huerta, Spain	marine sediments	-1.65	EF	(Boluda-Botella et al. 2023)	
	Albufereta, Spain		-2.45			
	San Gabriel, Spain		-4.45			
	Cabo de Santa Pola, Spain		-3.78			
	Cabo de la Huerta, Spain		10.00			
	Albufereta, Spain		5.40			
	San Gabriel, Spain		2.15			
	Cabo de Santa Pola, Spain		2.00			
	industrial parks, Taiwan	soil profile (horizon A)	(0.46 to 10.2)	(Liu et al. 2021)		
		soil profile (horizon B)	(0.5 to 6)			
		all soil profile	<0		PLI	
			<0.6			
	Lake Prošće, Croatia	sediments	24%	EDTA-extracted	EF	(Bačić et al. 2021)
			(1.0 to 1.1)	(1.0 to 1.0)		
Lake Kozjak, Croatia			(0.8 to 1.1)	EF		
Lake Kaluđerovac, Croatia			(1.0 to 1.0)			
Visovac Lake, Croatia			(0.9 to 1.3)	EF		
Lake Mir, Croatia			(0.8 to 1.6)			
North sea (north side), Germany			(0.9 to 1.5)	I_{geo}	(Klein et al. 2022b)	
North sea (south side), Germany			-0.38			
Upper Rhine River, Germany			-0.12			
Middle Rhine River, Germany			-0.10			
Lower Rhine River, Germany			-0.03			
Tributaries of Rhine River, Germany						
Ge	Lake Prošće, Croatia	sediments	(0.8 to 1.5)	EF	(Bačić et al. 2021)	
	Lake Kozjak, Croatia		(0.7 to 1.4)			
	Lake Kaluđerovac, Croatia		(0.8 to 1.5)			
	Visovac Lake, Croatia		(0.9 to 1.2)			
	Lake Mir, Croatia		(0.7 to 2.0)			
	North sea (north side), Germany		(0.9 to 2.0)	I_{geo}	(Klein et al. 2022b)	
	North sea (south side), Germany		(0.8 to 1.5)			
	Upper Rhine River, Germany		-0.56			
	Middle Rhine River, Germany		0.10			
	Lower Rhine River, Germany		0.63			
Tributaries of Rhine River, Germany	0.31					

environments, especially for indium. Second, the analytical techniques employed are not only modern and advanced but are also compatible with various sample preparation procedures, facilitating different speciation analysis objectives. Previously, finding reference-certified materials (RCMs) to evaluate the quality of chemical analysis was problematic. However, numerous RCMs are now accessible, except for certain types of biological samples that may pose difficulties in conducting toxicological studies (Klein et al. 2022a, Reimann et al. 2018, Wiche et al. 2018, Wojcieszek et al. 2018).

Toxicity and health impacts of In, Ga and Ge

Indium

Studies on the toxicity of indium in fish species show that it is very toxic (Yang and Chen 2018). Acute toxicity studies on important chemicals in photovoltaic industry, such as copper gallium diselenide (CGS) and copper indium diselenide (CIS) indicate that CIS caused significantly greater pulmonary toxicity than CGS. Gallium and indium compounds are extensively used in electro-optical industry, consequently, industrial effluents containing Ga and In are discharged into rivers or irrigation systems, which may influence the growth and productivity of crops. Humans may also be exposed to Ga and In via the food chain, posing severe health risks (Su et al. 2018). Indium lung disease is recognized as a potentially fatal disease caused by the inhalation of indium-containing particles (Cummings et al. 2016). Indium phosphide (InP) is a probable human carcinogen. Chronic (low doses over extended time periods) exposure to inhaled indium phosphide (InP), in particular, has shown carcinogenic effects in animals (Tanaka et al. 2010). The speciation of indium and germanium is related to the pH value (Wernera et al. 2018). The geochemical fate of indium in natural water is still poorly understood (Rotureau et al. 2019). Ion forms of indium are used for *in vivo* biotransformations and could be used in strategies to drive the design of future applied materials for nanotechnology (Veronesi et al. 2019). Even at a moderately acidic pH, the solution chemistry of indium is often dominated by its strong hydrolysis.

When the alkalinity of the system increases, indium hydroxide precipitates due to its extremely low solubility. This explains the low concentrations of free indium in the environment. Given the relevant role of speciation in the ecotoxicological effects of a certain total amount of indium, it is crucial to develop proper techniques to determine free concentrations of indium (Tehrani et al. 2019). It has been shown that pH plays a critical role in the bioavailability measurements of the trivalent cations in natural water (Yang et al. 2019). The nature of the indium(III) chloride complexes present in the organic and aqueous phases during the solvent extraction of indium(III) is described in the work of Deferm et al. (2019). Bomhard (2018, 2020) conducted thorough reviews concerning the toxicity of In_2O_3 , Ga_2O_3 , and GaAs in mice and rats. Although all three compounds have relatively low toxicity, the lungs seem to be the most vulnerable organs, especially when the exposure levels are 0.16 mg/m^3 for Ga_2O_3 and 0.1 mg/m^3 for each of In_2O_3 , and GaAs. In addition, higher concentration levels have been linked to male fertility deterioration and blood abnormalities.

Chang et al. (2020b) assessed the potential toxicity of indium on *Arabidopsis thaliana* and found that the accumulation of indium in insoluble forms ($\text{In}(\text{OH})_3$ and $\text{In}(\text{PO})_4$) in roots caused stunted growth, oxidative stress, anthocyanization, and, most importantly, unbalanced phosphorus uptake. An additional finding was the secretion of citrate in the roots, which might be a potential detoxification strategy by precipitating or immobilizing indium in the root cell. Similarly, many studies in Taiwan and Japan estimated indium's environmental impact on the rice cultivation system. Indium accumulation in the roots led to phosphate deficiency and unbalanced uptake of Mg and Fe, resulting in specific phenotypes changes due to alterations in root anatomy. RNA sequencing indicated that rice responds immediately to the stress created by indium through specific gene activations related to heavy metal tolerance and phosphate deficiency responses (Cheah et al. 2022).

Gallium

Chen et al (2022) investigated gallium impact on rice. $\text{Ga}(\text{OH})_3$ precipitates seem to accumulate in the roots and are less found in the shoots and the grains. However, a potential risk was reported due to gallium accumulation in the grains' endosperm. Indoor air of gallium-associated workspaces in semiconductor factories can also be a significant exposure source, with inhalation being the main route of Ga exposure in humans. Research indicated that workers might be exposed to relatively high levels of gallium. Gallium can also enter the environment through fossil fuels combustion.

Studies on the toxicity of Ga on fish species show that 96-h 50% lethal concentration values ranged within 7.25-11.42 mg/L for *Danio rerio*, and 9.47-12.22 mg/L for *Rhodeus ocellatus* (Yang and Chen 2018). Gallium appears in all human and animal tissues; however, its role in living organisms is not fully understood yet. In terrestrial mammals, the amount of gallium is about 0.001-0.004 ppm, while in marine organisms it is 0.1-0.7 ppm (Yu and Liao 2011). Gallium ions in water can lead to immune system diseases and a reduced blood leukocyte count.

In the literature, there is little information about gallium species. Among the few papers on this subject, several publications should be noted. Due to the harmful effects of Ga(III) on living organisms, research was conducted on the thermodynamic changes and preservation of this form of Ga (Min et al. 2018). Laboratory tests were also carried out by Brun et al. (2016). The authors studied the leaching of Al, Cd, Cu, Ga, In, Fe, Mo, Se, Ag and Zn (CIGS cells), as well as, Al, In, Ag, Sn and Zn (OPV cells) from photovoltaic cells. Available LC50 data for Ga for different aquatic organisms indicate that high concentrations of Ga in the aquatic environment may pose a threat to aquatic life. Furthermore, even in diluted environments, Ga may be harmful to the health and life of certain organisms with prolonged exposures (Yuan et al. 2021). Due to the increasing demand for electronic products, the use of Ga is expected to grow rapidly, making the study of its environmental effects and physiological toxicity a matter of urgency. Current environmental concentrations of gallium in natural waters are in the ng L^{-1} range, suggesting that the current risks from gallium to the health of aquatic biota are insignificant. However, this may change if the predicted rapid growth in its use in photovoltaics and clean energy technologies materializes (Batley et al. 2022).

Germanium

Over the past 40 years, germanium supplements have been popular treatments for various diseases. Organic-germanium compounds are believed to promote health and aid in healing illnesses (Lehmann et al. 2019). These compounds have been described as antioxidants and immunostimulants in conditions such as cancer and AIDS, potentially aiding in cancer cell destruction. However, while organic Ge compounds are used in medicine, inorganic forms such as GeO_2 can have toxic effects. Studies with rats have shown that GeO_2 accumulates in significant organs and tissues, particularly the nerves and kidneys, and human studies have confirmed the harmful effects of inorganic germanium compounds on various organs (Krystek and Ritsema 2004).

Inorganic Ge(IV) is known to passively enter or exit cells through protein-lined pores that allow neutral solutes to traverse cell membranes (Nodulin 26-like intrinsic channel proteins or 'NIPs') (Pommerrenig et al. 2015). In contrast to solid germanium compounds, the gas germane (GeH_4) is highly toxic and can be lethal at concentrations near 150 ppm or higher (Glei 2004). As a result, the U.S. Occupational Safety and Health Administration (OSHA) has set a permissible exposure limit of 0.2 ppm GeH_4 over an 8-hour workday (Occupational Safety and Health Administration 2013a). Germanium-based solar electric applications show higher speeds and lower energy consumption compared to Si substitutes, particularly beneficial for wireless network devices. The future use of Ge is expected to increase due to its unique characteristics and expanding applications (Licht et al. 2015).

Conclusion

This paper reviewed indium, gallium, and germanium across four fundamental aspects: sources and implications, chemical speciation, recovery and recycling, and toxicity, health impacts and environmental impact evaluation methodologies. The literature study underscored the sources of these elements and highlighted how human activities release them into the environment through extraction and utilization in high-tech manufacturing. However, the study has also revealed concerns about the sustainability of these elements due to the low recovery rates and limited progress in recent years. Additionally, the behavior of chemical speciation exhibited significant variability, with In, Ga, and Ge showing distinct responses to conditions and stability of complexes with soils, organic matter, organic acids, and others. Finally, the paper discussed environmental impact evaluation methods, emphasizing the significant challenges that restrict the flexibility of assessment approaches.

The significance of this work is to highlight that despite the increasing importance of In, Ga, and Ge in various industries, the management of these resources still falls short of meeting sustainability targets, from the extraction to end-of-life phases. Consequently, there is a growing need for more life cycle assessment research on high-tech products currently in existence and those expected in the future. This research aims to better understand the environmental impact of these elements.

Developing a flexible methodology for assessing the environmental impact of trace elements will be crucial in the coming years, given the significant limitations compared to evaluating heavy metal pollutants. Despite the notable increase

in research on the speciation of In, Ga, and Ge in recent years, the majority of studies have focused on their technological applications or laboratory experiments. There remains a considerable gap in our understanding of the speciation of these elements in soil and water environments, necessitating further investigation.

Declaration of software utilization in the review article

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Ethics declarations

Conflict of interest

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Ind, gal i german jako pojawiające się zanieczyszczenia: występowanie, specjacja i ocena potencjalnego wpływu na środowisko.

Streszczenie: Rosnące zapotrzebowanie na ind, gal i german, powodowane przez przemysł zaawansowanych technologii, zachęca do wielu badań nad ich interakcją ze środowiskiem, pomimo ich rzadkiego występowania w skorupie ziemskiej. Zrozumienie mechanizmów powstawania form chemicznych tych pierwiastków, które mogą powstać od etapu produkcji do etapu unieszkodliwiania, a także przebiegu interakcji z otaczającym środowiskiem, są uważane za podstawę każdej przyszłej oceny oddziaływania na środowisko. Celem niniejszego artykułu jest zwrócenie uwagi na (i) związki indu, galu i germanu oraz ich zastosowanie w produkcji zaawansowanych technologii, (ii) kompleksy indu, galu i germanu oraz ich reaktywność i stabilność w określonych warunkach, (iii) możliwości odzyskiwania i recyklingu poprzez ługowanie lub ekstrakcję tych pierwiastków z produktów wycofanych z eksploatacji (EOL), (iv) toksyczność i wpływ na zdrowie, (v) wskaźniki zanieczyszczenia, na które mogą mieć wpływ stężenia tła tych pierwiastków pochodzące z gleb lub osadów. Pierwiastki te charakteryzują się niską produktywnością, ale także znacznie niższym wskaźnikiem recyklingu (IRI). Brak niektórych danych, a mianowicie dotyczących reakcji toksycznej, uważa się za główną przeszkodę w ocenie potencjalnego wskaźnika ryzyka ekologicznego (RI), a ponadto brak wystarczających danych podstawowych dotyczących stężenia tych pierwiastków w różnych próbkach środowiskowych, zachęca do konieczności przeprowadzenia dalszych badań w przyszłości.