Supporting information to:

# The global anthropogenic gallium system: Determinants of supply, demand and efficiency improvements

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This supporting information includes 24 pages, 3 figures and 3 tables.

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# 1. System description

The system definition is shown in Figure S1.

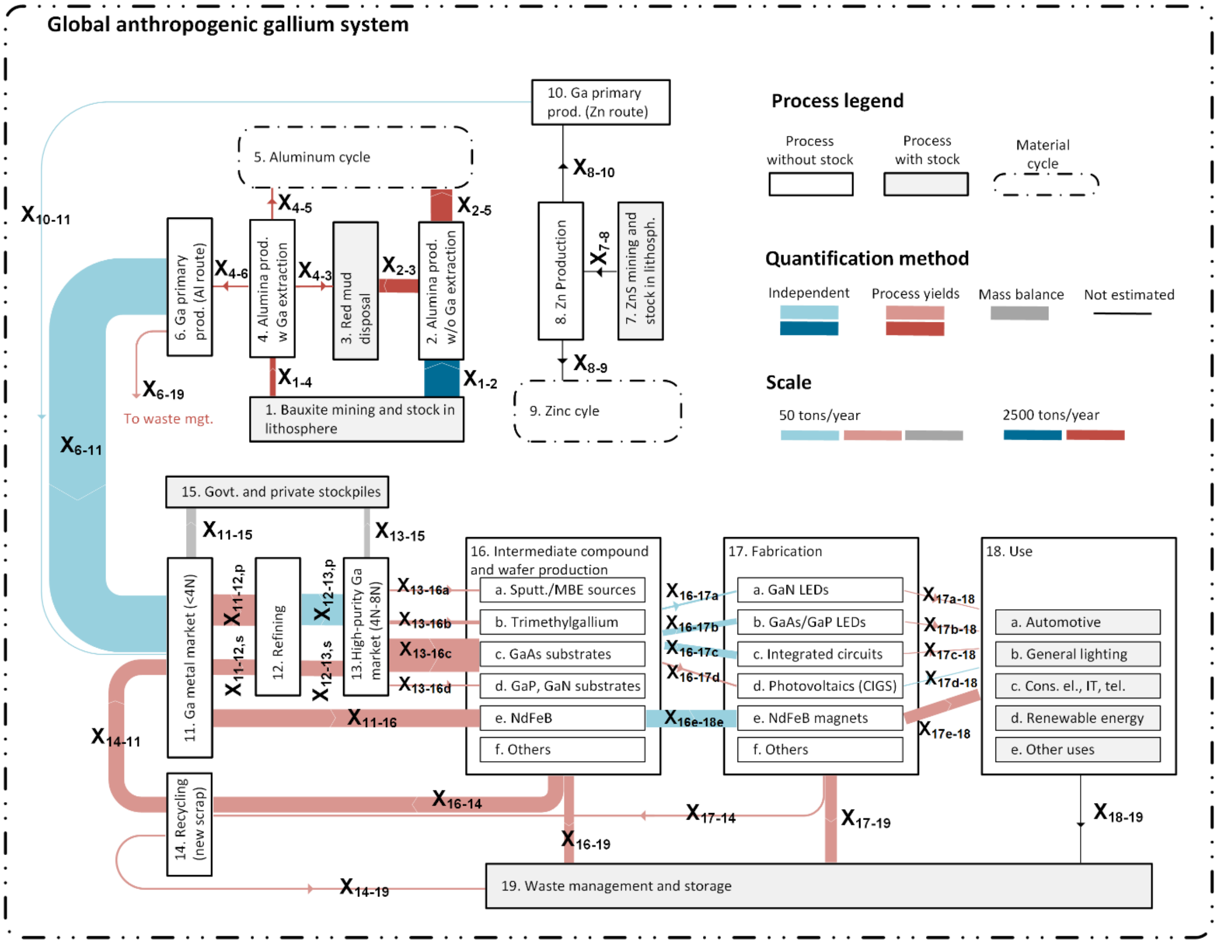


*Figure S1* System definition of the global system of gallium production, manufacturing, use and recycling. Flows to and from sub-processes 16a-e and 17a-e were also estimated.

**Geological resources.** Gallium occurs mainly as a trace element in earth's crust, with an estimated average concentration of about 17 ppm.[1] Minerals in which gallium forms a substantial part have been found only in uneconomic quantities.[2] Elevated concentrations are found in aluminum-containing rocks and minerals such as bauxite (<10-180 ppm), micas (7-170 ppm) and corundum (100 ppm), due to its chemical similarity to aluminum. Enrichments are also present in zinc blende (2-110 ppm) and magnetite (20-90 ppm). The world average gallium concentration in bauxite resources has been estimated to 57 ppm, with regional averages mostly between 28 ppm (Western Guanxi, China) and 75 ppm (Caribbean).[3]

**Primary production.** Gallium metal is produced as a by-product, mainly from the Bayer process for alumina production and to a lesser degree from the hydrometallurgical route for zinc production.[4] Alternative routes that are currently not used for large-scale production include recovery from aluminous clay,[5] fly ash from coal combustion[6,7] or gasification,[8] and phosphorous flue dust.[9] In the Bayer process, aluminum minerals in bauxite rock are dissolved in a sodium hydroxide solution, separated from iron oxides and silicates by filtration and then precipitated as aluminum hydroxide. About 30-50% of the gallium in bauxite will remain undissolved and therefore be disposed of in the so-called red mud together with iron oxides, silicates and undissolved aluminum hydroxides.[10,11] The alkaline solution (Bayer liquor) is recycled to process the next batch of bauxite. Gallium will accumulate in the liquor until it reaches a steady-state concentration, i.e. when the amount dissolved from bauxite equals the amount precipitated as an impurity in alumina.[12] When the concentration reaches a certain level, the liquor may be removed from the Bayer process to extract gallium in a series of processing steps. The most common method is the ion exchange process in which an organic compound is used to preferentially adsorb gallium. Further processing separates gallium from the organic resin and metallic impurities, and finally gallium metal is produced by electrolysis.[11]

**Secondary production.** Recycling of gallium from industrial scrap is commonly done, while no end-of-life recycling is known to occur.[13] The most important type of industrial scrap is GaAs in various forms: bulk crystal pieces, test wafers, broken wafers and slurries from grinding and cutting.[14,15] Bulk GaAs and clean wafers may be recycled internally at the crystal growth facilities by direct remelting.[14] From less pure scrap, gallium is typically recovered by dissolving GaAs in a hot acidic solution such as nitric acid, precipitation of $Ga_2O_3$, re-dissolution and electrolysis.[15,16] Another method involves heating the GaAs material to evaporate arsenic and obtain $Ga_2O_3$.[16] Recycled gallium metal may be further refined to obtain the same grades as from primary metal.

**Refining.** Refining of the metal to a purity of 99.9999% (6N) or higher for electronic applications, is achieved by a combination of methods such as vacuum refining,[17] washing with aqueous acids and alkalis, fractional crystallization,[18] zone melting[19,20] and/or single crystal growth.[21] Purification may also be conducted on gallium compounds such as gallium trichloride, which is sometimes produced directly at the gallium metal plant.[22] The overall yield of the refining process depends on the final purity and the methods used. As an example, purification from 4N to 7N by fractional crystallization could have a material yield in the range 70-80%.[23] However, the discarded material is reintroduced at an earlier stage in the process chain for an overall yield close to 100%.[24] This recovery is here defined as part of the refining process.

**Production of intermediate compounds and substrates.** The majority of gallium demand arises from its use in compound semiconductors, the most common ones being GaAs, gallium nitride (GaN), indium gallium nitride ($In_xGa_{1-x}N$, hereafter InGaN), gallium phosphide (GaP), aluminum gallium indium phosphide ($(Al_{1-x}Ga_x)_yIn_{1-y}P$, hereafter AlGaInP) and copper indium gallium diselenide ($CuIn_xGa_{1-x}Se_2$, CIGS). These are either grown as single crystals and cut into wafers or produced directly from precursor gases or other sources during the device fabrication process. GaAs and GaP single crystal ingots are produced by two techniques, the liquid-encapsulated Czochralski process and the vertical gradient freeze process. Both involve directional solidification of a single crystal from a melt to produce a cylinder-shaped ingot with a diameter of 50-200 mm and length of up to 300 mm.[25] The sides of the ingot are trimmed to an even diameter, the cone-shaped ends are cut off, and the ingot is sawed into thin wafers (<1mm thick) that are polished and used as substrates for device fabrication. Bulk losses such as the cone-shaped ends are usually recycled internally, while the wastes from sawing, trimming, polishing and etching are sent to an external recycler or disposed of.[14]

The other gallium-containing compounds are mainly produced during device fabrication by metalorganic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE) or sputtering deposition. These processes are described under “fabrication”. The main precursor gas for MOCVD of gallium compounds is trimethylgallium (TMG), $Ga(CH)_3$. TMG is synthesized from gallium trichloride and a metal alkyl such as trimethylaluminum,[26,27] or directly from gallium metal and methyl iodide.[28] Evaporation sources for MBE consist of pure gallium metal, while sputtering targets for CIGS production can be pure gallium metal or gallium in alloys with indium and/or copper.

**Fabrication.** Semiconductor devices such as integrated circuits (ICs) and light emitting diodes (LEDs) consist of a few microns thick *deposition layer* on top of the much thicker substrate. GaAs is used both for the substrate and the deposition layer in GaAs-based ICs and LEDs, and as substrate for GaAs/GaP-based LEDs.[29] GaN-based LEDs are produced on substrates of sapphire ($Al_2O_3$) or silicon carbide (SiC),[30] and therefore require very little gallium per device. The deposition layer is produced by MOCVD or MBE.[31] In an MOCVD process, precursor gases such as TMG and ammonia flow across the substrate surface in a reaction chamber to produce an epitaxial film of the desired compound. The MBE process is conducted in a vacuum chamber, where the low pressure causes the pure elemental sources (e.g. gallium metal) to sublimate. The beam of sublimated atoms is directed toward the heated substrate, and a thin film is formed. LEDs are mainly produced with MOCVD,[29] while ICs are produced with both MOCVD and MBE.[31,32] Thin film CIGS solar cells can be produced with a variety of techniques. Vacuum-based methods such as co-evaporation and sputtering are most common; methods with higher material utilization rates are being developed.[33,34] Material yields in deposition for LEDs and ICs are normally less than 20% and can be as low as 1%,[35] while the yield in thin film PV production is higher, typically 30-60% assuming sputtering deposition.[36]

The substrates for ICs and LEDs are much thicker than what is required for the operation of the device, 450-675 μm,[37] and is therefore thinned to a thickness of 50-100 μm in a “backgrinding” process to enable denser packaging and better heat dissipation.[38] Each wafer is normally used to produce up to several thousand identical devices, which are separated by cutting, leading to some additional loss. Finally, wafer breakage and non-working devices contribute to a total material loss that may reach above 90% including substrate material.[38–40] The majority of this loss is due to the backgrinding process.

In the production of NdFeB magnets, Ga is often added at approximately 0.5%wt to improve magnetic properties, corrosion resistance and the production process.[2,41,42] The magnets are produced by melting the constituent elements to form an alloy, milling to a fine powder, pressing, sintering and machining into the final shape. Material losses are typically 20-40% of the starting material.[43,44] Although it is common to recycle neodymium from the production scrap, gallium is not recovered in this process.[44]

**End-use.**

GaN-based LEDs are used to produce light with color ranging from ultraviolet to green.[45] The most important application is as a component of white LEDs, where a blue or ultraviolet LED is combined with a phosphor. White LEDs are today used in all key lighting markets such as residential, offices, outdoor, architectural and automotive; however, the penetration is still low compared to other lighting technologies. In addition, white LEDs are extensively used for backlighting in liquid crystal displays, especially in handsets and portable computers.[46]

GaAs/GaP-based LEDs can produce light with color ranging from green to red. They are used in automotive dashboards and exterior lights, traffic signal lighting, full-color displays and many other signage and display applications.[47] In the future, increased use may be seen in indoor general lighting where they can be used to improve the color temperature of white LED lamps.[48] Red LEDs can also be used together with green and blue LEDs to produce white light, but this is more expensive and therefore much less used than the phosphor-based white LED.[49]

GaAs ICs are mainly used in mobile phones and other wireless communication devices and infrastructure. More than 50% of the demand in 2011 has been attributed to mobile phones,[32] the majority of which comes from power amplifiers used to strengthen the signal before it is transmitted through the antenna. Due to the wide variety of air interface standards (e.g. GSM, EDGE, CDMA, LTE) and frequency bands, new handsets contain several power amplifiers for international compatibility including older standards.[32]

The main applications for NdFeB magnets are computers, electric motors and audio systems, each responsible for about 30% of demand.[50]

**Waste management.**

Currently, there is no recovery of gallium from end-of-life products, mainly due to the low concentrations with respect to other materials in the products, but also due to the lack of technologies for its recovery from end-of-life products.

The main end-of-life waste streams are, due to the end uses, end-of-life vehicles (ELV) and waste electrical and electronic equipment (WEEE). Gallium in automobiles is mainly in lighting systems and electrical motors;[51] in electronics it is found in printed circuit boards.[52] Typical recycling of ELV favors the recovery of bulk metals such as steel and aluminum and it can include depollution, dismantling, shredding and recovery of materials.[53] After shredding, gallium is found mainly in the automobile shredder residue (ASR) and in low concentrations in the bulk aluminum fractions, most likely as a native impurity in the base metal.[54] The ASR is subsequently incinerated or landfilled. Some processes exist to recover precious metals after incineration.[55] However, in such processes gallium is transferred to slags from which it is not recovered.[56]

Recycling of WEEE can include depollution, dismantling, crushing, separation and recovery of materials. As for ELV, it favors the recovery of bulk metals (steel, aluminum and copper), as well as the recovery of precious metals.[57] The final recovery of these metals is carried out in copper smelters or in integrated metals smelters in which gallium is transferred to slags and not recovered.[56]

# 2. Quantification of flows and decomposition

The system variables (flows) are listed and described in Table S1. $X_{m-n}$ refers to the flow from process *m* to process *n*. Letters *a-f* designate sub-processes, letters *p* and *s* stand for primary and secondary material respectively, *sc* stands for semiconductor applications (light emitting diodes, integrated circuits and photovoltaics), and *pe* stands for power electronics . All system variables refer to the gallium content in the flows.

*Table S1* System variables. All variables refer to the gallium content in the flows.

| *Variable name* | *Description of flow* |
|---|---|
| $X_{1-2}$ | Bauxite input to non-Ga Bayer process |
| $X_{1-4}$ | Bauxite input to Ga-extr. Bayer process |
| $X_{2-3}$ | Red mud from non-Ga Bayer process |
| $X_{2-5}$ | Alumina from non-Ga Bayer process |
| $X_{4-3}$ | Red mud from Ga-extr. Bayer process |
| $X_{4-5}$ | Alumina from Ga-extr. Bayer process |
| $X_{4-6}$ | Gallium entering extraction process from Bayer route |
| $X_{6-11}$ | Primary production of gallium metal from Bayer route |
| $X_{6-19}$ | Loss from extraction process |
| $X_{6-11}$ | Primary gallium to refining |
| $X_{10-11}$ | Primary production of gallium metal from zinc route |
| $X_{11-15}$ | Primary unrefined gallium going into stockpiles |
| $X_{11-12,p}$ | Refined gallium from primary production |
| $X_{11-12,s}$ | Refined gallium from recycling |
| $X_{14-11}$ | Recycled material going to refining |
| $X_{14-19}$ | Loss from recycling |
| $X_{13-15}$ | Gallium going into stockpiles |
| $X_{13-16a}$ | Refined gallium used in production of sputtering targets and MBE sources |
| $X_{13-16b}$ | Refined gallium used in the production of TMG |
| $X_{13-16c}$ | Refined gallium used in the production of GaAs substrates |
| $X_{13-16d}$ | Refined gallium used in the production of GaP and GaN substrates |
| $X_{13-16f}$ | Refined gallium used for other purposes |
| $X_{13-16}$ | Consumption of refined gallium |
| $X_{16b-19}$ | Loss from production of TMG |
| $X_{16c-19}$ | Loss from production of GaAs substrates |
| $X_{16d-19}$ | Loss from production of GaP and GaN substrates |
| $X_{16-19}$ | Loss to landfills from compound production |
| $X_{16c-14}$ | Recycling from production of GaAs substrates |
| $X_{16d-14}$ | Recycling from production of GaP and GaN substrates |
| $X_{16-14}$ | Recycling from compound production |
| $X_{16a-17}$ | Consumption of sputtering targets and MBE sources |
| $X_{16b-17}$ | Consumption of TMG |
| $X_{16c-17}$ | Consumption of GaAs substrates |
| $X_{16d-17}$ | Consumption of GaP and GaN substrates |
| $X_{16-17}$ | Consumption of intermediate compounds |

*Table S1 cont.*

| *Variable name* | *Description of flow* |
|---|---|
| $X_{16a\text{-}17c}$ | Use of sputtering targets and MBE sources for ICs |
| $X_{16a\text{-}17d}$ | Use of sputtering targets and MBE sources for PV |
| $X_{16b\text{-}17a}$ | Use of TMG for production of GaN LEDs |
| $X_{16b\text{-}17b}$ | Use of TMG for production of GaP/GaAs LEDs |
| $X_{16b\text{-}17c}$ | Use of TMG for production of ICs |
| $X_{16b\text{-}17f,\ pe}$ | Use of TMG for production of power electronics |
| $X_{16b\text{-}17}$ | Total use of TMG (estimated from substrates area) |
| $X_{16c\text{-}17b}$ | Use of GaAs substrates for GaP/GaAs LEDs |
| $X_{16c\text{-}17c}$ | Use of GaAs substrates for ICs |
| $X_{16d\text{-}17b}$ | Use of GaP substrates for GaP LEDs |
| $X_{16d\text{-}17f}$ | Use of GaN substrates for lasers and other applications |
| $X_{16e\text{-}17e}$ | Use of NdFeB to produce magnets |
| $X_{17a\text{-}19}$ | Scrap lost from production of GaN LEDs |
| $X_{17b\text{-}19}$ | Scrap lost from production of GaP/GaAs LEDs |
| $X_{17c\text{-}19}$ | Scrap lost from production of ICs |
| $X_{17d\text{-}19}$ | Scrap lost from production of PV |
| $X_{17e\text{-}19}$ | Scrap lost from production of NdFeB magnets |
| $X_{17f,\ pe\text{-}19}$ | Scrap lost from production of power electronics |
| $X_{17\text{-}19}$ | Total scrap loss to landfills from fabrication of devices |
| $X_{17b\text{-}14}$ | Collected scrap from production of GaP, GaAs LEDs |
| $X_{17c\text{-}14}$ | Collected scrap from production of ICs |
| $X_{17d\text{-}14}$ | Collected scrap from production of PV |
| $X_{17\text{-}14}$ | Total collected scrap from fabrication |
| $X_{17a\text{-}18}$ | Total use of GaN LEDs |
| $X_{17b\text{-}18}$ | Total use of GaP/GaAs LEDs |
| $X_{17c\text{-}18}$ | Total use of ICs |
| $X_{17d\text{-}19}$ | Total use of PV |
| $X_{17e\text{-}18}$ | NdFeB magnets entering use |
| $X_{17f,\ pe\text{-}18}$ | Total use of power electronics |
| $X_{17\text{-}18}$ | Total gallium entering use |

The system was quantified using a combination of statistical data, market data and technical process parameters. The parameters used in the quantification are listed in Table S2.

*Table S2.* Parameters used in the quantification of the system.

| *Symbol* | *Description* |
|---|---|
| $B$ | Bauxite mining |
| $c_0$ | Ga concentration in bauxite |
| $c_1$ | Ga concentration in bauxite used for Ga recovery |
| $a$ | Share of bauxite used in Bayer process |
| $A$ | Alumina production |
| $b$ | Fraction of Ga in bauxite going to red mud |
| $p$ | Fraction of dissolved Ga going to alumina |
| $y_1$ | Yield in gallium recovery from Bayer liquor |
| $Y$ | Primary gallium production |
| $Z$ | Primary gallium production from zinc route |
| $R$ | Refined gallium production |
| $c_2$ | Concentration of gallium in alumina |
| $T$ | Trimethylgallium production |
| $G_1$ | GaAs semi-insulating (SI) substrate prod. |
| $g_2$ | GaAs semiconducting substrate production relative to GaAs SI substrate production |
| $g_3$ | GaP substrate production relative to GaAs SI substrate production |
| $g_4$ | GaN substrate production relative to GaAs SI substrate production |
| $g_5$ | Sapphire and SiC substrate production relative to GaAs SI substrate |
| $d_1$ | Density of GaAs |
| $d_2$ | Density of GaP |
| $d_3$ | Density of GaN |
| $m_1$ | Molar mass of Ga |
| $m_2$ | Molar mass of As |
| $m_3$ | Molar mass of P |
| $m_4$ | Molar mass of N |
| $t_{1a}$ | Thickness of GaAs substrates for IC fabrication |
| $t_{1b}$ | Thickness of other substrates |
| $y_4$ | Yield in trimethylgallium production |
| $y_5$ | Yield in crystal growth and substrate production |
| $r_2$ | Collection rate, crystal growth and substrate production scrap |
| $y_7$ | Yield in MOCVD deposition |
| $y_9$ | Yield in MBE deposition |
| $y_{10}$ | Yield in sputtering deposition |
| $q_1$ | Wafer breakage and non-working devices loss, fabrication |
| $q_2$ | Backgrinding loss in IC fabrication |
| $q_4$ | Backgrinding/epitaxial lift-off loss in LED fabrication |
| $q_3$ | Dicing and edge loss in device fabrication |
| $M$ | Mass of gallium used in production of magnets |
| $y_{11}$ | Yield in fabrication of NdFeB magnets |
| $r_4$ | Collection rate broken wafers and non-working devices scrap |
| $r_5$ | Collection rate backgrinding and dicing scrap from IC fabricators |
| $r_6$ | Collection rate backgrinding/epitaxial lift-off scrap, LED |
| $t_2$ | LED deposition layer thickness |
| $t_4$ | Integrated circuit deposition layer thickness |
| $t_5$ | CIGS deposition layer thickness |
| $c_4$ | Concentration of gallium in CIGS |
| $W_1$ | CIGS PV production capacity |
| $W_2$ | PV total production capacity |
| $W_3$ | New installed PV electricity generation capacity |
| $t_6$ | Power electronics deposition layer thickness |
| $W_4$ | Power electronics GaN market |
| $w$ | Power electronics GaN substrate area per unit value |

**Calculation of flows**

The equations used to quantify the flows are explained in the following.

Primary production from zinc route:

$$X_{10-11} = Z$$

Primary production from aluminum route estimated as total primary production minus production from zinc route:

$$X_{6-11} = Y - Z$$

Loss during extraction from Bayer liquor estimated from process output and yield $y_1$ in the extraction process:

$$X_{6-19} = \frac{(Y - Z)(1 - y_1)}{y_1}$$

Input to Bayer liquor extraction process also estimated from process yield:

$$X_{4-6} = \frac{(Y - Z)}{y_1}$$

Ga ending up in alumina estimated from transfer coefficient *p*:

$$X_{4-5} = \frac{X_{4-6}p}{1 - p}$$

Likewise, Ga ending up in red mud was calculated from transfer coefficient *b*:

$$X_{4-3} = \frac{X_{4-6}b}{(1 - b)(1 - p)}$$

The amount of Ga entering the Bayer process *with* Ga extraction was back-calculated from output and the transfer coefficients *b* and *p* which designate the fractions ending up in red mud and alumina (as fraction of the gallium dissolved, i.e. not going to red mud) respectively.

$$X_{1-4} = \frac{X_{4-6}}{(1 - p)(1 - b)}$$

The amount of Ga entering the Bayer process *without* Ga extraction was estimated from the total bauxite production times the share of bauxite used for alumina production times the average concentration of Ga in bauxites minus the amount entering the Bayer process *with* Ga extraction:

$$X_{1-2} = Bac_0 - X_{1-4}$$

Ga to red mud from Bayer process *without* Ga extraction was estimated from transfer coefficient *b*:

$$X_{2-3} = X_{1-2}b$$

Ga to alumina from Bayer process *without* Ga extraction was estimated by mass balance (input minus the fraction ending up in red mud):

$$X_{2-5} = X_{1-2} - X_{2-3}$$

Refined Ga production was taken directly from statistics:

$$X_{12-13,p} = R$$

Since the yield was assumed to be 100%, the input to the refining process is the same as the output:

$$X_{11-12,p} = R$$

Sources of gallium used in molecular beam epitaxy (MBE) for integrated circuits (IC) was estimated from area of GaAs wafers used for IC production (semi-insulating wafers), $G_1$, times the thickness of the deposition layer, the density of GaAs, the share of ICs produced with MBE, the molar masses of gallium and arsenic, as well as the epitaxy yield factor, $y_9$:

$$X_{16a-17c} = \frac{G_1 t_4 d_1 (1 - h_1) 10^{-6} m_1}{(m_1 + m_2) y_9}$$

Ga in trimethylgallium (TMG) consumed was estimated from the consumption of TMG times the concentration of gallium in TMG:

$$X_{16b-17} = T c_3$$

Ga in GaAs semiconducting (SC) substrates for LEDs was estimated from the area of GaAs semi-insulating (SI) substrates, the area of SC substrates relative to SI substrates, the thickness of SC wafers, the density of GaAs and molar masses of Ga and As:

$$X_{16c-17b} = g_2 G_1 t_{1b} d_1 \frac{m_1}{m_1 + m_2} 10^{-6}$$

Ga in GaAs substrates for ICs was estimated from the area of GaAs SI substrates, the thickness of SI wafers, the density of GaAs and the molar masses of Ga and As:

$$X_{16c-17c} = G_1 t_{1a} d_1 \frac{m_1}{m_1 + m_2} 10^{-6}$$

Total Ga in GaAs substrates was calculated from the sum of Ga in SC and SI substrates:

$$X_{16c-17} = X_{16c-17b} + X_{16c-17c}$$

Ga in GaP substrates was estimated from the area of GaAs SI wafers, the area of GaP wafers relative to GaAs SI wafers, $g_3$, the thickness of GaP substrates (assumed same as GaAs SC substrates), the density of GaP, and the molar masses of Ga and P. It was assumed that all GaP substrates are used to manufacture light-emitting diodes (LEDs).

$$X_{16d-17b} = g_3 G_1 t_{1b} d_2 \frac{m_1}{m_1 + m_3} 10^{-6}$$

Ga in GaN substrates was estimated from the area of GaAs SI wafers, the area of GaN wafers relative to GaAs SI wafers, $g_4$, the thickness of GaN wafers (assumed same as GaAs SI substrates), the density of GaN, and the molar masses of Ga and N. It was assumed that all GaN substrates are used to produce solid state lasers (other applications).

$$X_{16d-17f} = g_4 G_1 t_{1a} d_3 \frac{m_1}{m_1 + m_4} 10^{-6}$$

Total Ga in GaP and GaN substrates was calculated from the sum of the two:

$$X_{16d-17} = X_{16d-17b} + X_{16d-17f}$$

Ga in NdFeB semi-finished products was calculated directly from the estimated amount used:

$$X_{16e-17e} = M$$

Ga going into use was calculated by the material yield in fabrication of magnets:

$$X_{17e-18} = y_{11}M$$

The rest of the flows related to magnets were calculated by simple mass balances.

Ga in CIGS photovoltaics (PV) going into use was estimated from the generation capacity of newly installed CIGS PV, the standard test condition irradiance, the efficiency of the cells, the thickness of the deposition layer and the concentration of Ga in the material. The newly installed capacity of CIGS cells is not reported. Therefore, this was estimated from the total newly installed PV capacity $W_3$ (all technologies), and the share of CIGS in the *production* capacity in the PV industry ($W_1/W_2$). Since the generation capacity of PV is based on testing under standard conditions ($k$=1000W/m$^2$), this value was used to find the area of the cells from the electricity generation capacity.

$$X_{17d-18d} = \frac{W_1 W_3 t_5 c_4 10^5}{W_2 e_1 k}$$

Consumption of sputtering targets (assuming all CIGS cells are produced with sputtering) was back-calculated from the amount of Ga in installed CIGS cells, assumed breakage rate in the manufacturing process, and the yield in sputtering deposition. Note that the uncertainties of these process yield parameters are quite high.

$$X_{16a-17d} = \frac{X_{17d_18d}}{y_{10}(1-q_1)}$$

Scrap collected from CIGS production was estimated from the input to the production process, the deposition yield and the breakage rate in manufacturing, assuming that all broken cells are recycled.

$$X_{17d-14} = X_{16a-17d}\, y_{10} q_1$$

Uncollected scrap (*i.e.* undeposited Ga) was calculated by mass balance:

$$X_{17d-19} = X_{16a-17d} - X_{17d-14} - X_{17d_18d}$$

Total CIGS into use is equal to the CIGS going into sub-process *18d*:

$$X_{17d-18} = X_{17d-18d}$$

Total use of MBE sources and sputtering targets was calculated from the sum of the two:

$$X_{16a-17} = X_{16a-17c} + X_{16a-17d}$$

The amount of Ga in TMG used for power electronics was estimated from the GaN power electronics market size in monetary value, $W_5$, the area of GaN wafers per unit value, $w$, the thickness of the deposition layer, the density of GaN, and the yield in the deposition process assuming metal-organic chemical vapor deposition (MOCVD).

$$X_{16b-18f,pe} = \frac{m_1}{(m_1+m_4)} \frac{W_5 w t_6 d_3 10^{-6}}{y_7}$$

The amount of Ga in power electronics going into use was estimated from the input to the manufacturing process times the deposition yield, breakage loss rate, and dicing loss rate:

$$X_{17f-18,pe} = X_{16b-18f,pe}\, y_7 (1-q_1)(1-q_3)$$

Uncollected scrap was estimated by mass balance, assuming that no scrap is collected from this process:

$$X_{17f-19,pe} = X_{16b-18f,pe} - X_{17f-18,pe}$$

Total use of intermediate compounds (sputtering/MBE targets and sources, GaAs wafers, GaP wafers, GaN wafers and TMG) was calculated by summing up the individual flows:

$$X_{16-17} = X_{16a-17} + X_{16b-17} + X_{16c-17} + X_{16d-17} + X_{16e-17}$$

Use of refined Ga for producing sputtering targets and MBE sources was set as equal to the consumption of these, assuming no loss in this process or 100% recycling (likely because it is high purity Ga metal and simple manufacturing process).

$$X_{13-16a} = X_{16a-17}$$

Use of refined Ga for TMG production was calculated from TMG consumption, concentration of Ga in TMG and the yield in the production process:

$$X_{13-16b} = T\frac{c_3}{y_4}$$

Use of refined Ga for production of GaAs substrates was calculated from the consumption of GaAs substrates (see individual calculations above), and the yield in substrate production, $y_5$:

$$X_{13-16c} = \frac{(G_1 t_{1a} + g_2 G_1 t_{1b})d_1}{y_5}\frac{m_1}{m_1 + m_2}10^{-6}$$

Likewise, refined Ga for GaP and GaN substrates was back-calculated from the Ga in produced substrates (see equations above) and the substrate production yield, $y_5$. It was assumed that the substrate production yield is the same as for GaAs substrates.

$$X_{13-16d} = ((g_3 G_1 t_{1b} d_2 \frac{m_1}{m_1 + m_3}) + (g_4 G_1 t_{1b} d_3 \frac{m_1}{m_1 + m_4}))\frac{10^{-6}}{y_5}$$

Total consumption of refined Ga was then calculated by summing up individual flows:

$$X_{13-16} = X_{13-16a} + X_{13-16b} + X_{13-16c} + X_{13-16d}$$

Loss from TMG production process was calculated from input to process times the loss rate (1 minus production yield). It was assumed that none of this is recycled.

$$X_{16b-19} = X_{13-16b}(1 - y_4)$$

Uncollected scrap from GaAs substrate production was calculated from process input, production yield and collection rate, $r_2$:

$$X_{16c-19} = X_{13-16c}(1 - y_5)(1 - r_2)$$

Likewise, the uncollected scrap from GaP and GaN substrate production were calculated:

$$X_{16d-19} = X_{13-16d}(1 - y_5)(1 - r_2)$$

Total uncollected scrap from production of intermediate compounds was found by summing up individual flows:

$$X_{16-19} = X_{16b-19} + X_{16c-19} + X_{16d-19}$$

Collected scrap from GaAs substrate production was calculated from process input, yield and collection rate:

$$X_{16c-14} = X_{13-16c}(1 - y_5)r_2$$

Collected scrap from GaP and GaN substrate production was estimated by the same procedure:

$$X_{16d-14} = X_{13-16d}(1 - y_5)r_2$$

Total amount of collected scrap from production of intermediate compounds was found by summing up the collected scrap from GaAs substrate production and GaP/GaN substrate production:

$$X_{16-14} = X_{16c-14} + X_{16d-14}$$

Use of Ga in TMG for GaN LED (white, blue, violet, green LED) production was estimated from the area of sapphire and silicon carbide substrates relative to GaAs SI substrates, the area of GaAs SI substrates, the thickness of the deposition layer, the density of GaN, the molar masses of Ga and N, and the deposition yield:

$$X_{16b-17a} = g_5 G_1 t_2 d_3 \frac{m_1}{m_1 + m_4} \frac{10^{-6}}{y_7}$$

Use of Ga in TMG for InGaP-based LEDs (red, orange, yellow LEDs) was estimated from the area of GaAs SC substrates and GaP substrates relative to the area of GaAs SI substrates, the area of GaAs SI substrates, the thickness of the deposition layer, the density of GaP, the molar masses of Ga and P, and the deposition yield. The factor 0.15 was introduced to correct for the stoichiometry of the InGaP deposition layer compared to GaP.

$$X_{16b-17b} = (g_2 G_1 + g_3 G_1) 0.15 t_2 d_2 \frac{m_1}{m_1 + m_3} \frac{10^{-6}}{y_7}$$

Ga in TMG used for production of integrated circuits was estimated from area of SI substrates, thickness of the deposition layer, the density of GaAs, the molar masses of Ga and As, the share of GaAs ICs produced with MOCVD, and the deposition yield:

$$X_{16b-17c} = G_1 t_4 d_1 10^{-6} \frac{m_1}{m_1 + m_2} \frac{h_1}{y_7}$$

The amount of scrap collected from production of InGaP LEDs was estimated from inputs into the process, the loss rates in the different fabrication stages and the assumed collection rate:

$$X_{17b-14} = X_{16b-17b} y_7 (q_1 r_4 + (1 - q_1) q_3 r_6) + \\ (X_{16d-17b} + X_{16c-17b})(q_1 r_4 + (1 - q_1) q_4 r_6 + (1 - q_1)(1 - q_4) q_3 r_6)$$

Scrap collected from production of ICs was estimated from process inputs, losses in the different fabrication stages, and the assumed collection rate:

$$X_{17c-14} = (X_{16a-17c} y_9 + X_{16b-17c} y_7)(q_1 r_4 + (1 - q_1) q_3 r_5) + \\ X_{16c-17c}(q_1 r_4 + (1 - q_1) q_2 r_5 + (1 - q_1)(1 - q_2) q_3 r_5)$$

The total collected scrap in fabrication was found by summing up individual flows:

$$X_{17-14} = X_{17b-14} + X_{17c-14} + X_{17d-14}$$

The amount of Ga in GaN LEDs going into use was calculated from inputs to the fabrication process, the deposition yield and the loss rates due to breakage/non-functioning devices and dicing:

$$X_{17a-18} = X_{16b-17a} y_7 (1 - q_1)(1 - q_3)$$

The amount of Ga in InGaP LEDs going into use was calculated from inputs to the fabrication process, deposition yield and loss rates due to breakage/non-functioning devices, dicing and backgrinding/epitaxial lift-off. Note that backgrinding/epitaxial lift-off loss, $q_4$, is only included for the substrate term, not the deposition layer:

$$X_{17b-18} = X_{16b-17b} y_7 (1 - q_1)(1 - q_3) + (X_{16c-17b} + X_{16d-17b})(1 - q_1)(1 - q_4)(1 - q_3)$$

The Ga in integrated circuits going into use was calculated from fabrication process inputs, MOCVD and MBE yields and loss rates due to breakage/non-functioning devices, dicing and backgrinding. Note that backgrinding loss only applies to the substrate term:

$$X_{17c-18} = (X_{16a-17c} y_9 + X_{16b-17c} y_7)(1 - q_1)(1 - q_3) + X_{16c-17c}(1 - q_1)(1 - q_2)(1 - q_3)$$

Total amount of Ga going into use in the form of semiconductor devices (LEDs, ICs, power electronics and CIGS photovoltaics) was calculated by summing up individual flows:

$$X_{17-18} = X_{17a-18} + X_{17b-18} + X_{17c-18} + X_{17d-18} + X_{17f-18,pe}$$

Uncollected scrap from production of GaN LEDs was calculated by mass balance:

$$X_{17a-19} = X_{16b-17a} - X_{17a-18}$$

Uncollected scrap from fabrication of InGaP LEDs was calculated by mass balance:

$$X_{17b-19} = X_{16b-17b} + X_{16c-17b} + X_{16d-17b} - X_{17b-18} - X_{17b-14}$$

Uncollected scrap from fabrication of GaAs ICs was calculated by mass balance:

$$X_{17c-19} = X_{16a-17c} + X_{16b-17c} + X_{16c-17c} - X_{17c-18} - X_{17c-14}$$

Total uncollected scrap from fabrication was found by summing up individual flows:

$$X_{17-19} = X_{17a-19} + X_{17b-19} + X_{17c-19} + X_{17d-19} + X_{17f-19,pe}$$

Recycled material going to refining was calculated from inputs to recycling and the recycling yield, $y_3$, assuming that all recycled Ga is refined. This is likely, because it is the same companies doing recycling and refining, who mostly serve the semiconductor device industry.

$$X_{11-12,s} = y_3 (X_{16-14} + X_{17-14})$$

Refined production from secondary material (production scrap), is assumed to be the same as input to refining, since the refining process has a net yield close to 100%:

$$X_{12-13,s} = X_{11-12,s}$$

Loss from the recycling process was calculated from input to recycling and recycling yield:

$$X_{14-19} = (X_{16-14} + X_{17-14})(1 - y_3)$$

Stockpiling of refined gallium was estimated by mass balance:

$$X_{13-15} = X_{12-13,s} + X_{12-13,p} - X_{13-16}$$

**Decomposition of flows (Figure 2 in main paper)**

The decomposition of primary Ga demand, demand for refined Ga and demand for Ga in intermediate compounds was done using the following equations:

Primary demand from GaN-based LEDs:

$$Primary_{LED1} = \frac{X_{16b-17a}}{y_4 y_2}$$

Primary demand from InGaP-based LEDs. This takes into account the that some of demand is covered by secondary material (the last two terms).

$$Primary_{LED2} = \frac{X_{16b-17b}}{y_4 y_2} + \frac{X_{16c-17b}}{y_5 y_2} - X_{16c-17b}\frac{(1-y_5)r_2 y_3 y_2}{y_5} - X_{17b-14}\, y_3 y_2$$

Primary demand from integrated circuits, also taking into account recycling (last two terms):

$$Primary_{IC} = \frac{X_{16a-17c}}{y_2} + \frac{X_{16c-17c}}{y_5 y_2} - X_{16c-17c}\frac{(1-y_5)r_2 y_3 y_2}{y_5} - X_{17c-14}\, y_3 y_2$$

Primary demand from photovoltaics, also taking into account recycling (second term):

$$Primary_{PV} = \frac{X_{16a-17d}}{y_2} - X_{17d-14}\, y_3 y_2$$

The total refined metal (primary and secondary) for GaN-based LEDs:

$$Metal_{LED1} = \frac{X_{16b-17a}}{y_4 y_2}$$

The total refined metal (primary and secondary) for InGaP-based LEDs:

$$Metal_{LED2} = \frac{X_{16b-17b}}{y_4 y_2} + \frac{X_{16c-17b}}{y_5 y_2}$$

The total refined metal (primary and secondary) for integrated circuits:

$$Metal_{IC} = \frac{X_{16a-17c}}{y_2} + \frac{X_{16c-17c}}{y_5 y_2}$$

The total refined metal (primary and secondary) for photovoltaics:

$$Metal_{PV} = \frac{X_{16a-17d}}{y_2}$$

Ga in intermediate compounds for GaN-based LEDs:

$$Semi_{LED1} = X_{16b-17a}$$

Ga in intermediate compounds for InGaP-based LEDs:

$$Semi_{LED2} = X_{16b-17b} + X_{16c-17b}$$

Ga in intermediate compounds for integrated circuits:

$$Semi_{IC} = X_{16a-17c} + X_{16c-17c}$$

Ga in intermediate compounds for photovoltaics:

$$Semi_{PV} = X_{16a-17d}$$

**Model for accumulation of Ga in Bayer liquor**

The fraction of Ga lost to alumina depends on how long the gallium is allowed to accumulate in the Bayer liquor before it is extracted. In the case that no Ga extraction occurs (assuming that the liquor is not discarded after a certain number of loops), the system will reach steady state, and the amount of Ga dissolved in the liquor for each batch will be the same as that precipitated to aluminum hydroxides, *i.e.* the loss to alumina is 100%. This fact, combined with the typical concentration of Ga in aluminum (100-200 ppm),[58] was used to back-calculate how much of the Ga ends up in the red mud, and it was found to be 30-50%. It was assumed that most alumina is produced without a Ga extraction loop, which later was confirmed by quantification of the other flows. To estimate how much gallium is lost to alumina when Ga is extracted from the liquor, it is necessary to make an assumption about how long the gallium is allowed to accumulate, *i.e.*, until what concentration does Ga accumulate before the liquor is removed for Ga extraction. There is not much information available about this, and it is also likely that this varies a lot between different producers. A higher concentration of Ga is better for the extraction process, but leads to a higher loss to alumina. However, since there is currently an oversupply of gallium, it was assumed that a more efficient extraction process is favored over larger amounts produced. We made a model similar to that used by Hudson to estimate the relationship between the number of accumulation cycles and Ga concentration in Bayer liquor. Figure S2 shows how Ga builds up in the Bayer liquor. The model was calibrated against the results presented by Hudson,[12] which gave a distribution coefficient of 0.3 between the concentration of Ga in precipitated hydrates and the concentration in the liquor. We assumed that Ga accumulates in the liquor until it reaches 90% of the steady state concentration, i.e. 0.14 g/l, meaning that 40% of the Ga dissolved from bauxite enters the Ga extraction process.

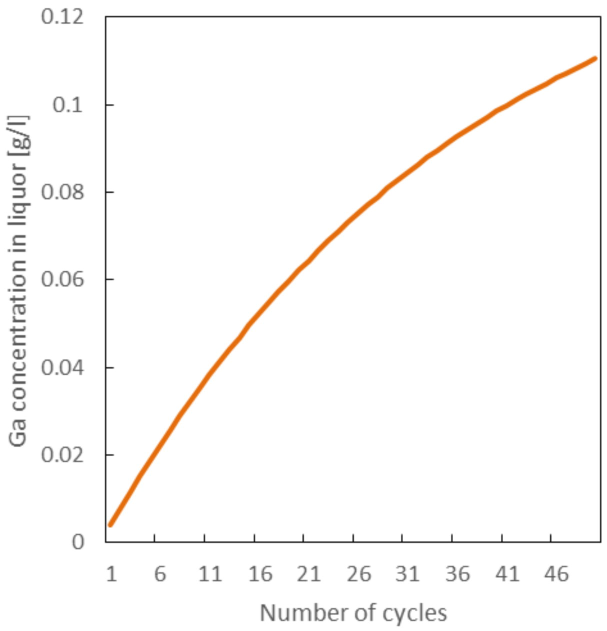


*Figure S2.* Gallium concentration in Bayer liquor as function of the number of cycles of dissolving bauxite and precipitation of aluminum hydroxide.

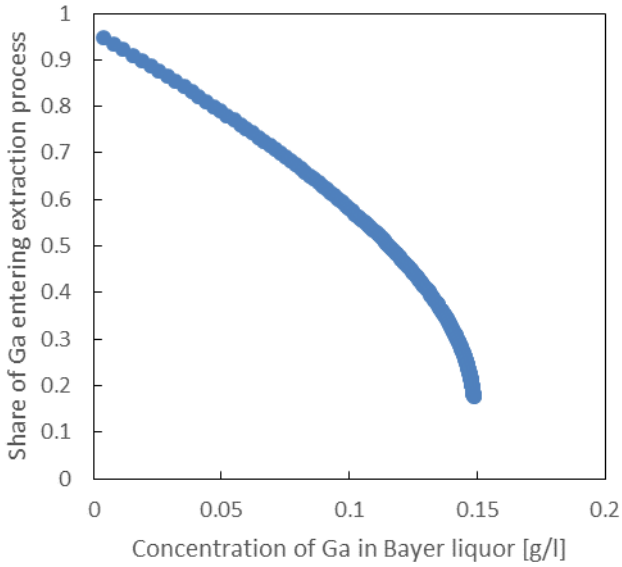


*Figure S3.* Share of Ga entering extraction process as a function of the concentration to which Ga is allowed to accumulate in the Bayer liquor, assuming 33 ppm Ga in bauxite. Higher concentrations lead to lower amount of Ga entering the extraction process. Steady state can be observed around 0.15 g/l. We assumed that the concentration builds up to 0.14 g/l, which means that 40% of the Ga would enter the extraction process.

# 3. Monte Carlo simulation

The Monte Carlo simulation was performed with MATLAB.[59] All parameters with uncertainty above zero were treated as random variables. Transfer coefficients (parameters limited between 0 and 1) were given a beta distribution and all other parameters were given a normal distribution. Uncertainties (standard deviations) were estimated based on the quality of data and knowledge about processes. The beta distribution is defined by the parameters $\alpha$ and $\beta$, which are related to the standard deviation and mean by the following relations:

$$\alpha = \mu^2 \left( \frac{1-\mu}{\sigma^2} - \frac{1}{\mu} \right)$$

$$\beta = \alpha \left( \frac{1}{\mu} - 1 \right)$$

Using the defined probability distributions, 100 000 sets of the parameters were drawn, and for each of the sets, a complete system quantification was done using the equations in chapter 2 of this supplementary information. Confidence intervals, mean and median were calculated for each system variable.

# 4. Detailed results

The detailed results of the quantification and Monte Carlo simulation are shown in Table S3. Note that the consumption of TMG, $X_{16b\text{-}17}$ was calculated using two approaches and is therefore listed twice.

*Table S3.* Results from the Monte Carlo simulation. All values are in metric tons/year.

| *Variable* | *Description* | *Mean* | *Stand. dev.* | *16th percentile* | *Median* | *84th percentile* |
|---|---|---|---|---|---|---|
| $X_{1\text{-}2}$ | Bauxite input to non-Ga Bayer process | 9290 | 2284 | 7124 | 9254 | 11504 |
| $X_{1\text{-}4}$ | Bauxite input to Ga-extr. Bayer process | 1521 | 993 | 830 | 1265 | 2125 |
| $X_{2\text{-}3}$ | Red mud from non-Ga Bayer process | 3508 | 1225 | 2319 | 3396 | 4702 |
| $X_{2\text{-}5}$ | Alumina from non-Ga Bayer process | 5782 | 1772 | 4055 | 5694 | 7514 |
| $X_{4\text{-}3}$ | Red mud from Ga-extr. Bayer process | 605 | 492 | 261 | 476 | 909 |
| $X_{4\text{-}5}$ | Alumina from Ga-extr. Bayer process | 613 | 558 | 234 | 462 | 945 |
| $X_{4\text{-}6}$ | Gallium entering extraction process from Bayer route | 304 | 47 | 257 | 303 | 350 |
| $X_{6\text{-}11}$ | Primary production of gallium metal from Bayer route | 288 | 44 | 244 | 288 | 332 |
| $X_{6\text{-}19}$ | Loss from extraction process | 15 | 10 | 6 | 13 | 25 |
| $X_{6\text{-}11}$ | Primary gallium to refining | 160 | 16 | 144 | 160 | 176 |
| $X_{10\text{-}11}$ | Primary production of gallium metal from zinc route | 4 | 1 | 3 | 4 | 5 |
| $X_{11\text{-}15}$ | Primary unrefined gallium going into stockpiles | 47 | 50 | -2 | 47 | 96 |
| $X_{11\text{-}12,p}$ | Refined gallium from primary production | 160 | 16 | 144 | 160 | 176 |
| $X_{11\text{-}12,s}$ | Refined gallium from recycling | 82 | 22 | 60 | 80 | 103 |
| $X_{14\text{-}11}$ | Recycled material going to refining | 82 | 22 | 60 | 80 | 103 |
| $X_{14\text{-}19}$ | Loss from recycling | 9 | 5 | 4 | 8 | 14 |
| $X_{13\text{-}15}$ | Gallium going into stockpiles | 27 | 29 | -2 | 28 | 56 |
| $X_{13\text{-}16a}$ | Refined gallium used in production of sputtering targets and MBE sources | 13 | 5 | 8 | 12 | 17 |
| $X_{13\text{-}16b}$ | Refined gallium used in the production of TMG | 15 | 2 | 12 | 15 | 17 |
| $X_{13\text{-}16c}$ | Refined gallium used in the production of GaAs substrates | 176 | 34 | 143 | 174 | 209 |
| $X_{13\text{-}16d}$ | Refined gallium used in the production of GaP and GaN substrates | 12 | 3 | 9 | 12 | 15 |
| $X_{13\text{-}16}$ | Consumption of refined gallium | 215 | 37 | 179 | 213 | 251 |
| $X_{16b\text{-}19}$ | Loss from production of TMG | 1 | 1 | 0 | 1 | 2 |
| $X_{16c\text{-}19}$ | Loss from production of GaAs substrates | 42 | 15 | 28 | 41 | 57 |
| $X_{16d\text{-}19}$ | Loss from production of GaP and GaN substrates | 3 | 1 | 2 | 3 | 4 |
| $X_{16\text{-}19}$ | Loss to landfills from compound production | 47 | 16 | 31 | 45 | 62 |
| $X_{16c\text{-}14}$ | Recycling from production of GaAs substrates | 72 | 20 | 53 | 70 | 91 |
| $X_{16d\text{-}14}$ | Recycling from production of GaP and GaN substrates | 5 | 2 | 3 | 5 | 6 |
| $X_{16\text{-}14}$ | Recycling from compound production | 77 | 21 | 57 | 75 | 97 |
| $X_{16a\text{-}17}$ | Consumption of sputtering targets and MBE sources | 13 | 5 | 8 | 12 | 17 |

*Table S3 cont.*

| ***Variable*** | ***Description*** | ***Mean*** | ***Stand. dev.*** | ***16th percentile*** | ***Median*** | ***84th percentile*** |
|---|---|---|---|---|---|---|
| $X_{16b\text{-}17}$ | Consumption of TMG | 13 | 2 | 11 | 13 | 15 |
| $X_{16c\text{-}17}$ | Consumption of GaAs substrates | 61 | 10 | 51 | 61 | 71 |
| $X_{16d\text{-}17}$ | Consumption of GaP and GaN substrates | 4 | 1 | 3 | 4 | 5 |
| $X_{16e\text{-}17e}$ | Ga in NdFeB to produce permanent magnets | 85 | 17 | 68 | 85 | 102 |
| $X_{16\text{-}17}$ | Consumption of intermediate compounds | 176 | 21 | 155 | 176 | 197 |
| $X_{16a\text{-}17c}$ | Use of sputtering targets and MBE sources for ICs | 1 | 1 | 0 | 1 | 1 |
| $X_{16a\text{-}17d}$ | Use of sputtering targets and MBE sources for PV | 12 | 5 | 7 | 11 | 16 |
| $X_{16b\text{-}17a}$ | Use of TMG for production of GaN LEDs | 10 | 8 | 5 | 8 | 15 |
| $X_{16b\text{-}17b}$ | Use of TMG for production of InGaP LEDs | 0 | 0 | 0 | 0 | 1 |
| $X_{16b\text{-}17c}$ | Use of TMG for production of ICs | 1 | 1 | 0 | 1 | 1 |
| $X_{16b\text{-}17f,\ pe}$ | Use of TMG for production of power electronics | 0 | 0 | 0 | 0 | 0 |
| $X_{16b\text{-}17}$ | Total use of TMG (estimated from substrates area) | 11 | 8 | 5 | 9 | 16 |
| $X_{16c\text{-}17b}$ | Use of GaAs substrates for InGaP LEDs | 26 | 6 | 20 | 25 | 32 |
| $X_{16c\text{-}17c}$ | Use of GaAs substrates for ICs | 35 | 6 | 30 | 35 | 41 |
| $X_{16d\text{-}17b}$ | Use of GaP substrates for InGaP LEDs | 3 | 1 | 3 | 3 | 4 |
| $X_{16d\text{-}17f}$ | Use of GaN substrates for lasers and other applications | 1 | 0 | 1 | 1 | 1 |
| $X_{17a\text{-}19}$ | Scrap lost from production of GaN LEDs | 9 | 7 | 4 | 7 | 14 |
| $X_{17b\text{-}19}$ | Scrap lost from production of InGaP LEDs | 17 | 6 | 11 | 17 | 23 |
| $X_{17c\text{-}19}$ | Scrap lost from production of ICs | 28 | 7 | 22 | 29 | 35 |
| $X_{17d\text{-}19}$ | Scrap lost from production of PV | 7 | 4 | 3 | 6 | 10 |
| $X_{17e\text{-}19}$ | Scrap lost from production of NdFeB magnets | 26 | 10 | 16 | 24 | 35 |
| $X_{17f,\ pe\text{-}19}$ | Scrap lost from production of power electronics | 0 | 0 | 0 | 0 | 0 |
| $X_{17\text{-}19}$ | Total scrap loss to landfills from fabrication | 87 | 18 | 70 | 86 | 104 |
| $X_{17b\text{-}14}$ | Collected scrap from production of InGaP LEDs | 8 | 5 | 4 | 7 | 14 |
| $X_{17c\text{-}14}$ | Collected scrap from production of ICs | 5 | 6 | 1 | 3 | 8 |
| $X_{17d\text{-}14}$ | Collected scrap from production of PV | 0 | 0 | 0 | 0 | 1 |
| $X_{17\text{-}14}$ | Total collected scrap from fabrication | 14 | 8 | 7 | 12 | 21 |
| $X_{17a\text{-}18}$ | GaN LEDs going into use | 0.6 | 0.2 | 0.5 | 0.6 | 0.8 |
| $X_{17b\text{-}18}$ | InGaP LEDs going into use | 3.7 | 2.0 | 1.8 | 3.4 | 5.7 |
| $X_{17c\text{-}18}$ | ICs going into use | 3.9 | 0.8 | 3.0 | 3.8 | 4.7 |
| $X_{17d\text{-}18}$ | PV going into use | 4.6 | 1.5 | 3.2 | 4.4 | 6.0 |
| $X_{17e\text{-}18}$ | NdFeB magnets going into use | 59 | 15 | 45 | 59 | 74 |
| $X_{17f,\ pe\text{-}18}$ | Power electronics going into use | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $X_{17\text{-}18}$ | Total gallium entering use | 72 | 15 | 57 | 72 | 87 |

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