Comprehensive Global and United States Cycles of Gallium, Germanium, Rhenium, and Tungsten in 2008

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Abstract
Metal life cycles for the scarcer elements are rarely compiled, in part because the data on which they must be based are rarely available in published documents. Drawing on published and unpublished material and on expert consultant knowledge, we have characterized the cycles of four scarce elements at both the global and U.S. levels: gallium, germanium, rhenium, and tungsten. The results are presented and discussed in this final research report.

1. Introduction
Metal life cycles are an important tool in assessing the sustainability of a material. They provide detailed information on the size and spatial allocation of production, use, and recycling flows, information that can be used to calculate a wide variety of indicators. Over the past decade, Yale’s Stocks and Flows (STAF) project at the Center for Industrial Ecology has developed a well-established methodology to characterize the human-related life cycles of metals over various spatial levels and time periods. As of today, comprehensive global cycles are available for seven metals, all based on more than 50 individual country cycles: iron (Wang et al. 2007), chromium (Johnson et al. 2006), nickel (Reck et al. 2008; Reck and Rotter 2012), copper (Graedel et al. 2004), zinc (Graedel et al. 2005; Graedel and Cao 2010), silver (Johnson et al. 2005), and lead (Mao et al. 2008). The multilevel cycles of stainless steel were produced as well (Reck et al. 2010).


The present study was conducted in collaboration between researchers from Yale University and USGS scientists, and in consultation with other representatives from academia and industry. It is planned that the detailed results of this study will be made available to the public through one or
more scientific publications (forthcoming later this year), and through presentations at academic and industry events.

2. Methodology

To characterize a metal life cycle we use the tool of material flow analysis (MFA), which is based on the mass balance principle. In MFA, a material life cycle is described by identifying (1) the main life stages (processes) of a material, (2) the main flows connecting these processes, (3) the stocks in which a material is accumulated over time, and (4) its release from these stocks. Flows are quantified by using a variety of data sources (e.g., literature, data bases), estimates, and mass balance. Logical connections between the flows make data challenges immediately apparent and provide guidance on where further investigations on data quality, reliability, and allocation are necessary.

The Yale Stocks and Flows (STAF) project defines a metal life cycle through four main processes: production, fabrication & manufacturing, use, and waste management & recycling (see Figure 1). These processes are interconnected through the generation and use of scrap in different forms and at different life stages.

![Figure 1](image-url) A simplified metal life cycle, showing metal production (P), fabrication & manufacturing (F&M), use (U), and waste management & recycling (WM). The life stages are connected through the generation and use of metal scrap.

In the life cycles of the four investigated metals, the production process yields the following:

- Gallium: Refined gallium,
- Germanium: Germanium chlorides, germanium oxides, and germanium metal,
- Rhenium: Ammonium perrhenate and rhenium metal,
- Tungsten: Tungsten powder.
In fabrication, intermediate products such as polymer catalysts in the case of germanium and superalloys in the case of rhenium are produced for use in manufacturing. In manufacturing the semi-fabricated products are processed into products for various end use sectors, e.g., construction, transportation, industrial and metal working machinery, and electrical and electronic products. These products are then used by the final customer, where they remain during corresponding lifetimes. Once a product reaches its end-of-life, it is either recycled or disposed of in landfills. The recycled scrap is used as a secondary raw material in production, with the exception of rhenium-containing superalloy scrap used in fabrication. At all levels, the metals can be traded between the US and the rest of the world (we introduce imaginary “markets”, allowing us to distinguish between domestic shipments and domestic use of a given commodity, with the difference being mostly net imports, and in some cases also stock changes). So-called phantom flows (marked as a dashed line) are introduced when independently collected data did not lead to mass balance for a process or market (most frequently, this is the case with the scrap market). A generic cycle is presented in Figure 2.
2.1 Production

2.1.2 Gallium

Gallium’s life cycle stage starts with the mining of bauxite and zinc ore, and its recovery as by-product. In the US, only refined gallium is traded, as it is only produced from scrap. The amount produced in the US is estimated using results from a depletion time model (see Section 2.4). The global primary (USGS 2009d) and total production (Jaskula 2010) as well as the US metal use are USGS estimates (USGS 2013d). USGS (2009d) indicated that only a portion of the gallium present in bauxite and zinc ores is recoverable, and that the factors controlling the recovery are proprietary. Due to a lack of available data, we assumed that 10% of the gallium present in the ores considered is recovered, the rest being lost in tailings. An overall production process efficiency of 81% is used in Classen et al. (2009), based on recovery rates of 90% for each electrolysis and purification (including partial reuse of waste) given in Meijer et al. (2003). This figure is used both for primary and secondary production.

2.1.2 Germanium

Germanium’s life cycle starts with the mining of zinc ore or coal, and its recovery as by-product. At this life stage, four commodities are actively traded: germanium concentrates, chlorides, oxides, and metal. The latter three components can also be produced from scrap. Global production as well as US production, government stockpiling, and use are estimated by USGS (USGS 2013c; Guberman 2010). In addition to these flows, the mining processing losses (based on zinc mining, Steblez, W., United States Geological Survey, Reston, Virginia, personal communication, 2001), the percentage of zinc not processed for germanium recovery (applies to indium, Mikolajczak 2009), the smelter and extraction losses (applies to indium, Mikolajczak 2009; Alfantazi and Moskalyk 2003), and the refinery losses (applies to indium, Stamp et al. 2014) were needed to determine all flows of the production stage.

2.1.3 Rhenium

Rhenium’s life cycle starts with the mining of copper, and the recovery of molybdenum as its by-product. Rhenium is in turn a by-product of molybdenum. Three commodities are actively traded: molybdenum concentrates, ammonium perrhenate, and rhenium metal. Ammonium perrhenate can be produced from spent catalysts as well (see Section 2.2.3). USGS and Roskill Information estimated the rhenium contained in mined molybdenum and the trade of ammonium perrhenate and rhenium metal (Polyak 2014), as well as the ammonium perrhenate and metal rhenium use worldwide (Roskill Information Services 2010) and in the US (USGS 2013b). Rhenium mine recovery rates from molybdenite containing 0.01 to 0.05% rhenium were indicated to be in excess of approximately 60% according to an industry expert; we used a recovery rate of 60% in the model. Primary and secondary production efficiencies stem from Millensifer (2000) and a personal communication with Desiree Polyak (USGS) in 2014, respectively.

2.1.3 Tungsten

Tungsten’s life cycle stage starts with the mining of wolframite. At this stage, three commodities are actively traded: tungsten concentrates, tungstates, and tungsten powder. The latter can also be produced from scrap. USGS estimates the US government stockpile shipments and secondary
production as well as global and US tungsten powder use (USGS 2013a). In 2008, USGS reports limited shipments from a mine in California (USGS 2009c). We assumed this amount corresponded to 5% of the sum of net imports and government stockpile shipments. The global split between primary and secondary production is estimated by Audion and Labbé (2012). International trade of tungsten concentrates and tungstates was accounted for with the United Nations commercial trade database (UN Comtrade Database, harmonized system, HS, United Nations Statistics Division 2010), multiplying amounts with respective tungsten contents. With respect to mining, recovery rates of 70 to 90% were cited by Smith (1994), and a recovery rate of 90% was used in this study as was used by Harper (2008). As for primary chemical treatment, losses are estimated at 4% (Harper 2008). We assumed the same for secondary production.

2.2 Fabrication

2.2.1 Gallium

Refined gallium is used to produce a number of intermediate gallium products, which we term first uses to distinguish them from the end-use sectors introduced in manufacturing. The former are optoelectronic devices, integrated circuits, and other gallium first uses. Data describing the relative importance of each first use in 2008 in the US are applied to the global cycle as well (USGS 2009d). Yield losses to new scrap and industrial waste applied to optoelectronic devices and integrated circuits are those of Eichler (2012). We assumed no yield losses for other gallium first uses.

International trade of semi-fabricated products was accounted for by identifying traded goods in the United States Census Bureau trade database (USCB 2008) and multiplying their amounts with respective gallium contents. Traded semi-fabricated products include semiconductors and related devices.

The use of semi-fabricated products in manufacturing was calculated by applying the mass balance principle to the semi-fabricated product market.

2.2.2 Germanium

Germanium chlorides, germanium oxides, and germanium metal are used to produce the following semi-fabricated products: infrared systems, semiconductors, fiber optics, radiation detectors, polymer catalysts, electrical/solar panels, and other germanium first uses. Data describing the relative importance of each first use in 2008 in the US and worldwide are from USGS (2009b). There are 60% yield losses to new scrap in the fabrication of fiber optics (USGS 2009b). We assumed no yield losses in the other first uses.

International trade of semi-fabricated products was accounted for by identifying traded goods in the United States Census Bureau trade database (USCB 2008) and multiplying their amounts with respective germanium contents. Traded semi-fabricated products include search, detection, and navigation instruments, optical instruments and lenses, fiber optic cables, and semiconductors and related devices.

The use of semi-fabricated products in manufacturing was calculated by applying the mass balance principle to the semi-fabricated product market.
2.2.3 Rhenium

Ammonium perrhenate and rhenium metal are used to produce the following semi-fabricated products: petroleum-reforming catalysts, superalloys, and rhenium mill products, wire, and alloys. Data describing the relative importance of each first use in 2008 in the US and worldwide are from USGS (2009a) and Roskill Information Services (2010), respectively. Ten percent of rhenium entering superalloy fabrication goes to scrap (Polyak 2011), a ratio applied to the US and the global level. We assume no yield losses at this stage.

International trade of semi-fabricated products was accounted for by identifying traded goods in the United Nations commercial trade database (UN Comtrade Database, harmonized system, HS, United Nations Statistics Division 2010) and multiplying their amounts with respective rhenium contents. Traded semi-fabricated products include catalysts of platinum and nickel superalloys.

The use of semi-fabricated products in manufacturing was calculated by applying the mass balance principle to the semi-fabricated product market.

2.2.3 Tungsten

Tungsten powder is used to produce the following semi-fabricated products: cemented carbides, tool steels, mill products, superalloys, and other tungsten first uses. Data describing the relative importance of each first use in 2008 in the US and worldwide are from Roskill (2007). A yield loss of 10% to new scrap is applied to all first uses (Pastor 2000; Roskill Information Services 2011).

International trade of semi-fabricated products was accounted for by identifying traded goods in the United Nations commercial trade database (UN Comtrade Database, harmonized system, HS, United Nations Statistics Division 2010) and multiplying their amounts with respective tungsten contents. Traded semi-fabricated products include tungsten carbides, ferrotungsten and ferrosilicon tungsten, and mill products.

The use of semi-fabricated products in manufacturing was calculated by applying the mass balance principle to the semi-fabricated product market.

2.3 Manufacturing

All intermediate gallium products flow to the electrical and electronic products end-use sector except for other gallium first uses flowing to miscellaneous end uses¹. All intermediate germanium products flow to electrical and electronic products except for polymer catalysts and other germanium first uses flowing to the food sector and miscellaneous end uses, respectively (Guberman 2010). While petroleum-reforming catalysts containing rhenium flow to the petroleum end-use sector, superalloys are used in the engine end-use sector. Rhenium mill products, wire, and alloys flow into miscellaneous end uses. Tungsten intermediate products are used in electrical and electronic products, transportation, industrial and metal working.

machinery, mining, and miscellaneous applications (Mesman, 2015). No yield losses were assumed in manufacturing.

International trade of end-use products was accounted for by identifying traded goods of the United States Census Bureau trade database (USCB 2008) for gallium and germanium and the United Nations commercial trade database (UN Comtrade Database, United Nations Statistics Division 2010) for rhenium and tungsten and multiplying their amounts with respective metal contents. Traded end use products include the following:

- **Gallium**: Optical instruments and lenses, electronic computers, computer storage devices, other computer peripheral equipment, audio and video equipment, electric lamp bulb and parts, broadcast and wireless communications equipment (all of which contain integrated circuits), search, detection, and navigation instruments, broadcast and wireless communications equipment (all of which contain optoelectronic devices).
- **Germanium**: Broadcast and wireless communications equipment.
- **Rhenium**: Turbo-jets, turbo-propellers, other gas turbines, helicopters, airplanes, and other aircraft.
- **Tungsten**: Various motor vehicles (e.g., fire fighting vehicles and concrete mixers), mobile cranes, mobile drilling derricks, turbo-jets, turbo-propellers, other gas turbines, helicopters, airplanes, and other aircrafts, flashbulbs, flashcubes, and the like, and lighting sets of a kind used for Christmas trees.

The flow of end use products from manufacturing to use was calculated by applying the mass balance principle to the end use product market.

### 2.4 Use

Petroleum-reforming catalysts (rhenium) and cemented carbides (tungsten) are dissipative uses. Dissipative metal losses were estimated based on a depletion time model we had developed for the US and the World (Graedel et al. 2012). This model estimates the end-of-life flows of metals depending on first uses and end uses (e.g., cemented carbides into mining, rhenium-containing superalloys into engines). Historical metal consumption data stem from the following sources:

- **Gallium**: Historical statistics for mineral and material commodities in the United States² and mineral commodity statistics³ for split among first uses, historical statistics for mineral and material commodities in the United States for total US and global consumption⁴
- **Germanium**: Historical statistics for mineral and material commodities in the United States⁵ and mineral commodity statistics⁶ for split among first uses, historical statistics

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for mineral and material commodities in the United States for total US and global consumption.

- **Rhenium**: Roskill (1983) and Roskill Information Services (2010) for global split among first uses, Roskill (1983) and mineral commodity statistics for the US split among first uses, historical statistics for mineral and material commodities in the United States and Audion et al. (2011) for the total global and US consumption, respectively.


The allocations of first uses into end uses remain those of 2008 for all years of the depletion time model. The model uses lifetime distributions of first uses according to Graedel et al. (2015). The model considers in-use dissipation as a fraction of the in-use stock (germanium in cemented carbides) or as a fraction of the flow entering use (rhenium in petroleum-reforming catalysts) with in-use dissipation rates from Ciacci et al. (2015).

The net addition to in-use stock was calculated by applying the mass balance principle to the use process.

Data on the international trade of end-of-life products was not available.

### 2.5 Waste Management and recycling

In waste management and recycling, end-of-life products are diverted to recycling with collection rates depending on the first use category and, in some cases, on the level of investigation (i.e., global level or US, Graedel et al. 2015).

The landfill flow was calculated by applying the mass balance principle to the waste management and recycling process.

### 2.6 Scrap market

Flows entering the scrap market are new scrap generated in fabrication, net scrap import flows, and old scrap from waste management. Flows leaving the scrap market are scrap used in fabrication and smelting and in refining/chemical treatment. The arithmetic difference between generation and use of scrap is a phantom flow, which might have several explanations, such as the build-up of a scrap stock or data uncertainty.

Net import of germanium scrap into the US was extrapolated from Jorgensen (2006), while net import of tungsten scrap into the US in 2008 is reported by Shedd (2011).

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3. Results of the cycle analysis

3.1 Global cycles 2008

Figure 3 shows the global cycles of gallium, germanium, rhenium, and tungsten in 2008. The differences are remarkable. Of the gallium mined together with bauxite or zinc ore (1,173 Mg/a), only 10% makes its way to smelting and refining. A third of the gallium flowing into smelting and refining is new scrap from fabrication (68 Mg/a). Yield losses to industrial waste in smelting and refining and fabrication are similar (35 and 28 Mg/a). No old scrap is rerouted to the gallium cycle.

The highest losses of the germanium cycle occur in smelting and refining (258 Mg/a), while its mining efficiency is relatively high with only 53 Mg/a of tailings. Like gallium, the main scrap flows are those from fabrication to smelting and refining (25 and 44 Mg/a, respectively). The model yields a high phantom flow (16 Mg/a).

Rhenium and tungsten exhibit similar global cycles, although on different orders of magnitude (Mg/a versus Gg/a). Losses occur in mining (48 Mg/a and 4 Gg/a, respectively) and waste management and recycling (15 Mg/a and 38 Gg/a, respectively). The main difference between the two cycles lies in fabrication, where rhenium scrap is used (6 Gg/a), while tungsten is lost as new scrap (6 Gg/a). In both cases, old scrap from waste management and recycling is supplied to production (18 Mg/a and 18 Gg/a, respectively).

3.2 US cycles 2008

Figure 4 illustrates the US cycles of gallium, germanium, rhenium, and tungsten. In the case of gallium, inputs to the US cycle are imports of refined gallium (18 Mg/a) and end-use products (8 Mg/a), while the majority of losses take place in waste management and recycling (9 Mg/a). The US flow entering end-use (15 Mg/a) is around a quarter of the global end-use flow (51 Mg/a).

Germanium is mined in Alaska and Washington State (i.e., Red Dog and Pend Oreille mines), and smelted and refined by Tech Cominco in Trail, British Columbia, Canada. This explains why most of germanium mined in the US is immediately exported (33 Mg/a). More is imported as germanium chlorides, metal, and oxides and processed in fabrication (49 Mg/a). Of the germanium flowing into use (49 Mg/a) [less than half of the global flow (115 Mg/a)], most of it was added to stock (33 Mg/a). As in the global case, the phantom flow from the scrap market is high (5 Mg/a).

Rhenium enters the US cycle almost exclusively as ammonium perrhenate and rhenium metal imports (37 Mg/a). More than half of the flow entering use, which represents more than half of the global end-use flow (46 and 70 Mg/a, respectively), is added to stock.

Finally, the tungsten cycle sees most of the metal entering the life cycle as tungsten ores and concentrates and tungstates (5 Gg/a). Interestingly, a similar quantity (6 Gg/a) leaves the cycle through waste management and recycling. Of the tungsten flowing into use (13 Gg/a, around a quarter of the 56 Gg/a global flow), little is added to the stock (2 Gg/a).
Figure 3  Global cycles of gallium (Mg/a), germanium (Mg/a), rhenium (Mg/a), and tungsten (Gg/a) in 2008.
Figure 4 US cycles of gallium (Mg/a), germanium (Mg/a), rhenium (Mg/a), and tungsten (Gg/a) in 2008.

4. Summary

This report presents the results for the global and US life cycles in 2008 for gallium, germanium, rhenium, and tungsten. The results show different cycles not only on the global level but also in the US. Of substantial significance is that the importance of the US cycle ranges from a quarter (gallium, tungsten) to more than half (rhenium) of the total global end-use flow. The main difference between the US cycles stems from the stage at which the metal enters these cycles, i.e., imports as ore and concentrates or refined metal, and from the importance of the scrap supply to production. The high phantom flows of germanium from the scrap market that are
derived indicate that further research should be dedicated to a better characterization of this particular issue.

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