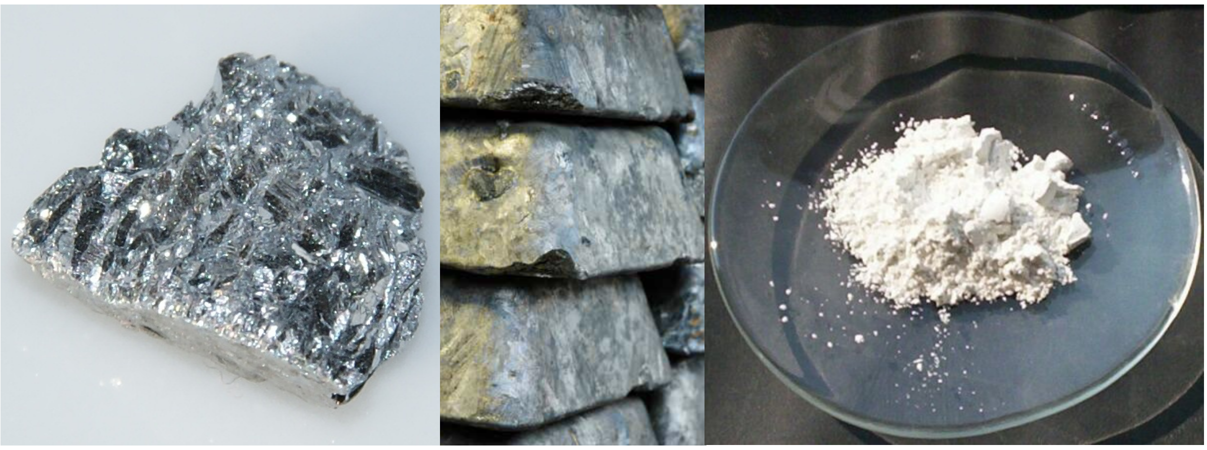

The Anthropogenic Antimony Cycle

Dynamic Analysis of Global Flows and Stocks of Antimony and Associated Environmental Impacts

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MSc. Thesis in Industrial Ecology

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THE ANTHROPOGENIC ANTIMONY CYCLE

DYNAMIC ANALYSIS OF GLOBAL FLOWS AND STOCKS OF ANTIMONY AND ASSOCIATED ENVIRONMENTAL IMPACTS

A thesis submitted by

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Cover images: Antimony crystal (Wikipedia 2015a), ingots (BGR 2010), and trioxide (Wikipedia 2015b)

PREFACE

This reports presents the study that I conducted for the Thesis Research Project in MSc. Industrial Ecology at the Delft University of Technology and Leiden University. Most of the research took place within the Technology and Society Lab at the Swiss Federal Laboratories for Materials Science and Technology (Empa), St. Gallen. I wish to acknowledge and express my gratitude to all those who supported me in carrying out this thesis.

First of all, the completion of this master's thesis marks the end of an academic adventure that started at the University of Lausanne a few years ago. I would like to thank all the people that helped me refine my way in the broad field of sustainability studies. In particular, I thank Dr. Suren Erkman for transmitting his passion for Industrial Ecology concepts and practices, and for advising me to follow the MSc. in Industrial Ecology at TU Delft/Leiden University.

I wish to thank Dr. Ester van der Voet for giving me the taste of tracking metal flows and stocks, and for her guidance and support throughout the thesis research project. I also express my gratitude to Dr.ir. Gijsbert Korevaar for his assistance as a second reader, as well as for his involvement in making the MSc. Industrial Ecology such a great study program.

I am very grateful for having been given the opportunity to integrate the Technology and Society Lab (TSL) at Empa for my thesis and would like to thank all my colleagues there for their advices, inspiration and encouragement during the six months I spent at Empa. This environment of quality allowed me to grow both professionally and personally, and provided me an excellent basis to go forward. I would particularly like to thank Dr. Patrick Wäger and Dr. Roland Hischier for supervising my internship, and Heinz Böni for giving me the possibility to conduct my research within the TSL and further accomplish my civil service duties within the Sustainable Recycling Industries program in India.

Very special thanks to my friends in the Netherlands and in Switzerland for their companionship throughout my studies.

Last but not least, I want to thank Laura and my family for their unconditional love and support.

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ABSTRACT

Antimony (Sb) is a rare metal – strictly speaking, a metalloid – that has been used for millennia, for various products and under diverse forms. As it is the case for most raw materials, the use of antimony has strongly increased during the last century as a result of technological developments and growing levels of population and wealth. Nowadays, antimony is mostly used as a flame-retarding compound (in synergy with halogens) in plastics contained in electronics, as well as an alloying element with lead in lead-acid batteries.

Mining of antimony is heavily concentrated in China, and has been increasingly constrained by political and geological factors over the last decade. As a result, antimony prices reached record highs in 2011. Geological reserves are reportedly dwindling, and supply risks are considerable. The recycling of antimony, which could reduce the need for mining, is limited as global recycling rates are low for most products using antimony. Besides those economic considerations, the growing use of antimony is of high concern for environmental and health reasons. It is a toxic element, with demonstrated harmful effects, including cancer, on animals and humans. As with other metals, the mining of antimony is also associated with severe environmental impacts.

Despite these problematic issues, little is known on the quantities of antimony that are being extracted, used, and disposed of by the global economy – that is, the global anthropogenic antimony cycle – and on the related environmental impacts. The aim of this master's thesis is to provide the first systemic picture of the global anthropogenic antimony cycle, explore its possible future development (at the 2050 horizon), and investigate its associated environmental impacts.

For this purpose, a model of the past, present, and possible future global flows and stocks of antimony was built using Material Flow Analysis (MFA). Associated environmental impacts were assessed based on the Life Cycle Assessment (LCA) methodology, as well as elements from risk assessment frameworks.

The results show that the current anthropogenic antimony cycle is characterized by high levels of resource extraction (about 190 Gg, or 190000 tons, per year) and landfilling (about 123 Gg/y), a relatively low overall recycling rate (estimated at 20-30%), and considerable emissions to the environment (about 23 Gg/y). Scenario analysis suggests that a resource crisis is probable within the next decade if demand continues to grow as it did during the last decade. Furthermore, significant environmental impacts were identified in relation with current mining levels, in terms of energy use, contribution to global warming, and damages to ecosystems.

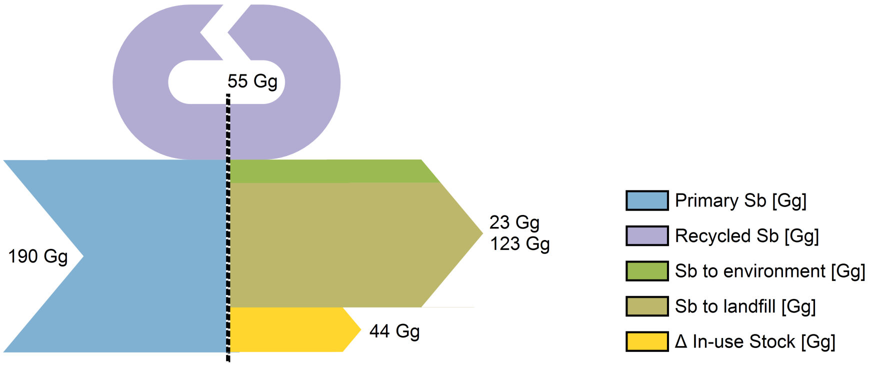

Figure 1: Global anthropogenic antimony cycle

Due to scope boundaries, data unavailability, inherent uncertainties, and model shortcomings, the results of this thesis should be regarded as estimates rather than accurate quantifications. As no study has previously been published on this topic and with such a scope, the validity of the research findings is difficult to assess. However, studies have been published on specific parts of the cycle, generally at a smaller geographical scope, and this study's results are generally in line with previous findings. Overall, it is considered that data sources and modeling assumptions used in this study represent the best currently available options to fill the knowledge gaps regarding past, current and possible future global antimony stocks, flows, and associated environmental impacts.

On the basis of the results of the research, several are strategies are proposed in order to reach a more sustainable anthropogenic antimony cycle:

1. Increase recycling rates for antimony-containing products, in order to decrease the demand for critical raw antimony, and to reduce the environmental impacts associated with the cycle. Results indicate that that secondary production of antimony can achieve energy savings of up to 95%, besides avoiding the environmentally damaging processes of primary production. According to the results, a considerable amount of antimony (about 1800 Gg) is currently being used in various products. This "in-use stock" is equivalent in size to the geological reserves. Much of the antimony contained in the in-use stock will potentially become available for recycling in the coming years. However, almost half of this in-use stock consists of plastics used in electronics, for which recycling rates are very low (<10%). Most of the remaining stock is made up of lead-acid batteries and other lead products, for which recycling rates are already quite high (>60%). Special attention should therefore be paid in the future to the recycling of antimony-containing plastics.
2. Substitute antimony for less problematic materials, such as aluminum and magnesium hydroxides in flame retardants, and calcium in lead alloys. These are plentiful elements and effective substitutes. Replacing antimony in those applications would drastically reduce the global demand and the associated environmental impacts.
3. Improve ore mining and processing technologies to increase efficiency and reduce emissions, and base as much as possible primary production processes on low-carbon energy sources. Mining and processing are by far the main sources of antimony emissions, they have a large carbon footprint, and they result in various pollutions.
4. Phase out the use of antimony in ammunition and in other dissipative applications such as brake linings, lubricants, pigments, and pesticides. Most of the emissions generated during the use of antimony products are related to these applications, although their share in the total consumption is very small. Substitutes exist for these applications.

Figure 2: Word cloud of the thesis report

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1 INTRODUCTION

1.1 TOWARDS A SUSTAINABLE METALS ECONOMY

Metals are essential to the functioning of industrial economies and few are the aspects of modern life that do not require their use. Over the past century, the global demand for metals has risen steeply as a result of population and economic growth. Furthermore, the palette of metals used in everyday products has expanded dramatically as a result of technological developments. With ever more people accessing material-intensive lifestyles globally, and the emergence of new technologies requiring the use of a large variety of metals (e.g. information and communications technologies, low-carbon power generation), these trends are expected to continue and possibly intensify in the future.

This heavy dependence on metal resources entails environmental and economic risks. The extraction, processing and refining of metal ores are energy intensive processes that contribute significantly to climate change. Production processes also use large amounts of water and can cause local environmental and health problems due to emissions of toxic substances into the air, soil, ground- and surface water. Furthermore, releases of metals into the environment throughout their anthropogenic life cycle – that is, from mining through manufacture, use, and disposal of metal-containing products – may harm humans and other living organisms. Risks for economies arise from the increasing dependence on the scarce, ultimately limited, and often geographically concentrated, resources that constitute metals. The issue is particularly pressing for countries with small domestic raw materials reserves and production, depending therefore strongly on imports to secure their supply. Most industrialized nations are in this situation. Many metals can thus be considered as "critical", a concept used to denote economic vulnerabilities due to insecure raw material supplies.

In this context, sustainable metals management has emerged as an international field of research and policy, arguably led today by the UNEP International Resource Panel (IRP) and its Working Group on Global Metal Flows (UNEP 2010a, 2011a, 2013a, 2013b). The IRP has identified six areas where research is needed to promote action towards a sustainable metals economy: (i) Stocks in society ("above-ground reserves"); (ii) Recycling rates; (iii) Environmental impacts; (iv) Geological stocks; (v) Future demand; and (vi) Criticality. Gathering information of those six areas of concern is considered as a prerequisite to develop effective policies for managing metal resources in a sustainable way. A growing body of knowledge related to those issues has already been developed. Information on societal stocks and flows of several metals – forming the so-called "anthropogenic metal cycles" – has been generated at various geographic scales, usually using the Material Flow Analysis methodology (MFA). With regard to environmental issues related to the production, use and disposal of metals, a large amount of literature has been developed in the field of environmental sciences. Furthermore, various governmental bodies, research institutions and NGOs have conducted studies on the criticality of different metals. However, important knowledge gaps exist for many metals, and existing information is dispersed and of varying quality and completeness.

This thesis proposes a contribution to this field of research by focusing on antimony, a metal about which surprisingly little is known in regards to the six research areas identified by the IRP, although it has been identified as both toxic and critical. This report presents the thesis research results.

1.2 ANTIMONY

1.2.1 PROPERTIES & SOURCES

Antimony (Sb), 51st element of the periodic table, is a shining silvery-white, brittle and crystalline semi-metal (or metalloid)[1]. Unlike typical metals, it is not malleable but hard and brittle, and can be crushed into a powder. Antimony is a poor conductor of heat and electricity. Its melting point is relatively low, at 630.6°C, and its common oxidation states are +5, +3, 0, and -3. Antimony is usually included in the list of heavy metals.

Antimony can be considered as a rare element with a crustal abundance of about 0.2 ppm, close to that of indium and cadmium. As its Greek etymology suggests, antimony – from "anti-monos", which can be translated into "not alone" – is rarely found in its native form. It is usually mixed with other elements in over 100 different mineral species, of which the principal source of mining is stibnite (Sb_2S_3) that gave antimony its chemical symbol. Antimony minerals tend to concentrate in sulfide ores along with copper, lead, and silver (Grund and colleagues 2011). With current prices and technologies, an ore grade of about 3% Sb is required to be economically extracted and smelted (Schwarz-Schampera 2014). Commercial ores are only found in significant volumes in a limited number of countries, the most important being China, Russia, Bolivia, Myanmar, Thailand, South Africa, Tajikistan and Kyrgyzstan. The world's largest antimony deposit is found in the Xikuangshan, near the city of Lengshuijiang in the Chinese Hunan province, where about 60% of the global primary supply originated in 2011 according to the U.S. Geological Survey (2012). Antimony deposits fall into two broad categories (Butterman and Carlin 2004): (i) Simple deposits consisting mainly of antimony-bearing minerals (mostly stibnite) with small quantities of other metallic minerals. Some of the world's largest sources of antimony are of this type, including top-producing mines in China, South Africa, Russia and Bolivia, where antimony is the main product. Valuable co-products can also be extracted, such a gold in the Consolidated Murchison mine in South Africa; (ii) Complex deposits containing mixtures of antimony (mostly sulfide) minerals and sulfosalts of iron, copper, lead, mercury or silver. In mines exploiting this type of deposits, antimony is generally a co-product. Complex deposits are the source of most antimony produced in Australia, Canada and the USA, as well as some of the Chinese production.

In 2014, about 160 Gg (thousand metric tons) of antimony were mined worldwide according to the U.S. Geological Survey (2015). With an estimated share of 80%, China was by far the largest producer of primary antimony, followed by Myanmar (6%), Russia (4%), Bolivia (3%), Tajikistan (3%) and South Africa (2%). In terms of reserves, China accounts for 52% of the total (1840 Gg), followed by Russia (19%) and Bolivia (17%). At the level of mine production in 2014, the world identified reserves would be used up in 12 years.

1.2.2 EVOLUTION OF DEMAND, SUPPLY AND PRICES

Antimony has been known and used as far back as the fourth millennium B.C. In the Antiquity, stibnite was used to produce "kohl", a thick black paste traditionally used as an eye cosmetic by Egyptian queens and noble women. Its use then spread in other African countries and in Asia. Antimony has also been used throughout the ages for medicinal purposes and particularly as a laxative. Ingested orally, this toxic heavy metal is violently rejected by the body, providing an unhealthy albeit effective cure for the chronically constipated. Reusable antimony pills and cups intended to induce therapeutic sweating, vomiting, and

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[1] Although antimony is strictly speaking a semi-metal, the term "metal" is used in this report.

[2] LC_{50} is the median lethal concentration, i.e. dose required to kill half the members of a tested population within 96

purging were popular in the 17th and 18th centuries (Tylenda and Fowler 2007). Reportedly, antimony drugs cured the King Louis XIV of France from typhoid fever (Cooper and Harrison 2009), whereas some believe that Mozart, an hypochondriac, died from abusing antimony medicines (Kean 2010).

In the Middle Ages, antimony became an object of fascination for alchemists who called it the “Black Dragon”. Isaac Newton, who wrote more on alchemy than on any other subject, became obsessed with the metallic form of antimony, which was called “regulus” by alchemists (meaning prince or little king) and whose crystalline structure evokes a bright silver star when the ore is heated in specific conditions (Dobbs 1983).

Because of its brittleness and lack of malleability, antimony is rarely used as a metal by itself. But as an alloying agent, it hardens and strengthens a variety of alloys, the most used being lead- and tin-based. Antimony has thus been used as an alloy for centuries in type metal (with tin and lead), Babbitt metal (with tin and copper) used in bearings, and in Britannia metal (with tin and copper) used in utensils and tableware.

Until the end of the 19th century, the number of uses for antimony and the amounts used remained small (Butterman and Carlin 2004). Demand took off in the early 20th century with the increasing use of the lead-acid batteries, whose (lead) plate grids were strengthened with the addition of antimony, and the use of antimony in artillery to harden lead ammunition.

Global primary production of antimony has increased twentyfold since the beginning of the twentieth century (Figure 3). About 7800 Gg of primary antimony has been produced since 1900, half of which since 1980. Production levels have fluctuated considerably according to technological, political, economic and demographic developments. The dramatic surge in demand for lead ammunition during the First World War translated into a peak in antimony production. In the following years, the development of the automobile industry created a demand for antimony-containing lead-acid batteries that slightly declined during the early years of the Great Depression. With the build-up of the Second World War, antimony production began to rise again and peaked in 1943 as a result of its use in ammunition as well as in lead-acid batteries for military vehicles and flame-retardants for military textiles (Butterman and Carlin 2004). Antimony does not provide flame-retarding properties by itself, but its oxides (mainly the trioxide) function as a synergist in combination with halogenated flame retardants, providing together a widely used and very effective flame-retarding system for plastics, textiles, and other inflammable materials.

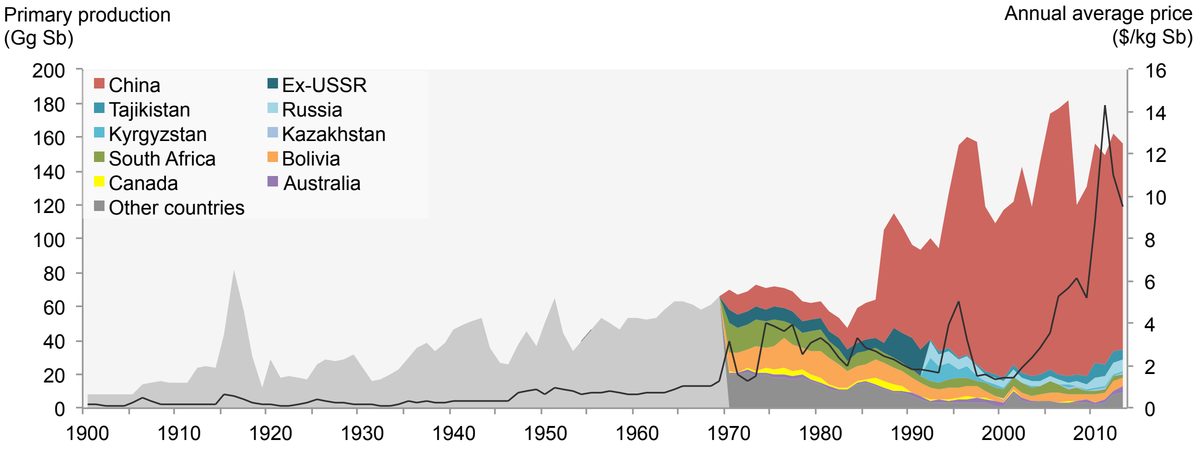


Figure 3: Global primary antimony production and nominal prices, 1900-2013 (U.S. Geological Survey 2014a; British Geological Survey 2015; Metalprices.com 2015).

Since the 1950s, lead-acid batteries and flame-retardants have remained the main applications for antimony and trends in those sectors have heavily influenced antimony demand and therefore primary production.

Lead-acid battery manufacturers began to replace antimony in grids with calcium in the 1970s, leading to a decrease in the demand for antimony. This technological development was due to the identification of two major drawbacks in the use of antimony as an alloying element in the battery grid. First, during discharge antimony tends to migrate from the positive to the negative plate, where it lowers hydrogen overvoltage and therefore accelerates the breakdown of water in the electrolyte. This increases the need for maintenance through regular addition of water. A second disadvantage is that antimony also deposits on the negative plate, which causes the self-discharge of the battery at a rate of up to 1% per day (Carlin 2006). As a result, manufacturers developed "low-maintenance" and "maintenance-free" batteries in which antimony is, respectively, partly or completely substituted by calcium in the grid plate. The average antimony content in lead alloys used in lead-acid batteries decreased from 8-12% in the 1960s to 0.5-3% nowadays (Linden and Reddy 2002; Grund and colleagues 2011). The decreasing antimony content in lead-acid batteries has however been, to an extent, offset by the global growth in demand for lead-acid batteries. As a result, lead-acid batteries still constitute the second largest end-use for antimony (Roskill 2011).

The development of strict fire safety regulations in recent decades fostered the use of flame retardant chemicals, including the use of antimony trioxide (ATO) as a synergist with halogenated flame retardants. This end-use is responsible for much of the tripling in antimony production since the mid-1980s and flame retardants now account for about half of the global antimony consumption (Roskill 2011). It is mainly used in the polymer sector and added to various thermoplastics (e.g. PVC, PP, PE, PS, ABS, PU, PBT), which are widely used in electrical and electronics parts (e.g., housings, cable insulation and printed circuit boards). Flame retardants used in textiles, rubber, paints and adhesives also use significant quantities of antimony compounds. Whether the use of antimony in flame retardants will increase or decrease in the future depends heavily on political and technological factors. On the one hand, increasing concerns in recent years over health and environmental risks of halogenated flame retardants and antimony have resulted in stricter regulations for several compounds in Europe and North America and fostered substitution to alternative flame-retarding compounds containing no antimony. On the other hand, more stringent fire safety regulations in the developing world could increase the demand for antimony-containing flame retardants.

Nowadays, flame retardants and lead-acid batteries together represent about 80% of the global antimony consumption (Roskill 2012). The remaining 20% is divided between the following applications:

- Metallurgical applications, using antimony as an alloying element: Lead alloys used in ammunition, rolled and extruded products, bearings, solders, type metals, etc., and tin alloys used as Babitt metal in bearings and as Brittania metal used in utensils and tableware. Small amounts of highly pure antimony metal are also used in the semiconductor industry.
- Non-metallurgical applications, using various antimony compounds: ATO used as a heat stabilizer in PVC, as a polymerization catalyst in the production of polyethylene terephthalate (PET), as a degasing agent in glass, and as an opacifier in porcelain enamels and pottery glazes. Sodium antimonate is used in the production of optical and CRT glass as a fining and degassing agent. Other minor non-metallurgical applications include pigments, brake linings, lubricants, pharmaceuticals, pesticides, fireworks and matches.

Secondary production of antimony is limited as antimony is mainly used in non-metallic products such as plastics, textiles, glass and ceramics, for which an adequate recycling infrastructure is lacking and global recycling rates are low. Recovered antimony comes mainly from the recycling of lead-acid batteries and, to a lesser degree, of other lead alloy products, and is usually reused in the same sectors. Some antimony may be unintentionally recovered through the recycling of plastic and glass products, although very little information exists on that matter. With the ongoing diminutions of antimony content and overall battery weight, secondary production of antimony could decrease in the future. According to Roskill (2012), secondary antimony production amounted to about 38Gg in 2011, which represents about 20% of the total supply assuming a primary production of 156Gg as given by the British Geological Survey (2015).

As visible in Figure 3, antimony prices fluctuated significantly in the last decades. In the late 1960s, demand for antimony in plastic products increased strongly, pushing up the prices. A few years later, supply restrictions in China combined with a high demand provoked another peak (European Commission 2014a). In 1994, floods in Chinese antimony mining regions caused interruptions in production and delays in shipping, leading to a surge in prices (Carlin 1995), which resulted in the multiplication of illegal exploitations in China (BRGM 2012) and eventually to an oversupply situation droving down the prices. Prices started to increase again in 2002, after the closure of several small and illegal exploitations in the Guangxi province following fatal flooding accidents in the Nandan mining region, where more than 80 people have died (Masters 2005). Between 2004 and 2008, antimony prices increased due to a growing global demand and the rapid depletion of high-quality Chinese deposits (Li 2013). Demand dropped with the Global Financial Crisis, leading to a decrease in prices in 2009. In March of the same year, the Chinese government's announced the introduction of production and export quotas, a freeze in granting of exploration and mining licenses, and a crackdown on small miners and smelters. This provoked the tripling of antimony prices within a year, peaking at 18$/kg in March 2011. With the outbreak of the European debt crisis in June-July, antimony prices started a decline that is still ongoing. At the end of February 2015, antimony prices were down to 7.7$/kg Sb, nearing their 2008 levels (Metalprices.com 2015).

1.2.3 CRITICALITY

The assurance of an adequate supply of raw materials at reasonable costs is of prime importance for many economic sectors. Supply disruptions and bottlenecks, and ensuing price surges are a great source of anxiety for enterprises and governments. The issue is particularly concerning in countries with small domestic raw materials reserves and production, depending strongly on imports to secure their supply, which is the case of most industrialized nations.

Over the past decades, natural resources extraction has strongly increased, with metals showing the highest growth rate, largely as a consequence of rapid industrialization in countries such as China and India (Behrens and colleagues 2007). Technological developments have also fostered the extraction of an increasingly large variety of metals with very specific properties (i.e. specialty metals), the supply of which is often concentrated in a few countries and controlled by a few companies, leading to oligopolistic markets.

In this context, the concept of criticality has emerged to quantify economic vulnerabilities due to insecure raw material supplies. Numerous attempts to assess the criticality of raw materials have been carried out in the past decade by governmental bodies, research institutions and private companies (extensive reviews by Erdmann and Graedel (2011), Speirs and Gross (2013) and Glöser and colleagues (2015)). Different criticality assessment methodologies have been developed, often resulting in different criticality hierarchies among raw materials. Many studies employ a "criticality matrix" defining criticality as the product of likelihood of supply disruptions (i.e., supply risk) and their economic consequences (i.e., vulnerability to supply disruptions), with different indicators used to quantify both dimensions. Other studies include additional dimensions, such as environmental implications.

Antimony has been identified as one of the most critical raw materials in several studies. In 2007, a German study on the "rarity" (measured by six criteria including price increase, scarcity of reserves, and concentration of supply) of metals used in electrical and electronic equipment (EEE) ranked antimony the second "rarest" after indium (Behrendt and colleagues 2007). In 2008, Oakdene Hollins (2008) published a study mandated by the British government on the "insecurity" of materials (eight criteria including geological scarcity, supply concentration, political instability in top-producing countries, and substitutability), ranking antimony as the seventh most "insecure" metal. In 2010, the German Geological Survey published its raw material risk assessment for antimony (BGR 2010). In 2011, researchers from the IZT institute assessed antimony as the third most critical raw material for Germany, after germanium and rhenium (Erdmann and Behrendt 2011). In the same year, antimony topped the "supply risk index" published by the British Geological Survey (2011), and it was ranked third after the rare earth elements and tungsten in the 2012 update (British Geological Survey 2012). Antimony was assessed as the third most critical raw material for the European Union in the latest report by the European Commission (2014b). Finally, antimony obtained the eighth highest combined score of all metals included in the criticality assessment of 62 metals and semi-metals conducted by Yale University researchers (Graedel and Nuss 2014; Graedel and colleagues 2015). Figure 4 presents the results of studies by the German Geological Survey (a), IZT researchers (b), Yale researchers (c) and the European Commission (d).

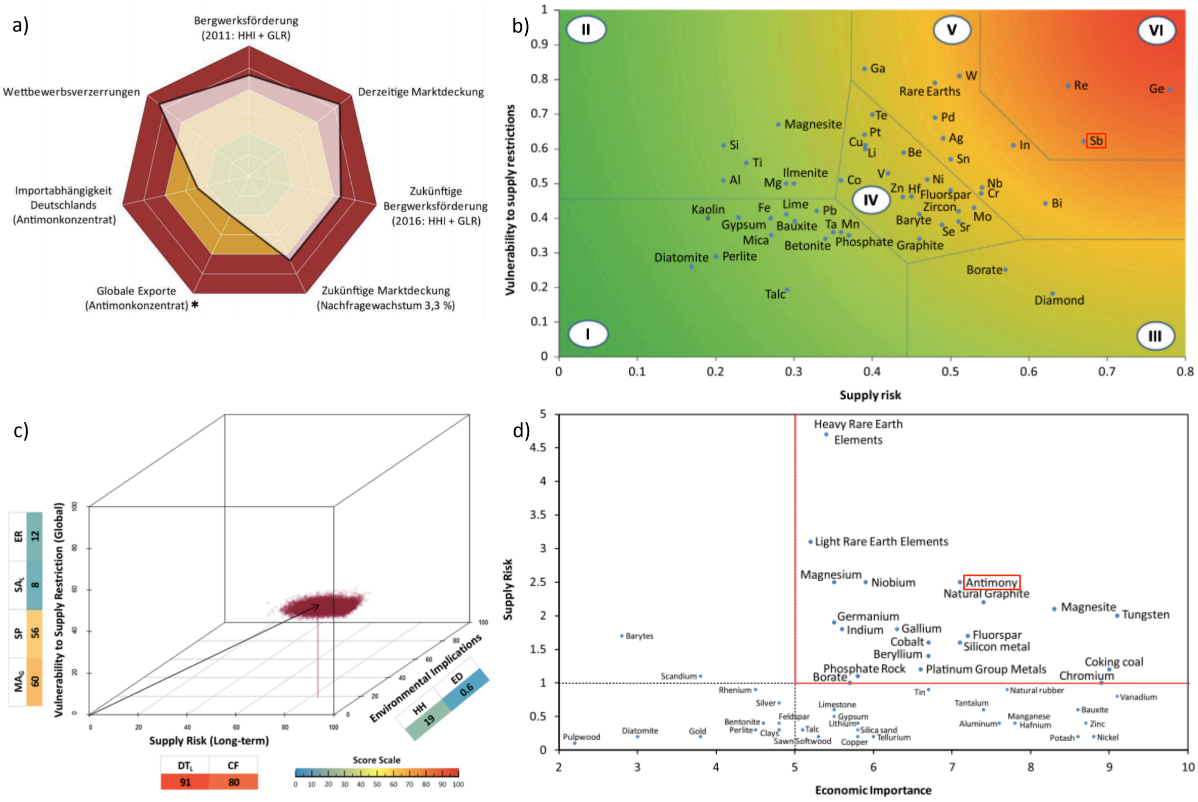


Figure 4: Antimony criticality studies

Legend: a) Raw material risk assessment for antimony conducted by the German geological survey (BGR 2010). (Zukünftige) Bergwerksförderung=(future) primary production; HHI=Herfindahl–Hirschman Index (indicator of country concentration); GLR=weighted country risk; Derzeitige/Zukünftige Marktdeckung=current/future market balance, Globale Exporte=global exports (diversity of exports from Germany), Importabhängigkeit Deutschlands=import dependence of Germany, Wettbewerbsverzerrungen=distortions of competition. b) Report on critical raw materials for Germany (Erdmann and Behrendt 2011). c) Criticality assessment conducted by Graedel and Nuss (2014). DTL=depletion time, long-term perspective; CF=companion metal fraction; HH=human health damage; ED=ecosystem damage; MAG=material assets; SP=substitution potential; SAL=substitute availability, ER=environmental impact ratio. d) Report on critical raw materials for the European Union (European Commission 2014b). Note that the axes are inversed compared to the matrix from Erdmann and Behrendt (2011).

A review of those six studies reveals that the criteria contributing the most for high criticality scores were related to the supply risk dimension. In particular, the high concentration of primary supply and reserves in China, combined with relatively low scores for governance indexes (as given by the World Bank, 2014), as well as the low reserves-to-production ratio contributed the most to a high ranking for antimony in all criticality assessments. Other factors contributed to high supply risk, such as low global recycling rates (included and estimated at <5% in the BGR assessment, and at 10% in the Yale study), and high price volatility (included only in the study by Behrendt and colleagues). Factors related to the vulnerability to supply disruptions dimension were generally less decisive for the criticality of antimony. The most relevant factors in this dimension were the limited substitutability of antimony in some applications and the high gross value added of main antimony-consuming economic sectors (chemicals, transportation, metals). Only Graedel and Nuss (2014) included environmental implications in the criticality assessment. They calculated human health and ecosystem damage scores related to antimony production and refining (i.e., cradle-to-gate) using the ecoinvent database (Classen and colleagues 2009) and the ReCiPe endpoint method (Frischknecht and colleagues 2007). The resulting weighted score was in the medium range compared to other metals assessed by Yale researchers (Graedel and colleagues 2015). As far as the author is aware, no criticality assessment methodology includes environmental implications related to latter stages of the metals' lifecycle (e.g. energy use and emissions during manufacture, use and waste management processes).

1.2.4 ENVIRONMENTAL AND HEALTH ASPECTS

Antimony is a heavy metal whose toxicological behavior is often compared to that of arsenic (Grund and colleagues 2011), although it is much less toxic (Tylenda and Fowler 2007). Antimony and its compounds are considered to be hazardous to human health and are classified as possibly carcinogenic by the International Agency for Research on Cancer (IARC 1989). Respiratory irritation, dermatitis, pneumoconiosis and gastrointestinal symptoms have been reported in workers in the antimony processing industry (Sundar and Chakravarty 2010). Furthermore, inhalation exposure to ATO produced lung cancer in female rats (Cooper and Harrison 2009). Antimony compounds are identified as pollutants of prime interest by the U.S. Environmental Protection Agency and the European Union, and are included in the list of hazardous substances under the Basel Convention (Filella and colleagues 2002). Yet, relatively little is known on the extent of global antimony pollution and its impacts on human health and ecosystems.

Antimony is naturally emitted into the environment as a result of volcanic eruptions, erosion of antimony-bearing rocks and minerals, soil runoff, forest fires and sea salt spray. Human activities are also a major source of emissions, which may originate in intentional applications, i.e. purposely using antimony for its intrinsic properties (antimony end-uses), or non-intentional applications, i.e. arising from the natural occurrence of antimony in fossil fuels, other metal ores, etc. Emissions from intentional applications occur through the mining, smelting and refining of antimony ores as well as during manufacture, use and disposal of antimony-containing products. In particular, high concentrations of antimony have been observed in soils, air and water surrounding: industrial areas where Sb is extracted, refined, or used for the manufacture of products; high-density traffic areas due to the abrasion of antimony-containing brake linings; and shooting ranges due to the use of antimonial lead ammunition (EU 2008a). Non-intentional emissions result from the production, use and disposal of other resources in which antimony occurs as a contaminant, mainly through mining and smelting of metal sulfide ores (especially Cu, Zn and Pb), combustion of fossil fuels (mainly coal), and incineration of municipal solid waste (Nriagu and Pacyna 1988). Most antimony emitted to the environment eventually ends up in soils where it attaches to minerals or compounds containing iron, aluminum or manganese and remains rather immobile due to the low solubility of most antimony compounds (EU 2008a). Although antimony has no known function for biological organisms, it can be readily taken up by plants and therefore enter the food chain (Okkenhaug and colleagues 2011). Humans are exposed to antimony through the use of antimony-containing products as well as through contact with contaminated air, food and water.

Concerns over the potential of antimony pollution to cause harm to humans and other living organisms have lead environmental agencies of the European Union, Canada and the USA to conduct risk assessments (EU 2008a; Environment Canada 2010; U.S. EPA 2014). The three studies focused on ATO, i.e. the most used form, and reached similar conclusions. Overall, human health risks associated with exposure of the general population to ATO in products and in the environment were considered too low to adopt additional risk reduction measures. Harm to aquatic and terrestrial organisms exposed to ATO was considered as unlikely, although considerable uncertainties in this area were acknowledged. Few studies assessed the risks related to exposure to other forms of antimony such as metallic antimony used in alloys or antimony trisulfide used in brake linings and lubricants, although those substances are used in dissipative applications.

Despites concerns, studies on the health and environmental impacts of antimony have so far not justified restrictions on the use of antimony in products. In several OECD nations, industrial actors have however adopted a precautionary approach and reduced or eliminated the use of antimony in PET, flame retardants, heat stabilizer, alloys, glass, ceramics and other products. Furthermore, stricter regulations and environmental concerns have indirectly impacted the use of antimony in some of its main end-uses because of the adverse health and ecological effects of substances used in conjunction with antimony, such as lead and halogenated flame retardants. The use of lead in many non-battery products has been progressively reduced or eliminated in industrialized countries since the 1980s (UNEP 2010b), and lead-free alternatives do not contain antimony. Due to their toxicity and persistence in the environment, several halogenated flame retardants have been banned or restricted in Europe and phased out in other regions. Halogen-free flame retardants – mainly inorganic-, phosphorus based-, and nitrogen-based compounds – are also antimony-free.

1.3 PROBLEM DEFINITION

Antimony (Sb) is a rare metal that has been used for millennia, for various products and under diverse forms. As it is the case for most raw materials, the use of antimony has strongly increased during the last century as a result of growing levels of population and affluence as well as of technological developments. Nowadays antimony is mostly used as a synergist in halogenated flame retardants and as an alloying element in lead-acid batteries. Sb is also used as a heat stabilizer and catalyst for plastics, and as a hardener in lead alloys used in ammunition, pipes and sheets, solders and bearings. Over the past decade, concerns have been raised over both the risk of supply disruptions for the economy and the risk of exposure to antimony for human and environmental health.

Primary supply of antimony is heavily concentrated in China (80% of world total), whose government implemented over the last few years a number of policies to tighten its control over the production and exports of antimony with the alleged purpose of conserving dwindling reserves and limiting environmental damage from mining. As a result antimony prices have sharply risen, starting below 2$ per kilogram in the early 2000s and peaking at 18$ per kilogram in 2011. Secondary supply is limited as antimony is mainly used in non-metallic applications lacking an adequate recycling infrastructure. Secondary antimony comes mostly from the recycling of lead-acid batteries. Widespread use coupled with constraints on primary supply and limited secondary supply led to the identification of antimony as one of the most critical raw materials in several studies (Behrendt and colleagues 2007; Oakdene Hollins 2008; BGR 2010; Erdmann and Behrendt 2011; British Geological Survey 2011; European Commission 2014b; Graedel and colleagues 2015).

Besides those economic preoccupations, concerns have been expressed regarding antimony's potential to harm humans and other living organisms. It is a toxic element with demonstrated harmful effects on human skin and lungs and suspected carcinogenicity. Exposure to antimony also represents a hazard for aquatic and terrestrial organisms, although knowledge on that matter is limited. Thus, the release of antimony to the environment during production, use and disposal processes is worrisome. Antimony compounds are identified as pollutants of prime interest by U.S. Environmental Protection Agency and the European Union, and are included in the list of hazardous substances under the Basel Convention.

Despite these problematic issues, little is known on the flows of antimony entering, circulating within and leaving the anthroposphere – i.e., the anthropogenic antimony cycle. Yet, this information is crucial to assess the criticality of antimony on the one hand, and the potential harm to humans and ecosystems engendered by losses of antimony to the environment on the other. Indeed, criticality essentially refers to the potential of future mismatches between supply and demand. Those are physically interconnected by material flows. Moreover, hazards to humans and other species depend, in part, on the magnitude of antimony flows from the anthroposphere to the biosphere.

Stemming from this problem definition, research aim, questions and scope are presented in the next section.

1.4 RESEARCH AIM, QUESTIONS AND SCOPE

This thesis aims to provide a first systemic picture of the global anthropogenic antimony cycle, explore its possible future development (at the 2050 horizon), and investigate its associated environmental impacts. In order to reach this threefold aim, the main research question is formulated as follows:

What characterizes the current and possible future global anthropogenic antimony cycle, in terms of supply, demand and environmental impacts?

This broad research question can be divided into the following sub-questions:

Regarding the current anthropogenic antimony cycle;

1. What is the system-wide material efficiency of the cycle? (How circular is it?)
2. What is the size of current in-use stocks?
3. How much antimony is lost to the environmental throughout the cycle, and in which environmental compartments? (How permeable is it?)
4. What are the environmental impacts associated with the cycle?

Regarding the future anthropogenic antimony cycle;

5. What are the trends in demand?
6. What is the outlook on primary and secondary supply?
7. How critical is the future antimony cycle according to different supply-demand scenarios?
8. How can associated environmental impacts be reduced in the future?

Given the limited time for this thesis research project and the broad geographical system boundaries (i.e., the world), answers to these questions are constrained. Hereafter, the main scope limitations of the study are given:

- This thesis focuses on the anthropogenic part of the global Sb cycle. Furthermore, non-intentional Sb flows – i.e., caused by forces other than the demand or need for Sb itself – are not accounted in the modeling. They are however included in the discussion.
- Due to the lack of transparency in the Sb supply chain, the insufficient disaggregation of available data, and the information gaps for large segments of the global Sb cycle, the accuracy of the information generated in this study cannot be guaranteed. It is however believed that this study makes uses of the best currently available options to characterize the global anthropogenic Sb cycle.
- By definition, it is not possible to provide accurate answers to sub-questions related to the future of the Sb cycle. Rather, a limited set of possible scenarios is generated, and their significance with regard to potential supply and environmental risks is discussed and compared.
- Regarding Sb losses into the environment, only first-order emissions are accounted. This means that the ultimate fate of Sb emissions in the environment is not modeled. This, coupled with the low spatial aggregation used in this study, renders a thorough environmental risk assessment unfeasible. Rather, a semi-quantitative analysis of the potential harm to humans and other living organisms is performed.

1.1 APPROACH & REPORT STRUCTURE

The research approach is visualized in Figure 5.

Prior to addressing the research sub-questions, an overview of the conceptual and methodological frameworks in which this research is grounded is given, respectively in Chapters 2 and 3. Conceptually, this study draws on the notion of industrial metabolism (Section 2.1), which considers the economy in terms of the flows of materials and energy entering, circulating within, and leaving the sphere of human activities (i.e., the anthroposphere). This approach is useful to gain a better understanding of societal uses of natural resources and related environment impacts. Another essential backdrop to this study is the debate over the scarcity of metal resources and its consequences for the economy. Within this debate, the notion of criticality has emerged in recent years. It denotes metals at relatively high risk of supply disruption and high importance for the economy (Section 2.2). Methodologically, this study employs Material Flow Analysis (MFA) to model the global stocks and flows of antimony in the anthroposphere (Section 3.1) and borrows notions from the Life Cycle Assessment (LCA) method to assess environmental impacts associated with the global anthropogenic antimony cycle (Section 3.2). An overview of previous studies combining MFA/LCA is given in Section 3.3 and the stepwise methodology used for this study in presented in Section 3.4.

Chapter 4 describes the static MFA model used to create a systematic picture of the current global anthropogenic antimony cycle, from ore extraction through manufacture, use, and disposal of antimony products. Relevant substances and processes are identified, and mass flows within and between each lifecycle stage are estimated for the year 2011 based on available data and assuming a steady-state situation (input=output for each lifecycle stage). This “snapshot” allows for a first assessment of the circularity (how much is recycled) and permeability (how much is lost to the environment) of the current global anthropogenic antimony cycle. The static model serves as a basis for dynamic analyses which are presented in Chapter 5. A dynamic MFA model is used to model the evolution of global antimony stocks and flows between 1900 and 2050. First, a retrospective analysis is performed to reconstruct past inflows to and outflows from use, resulting in a characterization of the current Sb cycle, including an estimation of in-use stocks (Section 5.2). A prospective approach using different demand scenarios is then used to simulate the development of the antimony cycle until 2050 (Section 5.3). Subsequently, the outlook on supply is investigated and possible future supply-demand mismatches are discussed (Section 5.3.5). Together, results of Chapters 4 and 5 provide the answers to sub-questions 1-3 and 5-7.

Sub-questions 4 and 8 are addressed in Chapter 6, where insights offered by the MFA models are combined with information on lifecycle environmental impacts of antimony. Current and possible future environmental impacts of antimony are investigated with a double focus on the energy demand of primary and secondary antimony production (Section 6.1), and on the toxicity potential of antimony releases to the environment (Section 6.2).

In Chapter 7, results are discussed, their validity is assessed, and reflections are given. Finally, in Chapter 8, conclusions are drawn, and recommendations are given.

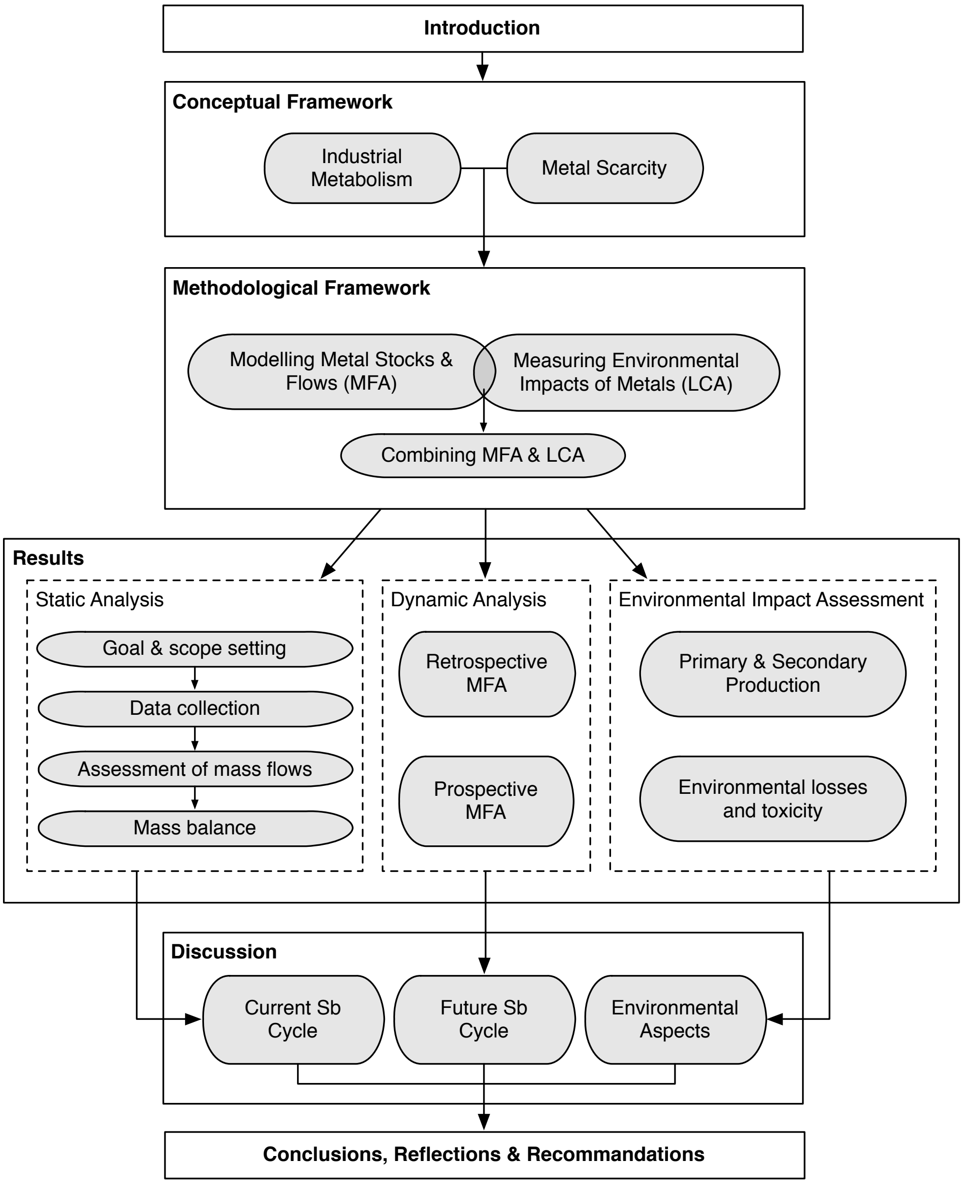


Figure 5: Research Approach

1.5 RELEVANCE OF THE RESEARCH

Answering the research questions raised in this thesis research project would provide useful information for a wide range of actors along the anthropogenic antimony cycle, in the industrial, political, academic, and financial realms.

Various industrial actors would benefit from a systematic and dynamic picture of the global anthropogenic antimony cycle. Primary antimony producers need to have an idea of how the demand for primary antimony can develop within the next decade due to the high lead time for mining projects (5-10 years). For manufacturers of antimony-containing products, early-detection of future supply restrictions and identification of environmental hazards are incentives for research and development of substitutes. Lastly, quantitative and qualitative projections of future waste streams are valuable for waste managers and recyclers.

Policy-makers involved in national and international resource security strategies are interested in detecting possible future resource constraints and assessing the recycling potential of scarce metals such as antimony. Furthermore, environmental protection agencies need to identify the sources of antimony pollution and quantify the emissions in order to assess human and ecological risks and implement protection measures.

In the academic sphere, this study fills a knowledge gap existing in the growing field of global metal cycles characterization, as no such characterization has been published for antimony so far. Furthermore, considerations of supply and environmental risks of antimony could be used in making material-related choices in product design. Initially, this study was commissioned by Empa to provide information on such risks in relation to the potential use of antimony nanocrystals in high-rate lithium and sodium ion batteries under research at ETH Zurich and Empa (He and colleagues 2014; Walter and colleagues 2015).

Consulting firms and investors in the commodity market might also be interested in such a study. Metals are increasingly bought for investment purposes, as the high volatility of their prices can be harnessed to rapidly increase wealth. Metal have an intrinsic value and their prices tend to increase in the long-term, so that the chance of gaining money appears higher than the risk of loosing some in the long-term. As a result of the steep increase in antimony prices between 2004-2011 and the restricted supply, this metal was seen as a particularly interesting investment metal (Bromby 2013; Topf 2013). Metal prices are determined by a number of factors related to the supply (itself governed by primary and secondary production capacity) and the demand (affected by substitution, technological developments, regulation, etc.). Several of those factors are included in the prospective MFA model, the results of which are therefore of prime interest for anticipating price evolutions.

2 CONCEPTUAL FRAMEWORK

This research draws on a set of basic ideas, assumptions and principles used to consider, understand and explain real phenomena. Those key concepts together constitute the conceptual framework in which this study is embedded and that provides its rationale. Hereafter, two central notions to this framework are presented; Industrial Metabolism and Metal Scarcity.

2.1 INDUSTRIAL METABOLISM

> 'Mankind's sphere of life, a complex technical system of energy, material, and information flows, is called the anthroposphere. It is part of planet Earth's biosphere. We think of the anthroposphere as a living system that evolves with its own history. In analogy to the physiologic processes in plants, animals, and ecosystems, the metabolism of the anthroposphere includes the uptake, transport, and storage of all substances, the total chemical transformations within the sphere, and the quantity and quality of all refuse' (Baccini and Brunner 2012).

Equivalent to the notion of "metabolism of the anthroposphere" used by Baccini and Brunner, the concept of industrial metabolism, as coined by Ayres (1989), draws on the analogy between the economy and the environment on a physical level. In this view, borrowing concepts to from the field of scientific ecology, the economy mobilizes, use and excrete materials to create 'technomass' similarly to the way ecosystems use materials to create biomass (Kleijn and colleagues 2000). Industrial metabolism therefore considers the economy in terms of the flows of materials entering, circulating within, and leaving the sphere of human activities (i.e., the anthroposphere). In contrast to mature ecosystems found in the billion years old biosphere and operating in a near-cyclical manner (i.e., "waste" generated by one organism becomes a resource for another), the economy can be considered as a young ecosystem characterized by a highly linear material functioning, low material recycling rates, and levels of resource extraction and waste generation that exceeds the regenerative and absorptive capacity of the biosphere. Developing strategies to "mature" the industrial ecosystem is core to the field of Industrial Ecology (Ayres and Ayres 2002).

The concept of industrial metabolism is operationalized through the application of the material balance principle (i.e., in its simplest form, input=output+accumulation), which is itself based on Lavoisier's Law of Conservation of Mass (i.e., in a closed system, mass can neither be created nor destroyed). This principle provides a mean to trace and understand the flows of materials linked to human activity, from their initial extraction through their societal use and, ultimately, their release into the environment. Material Flow Analysis (MFA) can be used to quantify these flows (see Section 3.1.2. for a description of MFA).

The industrial metabolism approach is therefore useful to obtain a better understanding of the societal uses of natural resources and their impact on the environment.

2.2 METAL SCARCITY

Another essential backdrop to this study is the debate over the scarcity of metal resources and its consequences for the economy. This section briefly presents the origins of the debate and its development under the concept of "criticality".

Metal ores can be considered as non-renewable resources, given that ore genesis – the process by which a deposit of ore is created, through plate tectonics, tectonic subsidence and crustal recycling – takes millions of years. The stark contrast between this natural, extremely slow process and the rapidly growing anthropogenic extraction of most metals has fueled concerns about metal resource depletion throughout the

20th century, often discussed within the larger debate of resource scarcity. First confined to the academic and political realms, the issue gained wide public attention with the publication of the 'Limits to Growth' study (Meadows and colleagues 1972), which argued, using a system dynamics model, that exponential growth of population, industrial activities and resource use would result in resource depletion and collapse of environmental quality by the middle of the 21st century. Shortly after, the 1973 oil crisis provided an evidence of the disruptive potential of resource scarcity for the global economy.

Metal scarcity received much attention during the first decade of the 21st century, with the "great metal boom" that ran from 2002 to 2008, during which the prices of many metals surged to unprecedented levels (Radetzki 2012). This boom in metal prices can be explained by the unusual strength of the demand – largely related to the rapid build-up of BRIC countries and especially China – and the lagged response of the mining and metals industry (Humphreys 2010). Metal prices dropped sharply in 2008, with the global economic slowdown. More recently, in 2009, the introduction of trade limits for rare earth elements (REE) by China – a country that produced at that time about 97% of the global primary supply and about 90% nowadays – caused the skyrocketing of REE prices. Those dropped in 2012 as a result of an increased supply from other countries, especially the USA and Australia. It is noteworthy that the conduct by China of a similar policy in the case of antimony resulted in comparable price hikes, although this issue received much less attention from scientists, policy makers, and media.

Price surges and supply constraints raised concerns over the supply risk of metals. In recent years, many governmental organizations, research institutes and other NGOs issued reports dealing with metals scarcity and its impact for the economy. Specifically, the "criticality" of different metals was addressed in numerous publications (e.g. Behrendt and colleagues 2007; Oakdene Hollins 2008; Angerer and colleagues 2009; Rosenau-Tornow and colleagues 2009; U.S. DOE 2011; Öko-Institut 2009; Achzet and colleagues 2011; British Geological Survey 2012; European Commission 2014b; Graedel and colleagues 2015). Although the definition of criticality differs among studies, the concept is usually used to denote materials that combine high economic importance and high risk of supply disruptions. It is a relative concept, in the sense that a metal is not critical by itself but to an actor (e.g. company, economic sector, country, group of countries) and over a certain time-horizon. Criteria to assess the criticality of a given metal differ from one study to another but are generally related to supply factors (including geological availability, supply concentration, geopolitical risk, recycling, etc.) and demand factors (e.g. added value of main consuming sectors, demand growth and future demand projections, substitutability). Some methodologies also include environmental aspects that can be for instance assessed in terms of the impacts of the metal's production on human health and ecosystems, according to life cycle inventories and impact assessment methods.

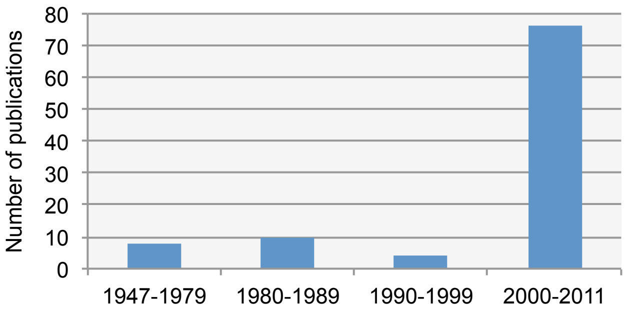


Figure 6: Publications on material criticality (data from Speirs and Gross 2013)

As shown in Figure 6, although the number of criticality studies considerably increased in the period 2000-2011, they have existed since the 1940s with similar underlying concerns, criticality assessment methodologies, and general conclusions, but a changing list of metals identified as critical (Kleijn 2012; Buijs and colleagues 2012).

Without common criticality definitions and assessment methodologies, the multiplication of studies has contributed to a general fuzziness surrounding the criticality concept and has fueled discussions as to whether or not a particular metal is critical, considered as 'sterile arguments' by the science director for minerals and waste at the British Geological Survey (Bloodworth 2014). Furthermore, mineral criticality studies suffer from a number of limitations (Erdmann and Graedel 2011; Polinares 2012a; Buijs and colleagues 2012; Knoeri and colleagues 2013):

1. Criticality studies typically provide a "snapshot" in time using static indicators and fail to account for dynamic changes in supply and demand. They therefore lack of predictive power beyond the short-term, and fail to distinguish between short-term and long-term problems. In fact, most of the minerals historically identified as critical have never caused significant problems for economic sectors and national economies;
2. By applying the same methodology for all minerals, they overlook the diversity and specificities of analyzed resource supply and demand systems. Furthermore, the necessity of a common database for the comparison of a large number of minerals prevents the consideration of factors that may be highly relevant but lacking a comparable database (e.g. recycling potential, emerging uses, cradle-to-grave environmental impacts);
3. They are often biased towards technology minerals, which are typically used in small quantities and for very specific applications, making price volatility and producer dominance much more likely but not necessarily problematic;
4. They tend to overstate the economic impacts of a possible supply disruption of "critical" minerals. Although they are widely used in the energy, ICT and electronics, and transport sectors, the fact that very small quantities per product are often used limits the impact of price hikes. Actual physical shortages and lack of supplies could have severe economic consequences, but strong prices increases generally result in increased supply (through increased primary and secondary production) or decreased demand (through substitution or increased efficiency) before serious problems arise.
5. They focus exclusively on risks related to the mining and export of raw materials, but disregard the rest of the supply chain (e.g. refining, transport, and trade in semi- finished-products).

To overcome these limitations, Bloodworth (2014), believes that 'a more holistic approach is needed', considering the issues of metals supply risks, low recycling rates, and environmental impacts 'as part of a one system that need to be wholly understood' through 'measuring technology-metal stocks and understanding how they flow through the whole supply chain — from mining to concentration, extractive and process metallurgy, manufacturing, use, reuse, recycling, dispersal and disposal'. The need to improve the understanding and quantification of the dynamic stocks and flows of critical metals has been highlighted in various studies (e.g., European Commission, 2014a; Knoeri et al., 2013; Polinares, 2012a; UNEP, 2010b; Patrick Wäger, Lang, Wittmer, Bleischwitz, & Hagelüken, 2012).

3 METHODOLOGICAL FRAMEWORK

Most environmental problems can be regarded as the result of unsustainable material circulation patterns through the economy. Resource depletion, climate change and pollution are different symptoms of the same fundamental issue: We, humans, extract natural resources and emit wastes at a rate that the planet cannot sustain.

With the growing awareness of environmental problems came a rising need to measure the pathway of material and substances through the economy and the emissions to the environment. Different methodologies have been developed, for various goals and with different strengths and shortcomings. Among them, Material Flow Analysis (MFA) and Life Cycle Assessment (LCA) stand out as widely used analytical tools for measuring economy-environment interactions. They both belong to the emerging field of Industrial Ecology.

3.1 MODELING METAL STOCKS AND FLOWS

3.1.1 INTRODUCTION

Metals are matter and are at such subject to the principle of mass conservation. Metal atoms extracted from the biosphere to be used in our technosphere (or anthroposphere) will eventually return to the environment. Some of them will remain "trapped" in our infrastructure and products for periods of time that can go from anything from a few days to millennia. Flows and stocks of metals within the technosphere – so-called anthropogenic flows and stocks of metals, originating in human activity – have been studied for decades. Material Flow Analysis has emerged as a methodology of choice for this purpose.

3.1.2 MATERIAL FLOW ANALYSIS

Definitions

According to Brunner and Rechberger (2004), Material Flow Analysis is a systematic assessment of the flows and stocks of materials within a system defined in space and time. The term "Substance Flow Analysis" can be used when the focus is on a single substance or group of substances.

MFA modeling is based on input-output analysis as developed by Leontief (1966) who wanted to 'describe economic reality as closely as possible' using a mathematic model of economy-wide flows between different sectors, expressed in monetary terms. MFA essentially uses a similar approach but consider the economy in its physical dimension, as described by Ayres (1989) with the concept of Industrial Metabolism' (Section 2.1). In this approach, materials flows entering, circulating within, and leaving a physical entity (e.g. a country) are systematically accounted, balanced by conservation of mass and expressed in physical units (e.g. tons). Such an analysis can be performed at different scopes, ranging from including the flows of all materials within a system (so-called "bulk MFA") or focusing on the flows a specific substance (e.g. a metal) through a system (Substance Flow Analysis). MFA can be used for different purposes, ranging from identifying the sources of regional pollutions (e.g. van der Voet 1996) to measuring the resource efficiency of a nation (e.g. Hammond and colleagues 1997).

A distinction is commonly made between static/steady-state and dynamic MFA studies. A MFA model is static if it describes a "snapshot" of a system at a certain point in time, usually a year. It is dynamic if it characterizes the evolution of a system over a time interval. The main difference between static and dynamic models is that the latter include stocks within society (van der Voet 2002). Those play an important role in determining future waste streams from discarded products and emissions to the environment. Combined with scenario analysis, future changes in stocks and flows can be assessed.

Stepwise MFA Methodology

Brunner and Rechtberger (2004) describe a generic stepwise MFA procedure (Figure 7):

1. Problem definition and goals setting;
2. Definition of system boundaries (spatial and temporal) and selection of relevant substances, processes and goods;
3. Assessment of mass flows of goods and substance concentrations in these flows;
4. Calculation of substance flows and stocks through mass balancing and evaluation of uncertainties;
5. Results intepretation and presentation in an appropriate way to visualize conclusions and facilitate implementation of goal-oriented decisions.

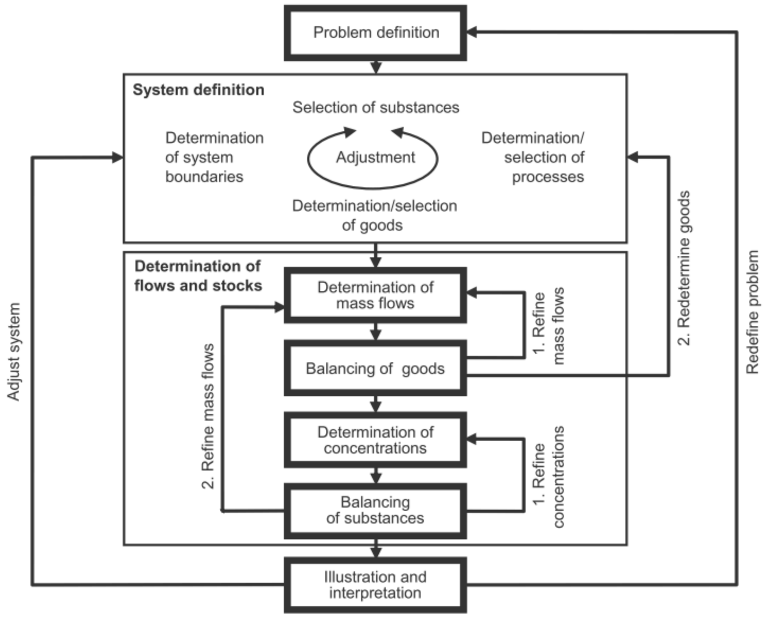


Figure 7: Step-by-step MFA procedure (Brunner and Rechtberger 2004)

As illustrated by the feedback loops, an MFA model has to be optimized iteratively. The authors note that it is in general ‘best to start with rough estimations and provisional data, and then to constantly refine and improve the system and data until the required certainty of data quality has been achieved’.

The determination of mass flows is carried out by gathering data from different sources, including direct measurements, governmental databases, scientific literature, company information, experts’ judgment, educated guesses, etc. They have different levels of accuracy and are rarely accompanied by information on their uncertainty. Data sources also differ in specificity and data often have to be aggregated or disaggregated to fit the investigate system which creates additional uncertainties. When data is lacking, they must be assumed or calculated using other uncertain values. The result is therefore inherently limited in accuracy and an uncertainty analysis is important, although often neglected.

Uncertainty in MFA

Several MFA practitioners (e.g. Rechberger and colleagues 2014; Laner and colleagues 2014) regret that it is not state-of-the-art to thoroughly consider uncertainties and their consequences on the results in MFA. Often, only mean values are used and uncertainty considerations are restricted to a qualitative discussion of the validity of results. Although the topic is receiving increasing attention, no systematic method for selection of appropriate uncertainty tools has been established in the field. Several approaches for including uncertainties in MFA can however be found in the literature, classified in three types by Laner and colleagues (2014): (i) qualitative and semi-quantitative approaches; (ii) approaches based on data classification; and (iii) statistical approaches.

Qualitative and semi-quantitative approaches are based on attributing confidence ratings to different flows and stocks according to the researcher's subjective assessment of the data reliability and quality. This approach, proposed by Moss and Schneider (2000) in the context of uncertainty assessment in IPCC reports, was notably used by Graedel and colleagues (2004) in their study of the global anthropogenic copper cycle. The authors used five confidence levels: very high (<±5%), high (±5–33%), medium (±33–67%), low (±67–95%) and very low (>±95%). Each flow was attributed a confidence level, assuming mining data to be generally of high accuracy (as it follows international metal markets data), information on use and waste management to be of moderate accuracy (as copper content in many of data flows is not well-known), and losses to the environment to be of low accuracy.

In a second type of approach, based on data classification, data is divided into different classes of uncertainty according to their reliability, completeness, temporality, scope, etc. In their study on urban heavy-metal flows, Hedbrant and Sörme (2001) introduced such a classification using asymmetric uncertainty intervals derived through multiplication and division of the data with the respective uncertainty factors. They therefore express uncertainty intervals in terms of magnitude ('probably X but maybe as much as 3*X or as little as 1/3*X') using the symbol '*/' instead of '±'. Data are categorized in classes of predefined uncertainty levels depending on the assumed reliability (e.g. recognized authorities or informal estimates) and scope (e.g. local or national) of their source. This approach was used by Thaler and colleagues (2011) in the context of MFA study on the nutrient balance in Austria (Table 1).

Table 1: Uncertainty levels and factors used by Thaler and colleagues (2011)

Uncertainty level	Uncertainty factor	Source type
0	*/1	Generic data (e.g. molecular mass)
1	*/1.1	Official statistics at national or regional level (e.g. mineral fertilizer use)
2	*/1.33	National and regional data; general data; experts estimate; modeled data
3	*/2	Modeled data; assumptions

In statistical approaches, input data are described by characterizing probability density functions and rigorous mathematical methods are applied to evaluate the sensitivity and/or uncertainty of model outputs. Three distinct statistical approaches can be distinguished:

1. The STAN software is a tool to perform material flow analysis that considers data uncertainties (Cencic and Rechberger 2008). In STAN, uncertain data are expressed by their mean value and standard deviation (that can either be manually entered or computed) and there are assumed to be normally distributed, which is convenient for error propagation but has the disadvantage that it can result in unrealistic negative flows. If the system is overdetermined (i.e. there is more equations than unknowns), conflicting uncertain data are reconciled in STAN by altering the mean values. The inverses of the variances of uncertain data are used as weighting factors in the reconciliation, meaning that highly uncertain values will be more strongly altered than values with low uncertainty. Uncertainties of unknown flows are calculated with the method of error propagation based on the least square method. According to its authors, STAN allows the reconciliation of inconsistent data in order to find the best fitting values without guessing (Cencic and Rechberger 2008). The interest of the possibility to use information redundancy in STAN to improve the

accuracy of data has been illustrated by Bonnin and colleagues (2013) in their study of the French anthropogenic copper cycle.

2. Probabilistic approaches that allows for assigning various probability distributions (e.g. uniform, triangular, log-normal, or Weibull distributions) to uncertain input flows, based on assumptions and/or observations. Monte Carlo simulation is usually applied to estimate the probability distribution of the model outputs. Gottschalk and colleagues (2010) proposed a detailed stepwise procedure for probabilistic MFA.
3. Finally, sensitivity analysis is a powerful statistical tool for assessing the importance of uncertainties in MFA. It can be combined with all approaches presented above. Sensitivity analysis can be used to study the effect of parameter variation on the model results by defining variation ranges for selected parameters. This allows evaluating the effect of uncertainties in input variables on the model results. It has been used in several dynamic MFA studies. For instance, in a study of the global copper cycle between 1910 and 2010, Glöser and colleagues (2013) investigated the effect of varying uncertainty of input variables (especially lifetime distribution and fabrication efficiency which were assessed as the most uncertain parameters) on calculated flows and recycling indicators. This approach can therefore be used to identify the parameters having the greatest influence on model results, for which uncertainty must be analyzed in priority.

The uncertainty analysis method developed for this study, described in Section 4.3.1, combines semi-quantitative and statistical approaches.

3.1.3 ANTHROPOGENIC METAL CYCLES

Definitions and State of the Art

A metal cycle is the quantitative characterization of the flows and stocks of a specific metal into, within, and from a given system; the term anthropogenic is added when focusing mainly on the anthroposphere (Chen and Graedel 2012). In this context, the metal supply chain is typically divided into a few life cycle stages such as ore mining and processing, fabrication of semi-finished products and manufacture of goods, use of goods, and waste management (Figure 8).

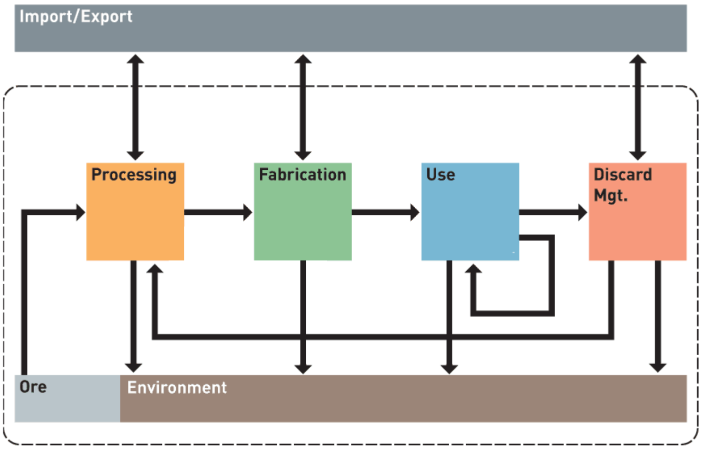


Figure 8: The anthropogenic life cycle of a metal (modified from UNEP, 2010)

Metal ores are mined from the lithosphere, and subsequently concentrated, smelted and refined into the metal itself (or its compounds). The refined products enter the fabrication of semi-finished products used as inputs in the manufacture of final goods, which are then put into use. Eventually, the goods reach the end of their service life and are either recycled or disposed into the environment. Losses to the soil, air and water occur at each lifecycle stage. During ore processing, significant quantities of the metal are lost in tailings and slag due to inefficient production processes. Fabrication, manufacture and waste treatment processes also result in air, water and soil pollution. During the use phase, consumptive losses are generated as a result of physical processes such as weathering, abrasive wear, and evaporation ("leaching"), as well as due to the inherently dissipative nature of some applications such as ammunition, biocides and fertilizers, where dispersion into the environment is part of the function itself (Ciacci and colleagues 2015).

Typically, the metal (in one form or another) moves rapidly through the production, fabrication, manufacture and waste management phases. In contrast, the metal contained in goods can remain in the use phase for an extended period of time, depending on the goods useful lifetime (or residence time), before being discarded or lost into the environment. Such "in-use stocks" of metals therefore represent potential future emission or waste flows. Their estimation provides crucial information on the quantity of metal that may be available for future recycling. For these reasons, the characterization of metal in-use stocks is a central focus in metal flows and stocks studies.

Anthropogenic metal cycles are usually constructed using MFA, which provides a way to quantify how much metal enters, circulates within and leaves the economy as wastes or emissions. Static and dynamic modeling can be used depending on the purpose as well as the availability of time and data. Dynamic MFA is especially useful for sustainable metal management as it allows for the estimation of in-use metal stocks. The terms "retrospective" and "prospective" can be employed when past or future, respectively, stocks and flows are investigated (Müller and colleagues 2014). MFA has been used to characterize the global anthropogenic cycles of several widely used metals, such as iron (Wang and colleagues 2007), aluminum (Cullen and Allwood 2013; Liu and colleagues 2012), copper (Glöser and colleagues 2013; Graedel and colleagues 2004), zinc (Graedel and colleagues 2005), nickel (Reck and colleagues 2008), tin (Izard and Müller 2010), and cobalt (Harper and colleagues 2012). Due to lack of data, few global-scale MFA studies have been conducted for less commonly used metals, with the notable exceptions of rare-earth elements (Du and Graedel 2011), indium (Yoshimura and colleagues 2013), tellurium (Kavlak and Graedel 2013b), selenium (Kavlak and Graedel 2013a), and gallium (Løvik and colleagues 2015). Out of 1074 anthropogenic metal cycles characterized in the 350 publications reviewed by Chen and Graedel (2012), more than 90% use static models, generally with a temporal boundary of one year. Although dynamic modeling provides much more insights, it is also more data intensive and time consuming. Several studies have nevertheless used dynamic MFA to understand how the flows and stocks of metal in the anthroposphere evolve over time. Specific aims include investigating the potential for future recycling of metals (e.g., Glöser and colleagues 2013; Hatayama and colleagues 2010), evaluating future scenarios of resource availability (e.g., Kapur 2005; Alonso and colleagues 2012; Elshkaki 2013), and assessing the evolution of environmental impacts related to changes in metal flows (e.g., Saurat 2006; Elshkaki 2013).

In-Use Metal Stock Characterization

In-use stocks are the quantities of metal contained in product currently providing services of various kinds to the society. They are the result of a greater rate of metal entering use than leaving it over time. As stated above, the size of in-use stocks informs on future waste streams and emission flows. Furthermore, regionally quantified in-use stocks can serve as an indicator of the quantity of metals less-developed countries would need to put in use in order to reach comparable material services (Gordon and colleagues 2006). Indeed, because they are directly related to the levels of material consumption, the size of the metal in-use stocks of a region reflects that region's affluence level (Gerst and Graedel 2008).

A review of 54 studies addressing the stocks in society of 24 different metals (Gerst and Graedel 2008) has shown that enough information to give a reliable estimate of the global metal in-use stocks exist only for five base metals (aluminum, copper, iron, lead and zinc). Sparse, and often regional, information exist for 19 other metals. Furthermore, the authors note that dynamic information is absent in most of the cases, with most stock estimates being no more than 'snapshots in time', although dynamic stock information provides much richer insights into metal supply and demand systems.

Two approaches can be distinguished to estimate in-use stocks of metals. First, the "bottom-up" approach, the quantities of metal used in each application is estimated by combining inventories of the different products that contain the metal of interest (e.g. vehicles, buildings) with the average metal content of those products. Mathematically, this can be expressed as:

$$S_t = \sum_{i=1}^{A} N_{it} \times m_{it} \tag{1}$$

where S_t is the in-use stock at time t, N_{it} is the quantity of product i in use at time t, m_{it} is the metal content of in-use product i, and A is the number of different types of metal-containing products. This method is very data intensive and mostly used in in-use stocks characterization with a small spatial scale (e.g. a city) where census information on the number of units of metal-containing products in use is available or can be easily derived. For regional or global estimates, data availability is an issue. Furthermore, the metal content can vary considerable for the same type product, which leads to large uncertainties over the results of in-use stocks estimated with the bottom-up approach.

More appropriate for studies with larger temporal and spatial scales (Gerst and Graedel 2008), the "top-down" approach consists of computing the cumulative difference between the inflows to and outflows from use, usually for each year. Mathematically, S_{t+1}, the in-use stock at time $t + 1$, is estimated in discrete time steps as:

$$S_{t+1} = \sum_{t=T_0}^{T} (inflow_t - \ outflow_t) + \ S_0 \tag{2}$$

where T_0 is the time of the initial time step, T the current time step, and S_0 he stock at the initial time step. Initial in-use stocks are often assumed to be zero when metal MFA analyses go far back in time (typically 1900), as metal production and consumption was then insignificant compared to current levels (Müller and colleagues 2014).

Inflows are the quantities of metal entering the Use phase yearly. Outflows from use can have different origins and fates: (i) End-of-life outflows are generated when products reach the end of their useful life and are transferred to the Waste Management phase; (ii) leaching outflows occur as a result of physical processes such as weathering, abrasive wear, and evaporation; (iii) dissipative uses where loss into the environment is part of the function itself (e.g. ammunition, fertilizers). The magnitude of end-of-life flows and that of leaching flows can be estimated using respectively delay and leaching models (Kleijn and colleagues 2000; Van der Voet and colleagues 2002; Elshkaki and colleagues 2005). The delay model uses historical inflow data and products lifetime distributions, and describes the outflow as a delayed inflow. The leaching model express leaching flows as a fraction of the in-use stocks. As for inherently dissipative applications, it can be considered that loss into the environment occurs as soon as the product enters the Use phase, and outflows from dissipative uses can therefore be modeled as a fraction of the inflow (e.g. Ayres and Ayres 1994, Chen and colleagues 2010).

For this study, it is therefore considered that the outflow at time t depends on delay, leaching and dissipative uses:

$$outflow_t = delay_t + leaching_t + dissipation_t \tag{3}$$

Outflows from in-use stock at time t resulting from delay and leaching processes are estimated using the following relations:

$$delay_t = inflow_t * f \tag{4}$$

where f is the probability density of the lifetime distribution function.
The symbol "*" denotes a convolution.

$$leaching_t = l \times S_t \tag{5}$$

with S_t the stock at time t and l the leaching factor, i.e. a constant for the fraction of the stock becoming a leaching outflow per unit of time.

$$dissipation_t = d \times inflow_t \tag{6}$$

where d is the dissipation factor, i.e. a constant for the fraction of the inflow becoming being lost into the environment as a result of dissipative uses.

Three approaches can therefore be used to estimate outflows whether they are due to the delay mechanism, leaching processes, or dissipative uses. The delay model describes outflows as a delayed inflow and requires information on past inflows to use as well as on the products lifetime distributions. In the leaching model, outflows are considered to be proportional to the amount of products in use and are expressed as a fraction of the in-use stock. For the dissipation model, it is assumed that metals used in inherently dissipative applications are essentially lost to the environment as soon as they enter into service.

Different lifetime distribution functions can be used for the delay model (Table 2). The choice of one function or the other depends on the available lifetime data as well as on the authors' assumptions. The effect of applying different lifetime distribution on the model results were explored in several dynamic metal flows and stocks studies, reviewed by Müller and colleagues (2014). It has been observed that, when the Dirac delta function (i.e., average and constant lifetime) is applied, some model outputs such as the outflows from use can be highly influenced by fluctuations of the inflows. Probability density functions such as the normal, lognormal and Weibull distributions smooth out the effects of fluctuating inflows on scrap flows, and choosing one of those functions over the other does not have significant consequences on the model inputs if shape, scale and location parameters are similar. All in all, model results were found to be most sensitive to the mean values of the lifetimes, regardless of the distribution function chosen.

Regarding the leaching model, different leaching factors can be established for each application. Such coefficients have been estimated for several metals in previous studies (e.g., for Ag, As, Cd, Cr, Cu, Hg, Pb and Zn in Karlsson and colleagues (1997)). However, considerable uncertainties accompany such estimates as leaching behavior strongly varies depending on local characteristics (Tukker and colleagues 2001).

Dissipation factors can often be inferred from common sense. For instance, it can be reasonably assumed that all metal being used as a fertilizer is lost to the environment. In applications where not all the metal is lost, factors have to be assumed rather arbitrarily (Ayres and Ayres 1994)

Table 2: Lifetime distribution functions frequently used in MFA of metals (Müller and colleagues 2014)

Distribution function	Formula	Parameters	Strengths (+) and weaknesses (-)
Delta (or Dirac delta)	$f_t = \bar{\mathrm{l}}$	$\bar{\mathrm{l}}$: average lifetime	+ Parameter easily derived from available data - Strong simplification - High influence of fluctuations in inflows on calculated outflows - Can significantly under or overestimate outflows
Normal (or Gaussian)	$f_t = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{t-\mu}{\sigma}\right)^2}$	μ: mean σ: standard deviation	+ Parameters are understandable and easily derived from available data - Values of distribution can be negative - Inflexible shape
Lognormal	$f_t = \frac{1}{t\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{\ln t-\mu}{2\sigma^2}\right)^2}$	μ: scale parameter σ: shape parameter	+ f(t) = 0 if t ≤ 0
Weibull	$f_t = \begin{cases} \alpha \times \beta^{\alpha} \times (t-\gamma)^{\alpha-1} \times e^{-\left(\frac{(t-\gamma)}{\beta}\right)^{\alpha}} & \text{if t} > \gamma \\ 0 \text{ otherwise} \end{cases}$	α: scale parameter; controls 'tail' β: shape parameter γ: location parameter	+ Good fit to lifetime of many metal products (Melo 1999) + Flexible distribution, can attain many different shapes depending on the shape parameter + f(t) = 0 if t ≤ 0 - Data for parameters is most often not available and must be estimated or deduced from available data

Forecasting future metal cycles

Several approaches can be used to forecast future anthropogenic metal cycles. It can be assumed that the demand is the main driver of the metal cycle and therefore develop scenarios on the future demand for the metal, using constant, linear, exponential or logistic extrapolation from historical demand data and/or more sophisticated methods using a regression with exogenous variables (e.g. GDP, population), demand trends analysis, or the 'intensity of use hypothesis', which is based on the observation that the material use per unit GDP often follows an inverted U-shaped curve (van Vuuren and colleagues 1999). Individual production and consumption models for each end-use sector can also be developed, such as in Elshkaki (2007). Future stocks can then be estimated considering the expected inflow of metal into use and the assumed residence time.

Other approaches regard in-use stocks as the driver of the metal cycle and use the "stocks drive flows" concept, where future flows are computed backwards from assumed stock patterns and product lifetimes (e.g. Hatayama and colleagues 2010). It is generally considered that metal stocks do not grow indefinitely but saturate at some level. In their review of in-use metal stocks estimates, Gerst and Graedel (2008) observed that per capita metal in-use stocks were significantly higher (5 to 10 times) in more-developed countries (Australia, Canada, EU-15, New Zealand Sweden, Switzerland, the USA and Japan) than less-developed countries. Rauch (2009) showed that the correlation between gross domestic product and in-use stocks of aluminum, copper, iron and zinc was greater than 0.8 (>0.9 for Al and Cu). While this correlation has been confirmed for widely used metals, it might not be valid for more specialized metals. For instance, per capita in-use silver stocks appear to be higher in developing countries because of the large use of this metal in jewelry and decorations (Gerst and Graedel 2008).

Comparing the forecasted demand with the identified reserves and the potential for recycling allows for identifying the conditions in which supply can meet the demand, as well as hypothetical depletion cases. Furthermore, performing a sensitivity analysis allows for the identification of variables having the greatest impact on the model results. In this way, it is possible to identify sustainable and unsustainable scenarios, as well as the parameters playing a key role in this distinction.

Uncertainties in anthropogenic metal cycles characterization

Modeling the stocks and flows of metals is a data intensive process, compared by Chen and Graedel (2012) to 'a detective activity in which information of varying quality is assembled from a variety of sources and then harmonized'. Data can be especially difficult to find in the case of specialty metals, for which volumes are low and company concentration of mining, processing and recycling is high (Bloodworth 2014).

The level of uncertainty associated with data typically increases through the metal supply chain. Data for global primary production, refinery output and products fabrication tend to be well reported and relatively accurate, although their uncertainty is almost never reported. On the other hand, data on waste flows are generally not well documented, if at all. In-use stocks and end-of-life flows must be estimated using reported or inferred data regarding inflows and products lifetimes for the top-down approach, and metal content and stocks of metal-containing products for the bottom-up approach. Uncertainty associated with these data is difficult to assess, although comparing the results of using both in-use stock estimation approaches can be used to assess accuracy levels (cross-checking). Furthermore, considerable uncertainties exist over the quantities of metal dissipated throughout their anthropogenic lifecycle, which must often be estimated using assumptions and approximations with local monitoring data.

Therefore, the results of a study on local, regional or global flows and stocks of metals are inherently limited in accuracy. Yet, it is not state of the art to consider uncertainties in this field of research. Half of the 60 dynamic MFA of metals reviewed by Müller and colleagues (2014) did not consider data uncertainty. Sensitivity analysis was performed in 37% of the cases, whereas uncertainty intervals (such as proposed by Moss and Schneider (2000) or by Hedbrant and Sörme (2001)) and Gaussian error propagation (such as integrated in the STAN software) were used in only 6% and 5% of all studies, respectively.

3.2 MEASURING THE ENVIRONMENTAL IMPACTS OF METALS

3.2.1 LIFE CYCLE ASSESSMENT

Rebitzer and colleagues (2004) define Life Cycle Assessment (LCA) as a 'methodological framework for estimating and assessing the environmental impacts attributable to the life cycle of a product, such as climate change, stratospheric ozone depletion, tropospheric ozone (smog) creation, eutrophication, acidification, toxicological stress on human health and ecosystems, the depletion of resources, water use, land use, and noise – and others'. LCA can be used to evaluate the environmental burdens associated with a product or service by identifying and quantifying energy and materials used and wastes released to the environment throughout its life cycle, from cradle to grave (i.e. from raw material extraction through materials processing, manufacture, distribution, use, repair and maintenance, and disposal or recycling). It also allows the evaluation of opportunities to implement environmental improvements.

The LCA procedure is described in International Standardization Organization (ISO) 14040 series (2006). It consists of four steps:

1. Goal and scope definition: describes the context of the study and its intended application. It sets out the system boundaries in terms of time, space, technology, and level of detail. This step includes also the selection of the "functional unit", which defines the function that the considered product or service delivers and serves as a basis for allocating the inputs and outputs.
2. Life Cycle Inventory (LCI): Cradle-to-grave accounting of energy and material flows flowing into and out of the environment that are related to the functional unit defined in the first step. This step can be very data intensive depending on the product and the system boundaries. Several databases are available to support LCI, such as the ecoinvent database (Frischknecht and colleagues 2004) that contains more than 4000 data sets in the areas of agriculture, energy, transportation, chemicals, construction, waste treatment, and others, compiled by research institutions and LCA consultants. MFA can also be used as a method to establish the inventory for an LCA (Baccini and Brunner 2012).
3. Life Cycle Impact Assessment (LCIA): LCI data and societal preferences are used to calculate and interpret environmental impacts per functional unit. Environmental exchanges listed in the LCI are classified according to predefined impact categories such as acidification, eutrophication, ozone depletion, greenhouse gas emissions, depletion of resources, human health, eco-toxicity, noise, and others. The LCI flows are then characterized using one the many possible LCIA methods, i.e. the impacts are quantified by a specific unit for each category (e.g. kg CO2 equivalents for climate change). This allows for the aggregation of results of one category to a single score, the category indicator result. Additional steps may include normalizing and weighting the impact category scores leading to a single final score.
4. Interpretation: results are interpreted in terms of completeness, consistency, and sensitivity. Conclusions, limitations and recommendations are deduced.

3.2.2 LIFE CYCLE ENVIRONMENTAL IMPACTS OF METALS

Environmental impacts can be generated at different stages of a metal's lifecycle, from ore extraction through manufacture, use, recycling, and final disposal of products in which this metal is used.

The primary production of metals is probably the most preoccupying lifecycle stage from an environmental perspective. Mining, mineral processing, metal extraction and refining are very energy intensive processes that significantly contribute to global warming. It is estimated that primary metal production accounts for 7-8% of the total global energy use (UNEP 2013b). For most metals, extraction and refining processes consume much more energy than the mining and concentration stages (UNEP 2013b). Primary production processes also use large amounts of water and can cause local environmental and health problems due to air emissions and leaching of toxic substances into the ground- and surface water. It is generally observed that environmental impacts increase as metal ore grades decline (more energy, water, land, toxic substances needed), which is gradually happening for several metals (Norgate and Haque 2010; Kleijn 2012).

The use of metals can have direct and indirect environmental impacts. Direct impacts result from dissipation/leaching of metals into the environment, with potentially harmful effects on human health and ecosystems. Indirect impacts are related to the use of metal-containing products which can also causes adverse environmental impacts (e.g. energy or water consumption). In such cases, impacts are related to the product itself and not the materials that compose it, and allocating impacts to the metals is therefore tricky.

Waste management processes also generate environmental impacts. Incineration and discard of metals or metal-containing products can lead to emissions to the air (e.g. from incineration), water (e.g. from waste water treatment), and soils (e.g. from spreading of sewage sludge or landfilling). Recycling uses significant quantities of energy and water, and may also generate emissions into air, water and soils. However, those impacts are generally much lower than those of primary production. Energy savings of recycling typically range between 60% and 90% (UNEP 2013b).

Quantified information about the extraction and emissions of different substances during the mining, production, use and waste management processes of metals can be found in LCI databases, the richest being the ecoinvent database (Classen and colleagues 2009). This type of information is however available for a limited number of metals, generally the most commonly used ones, and often only for the primary production processes (cradle-to-gate). An overview of available LCI data for metal production can be found in the UNEP International Resource Panel report on environmental risks and challenges of metals (UNEP 2013b).

Toxicity of metals on the health of humans and other living organisms are assessed during the LCIA step of LCA studies. LCI flows into the environment can be characterized by relevant toxicity factors included in several impact assessment methods, such as CML 2001 (Guinée and colleagues 2001), ReCiPe (Goedkoop and colleagues 2009), USETox (Rosenbaum and colleagues 2008), and Eco-indicator 99 (Goedkoop and Spriensma 2001). Usually, toxicity potential for ecosystems and toxicity potential for humans are distinguished. A further distinction is often done between terrestrial and aquatic ecosystems toxicity. To calculate those factors, assumptions and models on fate, exposure and toxicity are used. They often differ between impact assessment methods, which results in great variations between different methods regarding the calculated human- and eco-toxicity potentials for the same metal (Pizzol and colleagues 2011a, 2011b). ReCiPe is the most used method for assessing eco-toxicity potential. The USETox method results from a consensus among international modeling experts and is regarded as the best current model for LCIA on human toxicity, although large uncertainties remain (UNEP 2013b).

3.3 COMBINATION OF METHODS

While these different methodologies developed and matured quite separately, research has also been increasingly devoted to building integrated models combining the best aspects of two or more methods. Hereafter, we give an overview of previous attempts to combine MFA and LCA through a selection of studies.

Tukker and colleagues (1998) combined MFA and LCA to assess the environmental impacts associated with the Swedish PVC chain. They inventoried all emissions related to PVC using MFA and translated into LCA scores. In order to do that, the authors extended the typical system definition used in MFA studies (track the flows of one substance in a defined region) by including an emission inventory for PVC production that is normally used in LCA. Each emission flows were multiplied by characterization factors as given by Heijungs and colleagues (1992) for human toxicity, aquatic and terrestrial eco-toxicity, acidification, eutrophication, depletion of the ozone layer, global warming and smog formation. However, due to high uncertainties concerning the emissions, fate and effect data of certain substances, they were unable to give LCA scores for the human- and eco-toxicology impact categories.

Bouman and colleagues (2000) compared MFA and LCA applied to a single, hypothetical example of a pollution problem (i.e. the production and consumption of lead and 'green' batteries). They applied each model to the problem separately and compared the consequences of changes aiming at: (i) reducing the use of virgin materials; (ii) abating the emissions to the atmosphere; (iii) reducing the waste disposal in landfills. They concluded that results of the two models are 'complementary rather than contradictory', and that 'a sequential application of a number of limited models may therefore be an approach that provides more useful information than the tedious construction and application of an encompassing model that integrates these models'. For a typical metal pollution problem, they recommend to start with MFA to identify the metal flows, distinguish the problematic flows and select the main flows to regulate and try out the problem solving potential of some technically defined options and then to use LCA to evaluate the alternatives (products, materials or processes) in terms of environmental impacts and problem shifting potential.

Wäger and colleagues (2011) combined MFA and LCA to calculate the overall environmental impacts of collection, pre-processing and end-processing for the existing Swiss WEEE collection and recovery systems, as well as of hypothetical incineration and landfilling scenarios. The authors carried out the MFA using input-output data reported by the contractors of the Swiss WEEE systems and calculated the amount of WEEE collected, sorted and dismantled. They then performed a simplified LCA to calculate the environmental impacts of three alternative recovery and disposal scenarios. The impact assessment was performed using the CML 2001 (Guinée and colleagues 2001) and the Eco-indicator 99 (Goedkoop and Spriensma 2001) methods.

Rochat and colleagues (2013) systematically combined MFA and LCA for supporting the choice of best end-of-life scenarios for polyethylene terephthalate (PET) waste in the municipality of Tunja, Colombia. MFA and LCA have been combined using 'the service offered by the total PET used during one year in the region' as the functional unit for the LCA. Life cycle inventory and impacts were calculated by multiplying MFA flows with LCA impacts per kilogram. They argue that the combination of MFA and LCA brings the added value of allowing for the assessment of the environmental impact of changes in MFA flows due to decisions taken by the relevant stakeholders.

3.4 STEPWISE METHODOLOGY

To answer the research questions raised by the problem definition, the following methodology was followed:

1. Extensive literature review: initially conducted to understand the challenges related to the global anthropogenic antimony cycle, as well as to develop the conceptual and methodological framework. Throughout the research, additional literature was reviewed to perform the assessment.
2. Static MFA model (Chapter 4): goal setting; delimitation of system boundaries, selection of relevant substances, processes and goods; assessment of mass flows based on an extensive data collection; assignment of uncertainty intervals to data sources; balancing of the model and error propagation using the STAN software; results visualization.
3. Dynamic MFA model (Chapter 5): transformation of static model into a relational data model using Microsoft Excel to allow dynamic analyses; data collection for retrospective dynamic MFA; analysis of 2011 cycle and comparison with previous studies; generation of scenarios for prospective dynamic MFA; results interpretation.
4. Environmental and health aspects (Chapter 6) gathering of information on environmental impacts related to primary and secondary production processes, as well as on toxicity potential of Sb emissions for human health and ecosystems; semi-quantitative assessment of environmental impacts risks by combining MFA results with LCA and risk assessment frameworks.
5. Results integration, interpretation, and discussion (Chapter 7).

4 STATIC MFA

4.1 GOALS

The aim of the static MFA is to understand the pathways of antimony in the anthroposphere i.e., the part of the environment that is made or modified by humans. This involves identifying and quantifying the flows of antimony entering, circulating within, and leaving the economy, from the extraction of the ore, its transformation into refined metal and compounds, the incorporation of these substances into products, the use of those products, and the waste management processes related to those products. Furthermore, the magnitude of flows of antimony being lost to the environment along these lifecycle stages is assessed.

4.2 SYSTEM DEFINITION

4.2.1 SPATIAL AND TEMPORAL BOUNDARIES

Antimony flows are interconnected at the global level; the spatial system boundary for this study is the world. Relevant processes, stocks and flows are identified along four basic lifecycle stages: Production, Fabrication and Manufacture, Use, and Waste Management. For reasons of data availability, the temporal boundary chosen is the year 2011.

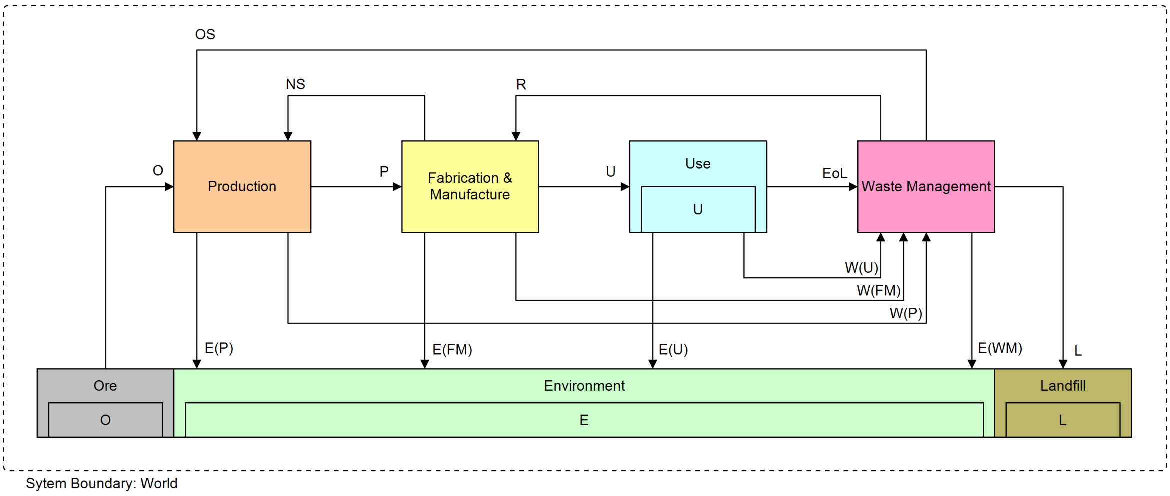


Figure 9: Simplified MFA model

Legend:

O	Sb from ore	W(P)	Sb in wastes from Production
P	Refined Sb	W(FM)	Sb in wastes from F&M
U	Sb entering use	W(U)	Sb in wastes from Use
EoL	Sb in End-of-life products	E(P)	Sb in emissions from Production
R	Sb in recycled plastic and glass	E(FM)	Sb in emissions from F&M
OS	Sb in old metal scrap	E(U)	Sb in emissions from Use
NS	Sb in new metal scrap	E(WM)	Sb in emissions from Waste Management
		L	Sb to landfills

4.2.2 ANTIMONY PRODUCTS AND APPLICATIONS

Antimony metal and compounds are required for the production of a wide range of products that can be grouped into metallic and non-metallic applications. An overview of the main antimony products in international trade and of their main end-uses is given in Figure 10.

Figure 10: Main antimony products and applications

Substance	Formula	Sb content	Code in the Harmonized System	End-uses		Remarks
Antimony ore and concentrates	Main: Sb_2S_3 (stibnite)	71.70%	261710 antimony ores & concentrates	Metallic uses	Lead-acid batteries	Sb used for antimonial lead used in the grid plates of lead-acid batteries
Primary antimony metal	Sb	<99%	811010 semi-refined unwrought antimony metal			
Antimonial lead	Alloy	4-25%	780191 unwrought lead, containing by weight antimony as the principal other element		Other alloys	Sb used as an alloying element in rolled and extruded lead products (pipes, tank linings, roofing, cable sheaths, etc.), ammunition, solders, bearings, type metals, pewter, etc.
Antimony oxides	Sb_2O_3 (trioxide) Sb_2O_5 (pentoxide) SbOCl (oxychloride)	83.50% 75.30% 70.30%	282580 antimony oxides	Non-metallic uses	Flame-retardants	Sb used as a synergist with halogenated (mostly bromine- but also chlorine-based) flame-retardants in plastics, textiles, paints, rubber, etc. Also used alone in applications where polymers already contain halogens (PVC).
					PET	Sb used as a catalyst in the manufacture of PET, used to produce synthetic polyester textiles, PET containers (e.g. drinking bottles) and polyester film for packaging
Sodium antimonate	$NaSbO_3$	62.30%	28419060 antimonates		Glass & Ceramics	Sb used as fining and degasing agent in CRT and optical glass, and as a opacifier in porcelain enamels and pottery glazes
					Other	Sb used in brake pads, semiconductors, fireworks and matches, pharmaceuticals, lubricants, pigments, etc.

Metallic uses

Due to its poor mechanical properties, antimony metal is not used directly but as an alloying element in various alloys, adding hardness and smoothness. The main antimony-containing alloy is antimonial lead, which contains between 1% and 15% Sb. The higher the antimony content is, the harder and more brittle the alloy will be. The main metallic applications of antimony are lead-acid batteries, rolled and extruded lead products, and ammunition.

Lead-acid batteries represent the main end-use sector for metallic antimony. Since the early developments of technology (mid-19th century), lead-antimony alloy has been used to increase the resistance of certain parts to corrosion and deformation. The largest of these parts is the plate grid, which provides a mechanical support to the active electrode materials and a conductive path for the electric current. In addition to its strengthening qualities, antimony simplifies and speeds up the casting of grids by enhancing the fluidity of the melt and minimizing shrinkage during cooling. Furthermore, antimony leached from the grid during use facilitates the recrystallization of the lead oxide, which keeps the plate grid firm and thus lengthens the service life of the battery. However, using antimony in lead-acid battery plates has two main drawbacks: first, during discharge antimony tends to migrate from the positive to the negative plate, where it lowers hydrogen overvoltage and therefore accelerates the breakdown of water in the electrolyte. This increases the need for maintenance through regular addition of water. A second disadvantage is that antimony also deposits on the negative plate, which causes the self-discharge of the battery at a rate of up to 1% per day (Carlin 2006). For these reasons, manufacturers started to decrease the antimony content in SLI batteries in the 1970s and developed ‘low-maintenance’ and ‘maintenance-free’ batteries in which antimony is, respectively, partly or completely substituted by calcium in the grid plate. The average antimony content in lead alloys used in lead-acid batteries decreased from 8-12% in the 1960s to 0.5-3% nowadays (Linden and Reddy 2002; Grund and colleagues 2011). The decreasing antimony content in lead-acid batteries has however been, to an extent, offset by the global growth in demand for lead-acid batteries.

Rolled and extruded lead products are the second largest metallic end-use for antimony. Containing 4-12% Sb, antimonial lead pipes and sheets are resistant to atmospheric corrosion and are mainly used in buildings for roofing, flashing, and gutters.

Ammunition has been a significant end-use for antimony since the 19th century, as a hardener in lead ammunition. Shrapnel shells, anti-personnel artillery munitions containing 10-13% Sb, were used so extensively during the First World War that antimony production peaked at levels not equaled until the late 1980s. Nowadays, antimony is mostly used in small arm lead ammunition containing on average 1-2% Sb (Butterman and Carlin 2004). Due to concerns over lead pollution, lead ammunition has been partially or completely banned in several countries (Avery 2009).

Other antimony-containing alloys are used to manufacture a wide range of metallic products with varying antimony content. Antimony-containing lead alloys are used in bearings metals (6-15%), cable sheathing (0.7-1%), solder metal (0.5-3% Sb), and type metals (2.5-25% Sb) used in the printing industry. Antimony is also added to tin alloys are used as Babitt metal in bearings (4.5-14% Sb), and as Brittania metal (7-20% Sb) used in utensils and tableware. Furthermore, lead-tin-antimony alloys are used as solder metal. Increasing amounts of very pure antimony metal (99.999–99.99999% Sb) are used as dopants in the manufacture of n-type semiconductors.

Non-metallic uses

Over half the global consumption of antimony occurs under its oxidized form, mainly as antimony trioxide (ATO). Other important compounds are sodium antimonate, antimony pentoxide, antimony trisulfide, and antimony triacetate. The main non-metallic applications of antimony are as synergist in halogenated flame retardants, as polymerization catalyst for PET, as fining agent in glass, and as opacifier in ceramics.

Flame retardants represent the largest application for antimony worldwide. Although antimony has no flame-retarding property by itself, its oxides (mainly the trioxide) act as synergists in combination with halogenated organic compounds (bromine- and chlorine- based) to provide a very effective flame retardant system used mainly in plastics and to a lesser textiles, rubber, paints and adhesives. Two mechanisms exist in the synergetic system. One the one hand, the halogenated antimony compounds act as dehydrating agents and inhibit ignition and pyrolysis in the solid, liquid and gas phases. On the other, the antimony oxides promote the formation of char on the substrate, which reduces oxygen availability and volatile gas formation. ATO is mostly used as a synergist when halogenated flame retardants are used additively (Morf and colleagues 2003), and mainly in thermoplastics such as polystyrene (PS), acrylonitrile butadiene styrene (ABS), polyvinyl chloride (PVC), polyethylene (PE), and polypropylene (PP). Brominated flame retardants are primarily used in electrical and electronics equipment (EEE), in plastic parts such as housings, cable insulation and printed circuit boards. Those plastics are typically HIPS (high impact polystyrene) and ABS. The ratio of ATO to bromine in brominated flame retardants typically lies between 1:2 and 1:4 (Morf and colleagues 2003). Concentrations of 330-690 ppm Sb were measured in the plastic fraction from mixed waste electrical and electronic equipment (WEEE), and of 1000-2600 ppm Sb in WEEE plastic from ICT equipment only (Wäger and colleagues 2010b). Chlorinated flame retardants are mainly added to PVC, mostly used for building materials (pipes and fittings, window frames, rain gutters, etc.). The ratio of ATO to chlorine ranges between 1:4 and 1:5 (Mathys and colleagues 2007). In PVC, antimony is also used as a thermal stabilizer, often in combination with its flame retarding properties. Typically, PVC contains 50-100 ppm Sb (Mathys and colleagues 2007).

Antimony trioxide and, to a lesser extent, antimony triacetate are the most used catalyst in the polymerization of polyethylene terephthalate (PET). PET is used in the manufacture of synthetic textiles (about 65% of total PET consumption), plastic containers (about 28%) and polyester film for packaging (about 7%) (Gibbs 2012). Thiele (2004) estimated that 90% of the world PET production was realized by adding 150-300 ppm antimony trioxide or triacetate. Concentrations of 190-300 ppm Sb are measured in PET bottles and of 160-240 ppm in polyester textiles (Shotyk and colleagues 2006; Belzile and colleagues 2011), indicating that most, if not all, antimony used as a catalyst is transferred into the product. Concerns over potential health hazards due to leaching of antimony from polyester products (especially food and water containers) have stimulated the research for antimony-free polymerization catalysts based on germanium, titanium, aluminum, magnesium or phosphorus. Several of such antimony-free PET catalysts have been on the market for more than a decade but have struggled to gain market acceptance due to concerns over the impacts that these catalysts may have on PET resin color, line yield and quality (Weissman 2014). In the glass sector, antimony in the form of sodium antimonate, and to a lesser extent ATO, is used as decolorizing and fining agents for high-quality transparent glass, mainly cathode ray tube (CRT) glass and optical glass (used in cameras, photocopiers, etc.). ATO is also used as opacifier in porcelain enamels that are used for iron bathtubs and sinks, as pottery glazes and as brick additives. Other minor non-metallic applications include the use of antimony trisulfide in brake linings, paints, pigments, lubricants, and matches, of antimony pentasulfide and trioxide in the vulcanization of rubber, and of various antimony compounds to produce pigments, pharmaceuticals, and pesticides. Most of these applications are inherently dissipative.

4.3 ASSESSMENT OF MASS FLOWS

4.3.1 DATA SOURCES

The main inputs to the model are primary antimony production, refined antimony production, demand of antimony by end-use sector, end-of-life products generation, as well as transfer coefficients related to production, manufacturing and waste treatment efficiencies, and emissions from production, consumption and waste management processes.

To quantify those flows and transfer coefficients, an extensive data collection was performed, involving various sources such as national geological surveys, metal trading companies reports, market consultant reports, product trade statistics, company product fact sheets, scientific literature, and expert judgment. All these sources differ in terms of temporal and spatial scope, completeness, reliability, etc., and rarely include information on uncertainties.

To deal with such "uncertainty over uncertainties", a five-point quantitative scale for confidence levels such as proposed by Moss and Schneider (2000) was used. Accordingly, different uncertainty intervals – very high (±10%), high (30%), medium (50%), low (75%) and very low (>100%) – were assigned to flows and transfer coefficients according the evaluated reliability and quality of the data. Following a method used previously in metal MFAs (e.g., Graedel and colleagues 2004; Kapur 2005; Graedel and colleagues 2005; Bonnin and colleagues 2013), each flow was attributed a confidence level assuming mining data to be generally of high accuracy as it follows international metal markets data, information on use and waste management to be of moderate accuracy as antimony content in many of data flows is not well-known, and losses to the environment to be of low accuracy, as their magnitude can widely differ between units (e.g. plant, product). This semi-quantitative approach to assess uncertainties therefore includes considerations of both epistemic uncertainty (due to a lack of information over specific parts of the life cycle) and stochastic uncertainty (due to inherent variability in processes along the life cycle).

Confidence levels and corresponding uncertainty intervals are presented in Table 3. For each level, examples of flows and transfer coefficients as well as the main sources used for their determination are given.

Table 3: Confidence levels and uncertainty intervals

Level	Interval	Examples of Flows (F) and Transfer Coefficients (TC)		Main sources
1	±10%	F	Primary production	U.S. Geological Survey (2014a), British Geological Survey (2015)
		F	Inflows to F&M	Roskill (2011)
		TC	Recycling efficiency	Carlin (2006)
2	±30%	F	Old metal scrap generation	Roskill (2011)
		TC	Primary production efficiency	Anderson (2012), Grund and colleagues (2011)
		TC	Refining efficiency	EU RAR (2008)
3	±50%	TC	Environmental fate of emissions	EU RAR (2008); Buser et al. (2007)
		TC	End-of-life recycling rates	US EPA (2014); Thiele (2007); Mao et al. (2008)
		TC	Antimony pathways in WWT	Mathys et al. 2007, Van Velzen et al. (1998)
4	±75%	TC	Incineration/landfill ratios	Assumptions
5	±100%	TC	Emission & waste factors	EU RAR (2008); OECD (2009); (EEA 2013); Mathys et al. (2007); Tian and colleagues (2014); Van Velzen et al. (1998); Paoletti et al. (2001);

4.3.2 LIFECYCLE STAGE: PRODUCTION (P)

The production stage includes primary production processes that transform antimony ores and concentrates into refined antimony metal, alloys and compounds, and secondary production processes that transform old and new antimony scrap into secondary antimony metal and alloys. Wastes and losses to the environment occurring in these processes are also modeled. Flows of antimony entering, circulating within, and leaving the Production stage are modeled in STAN as shown in Figure 11.

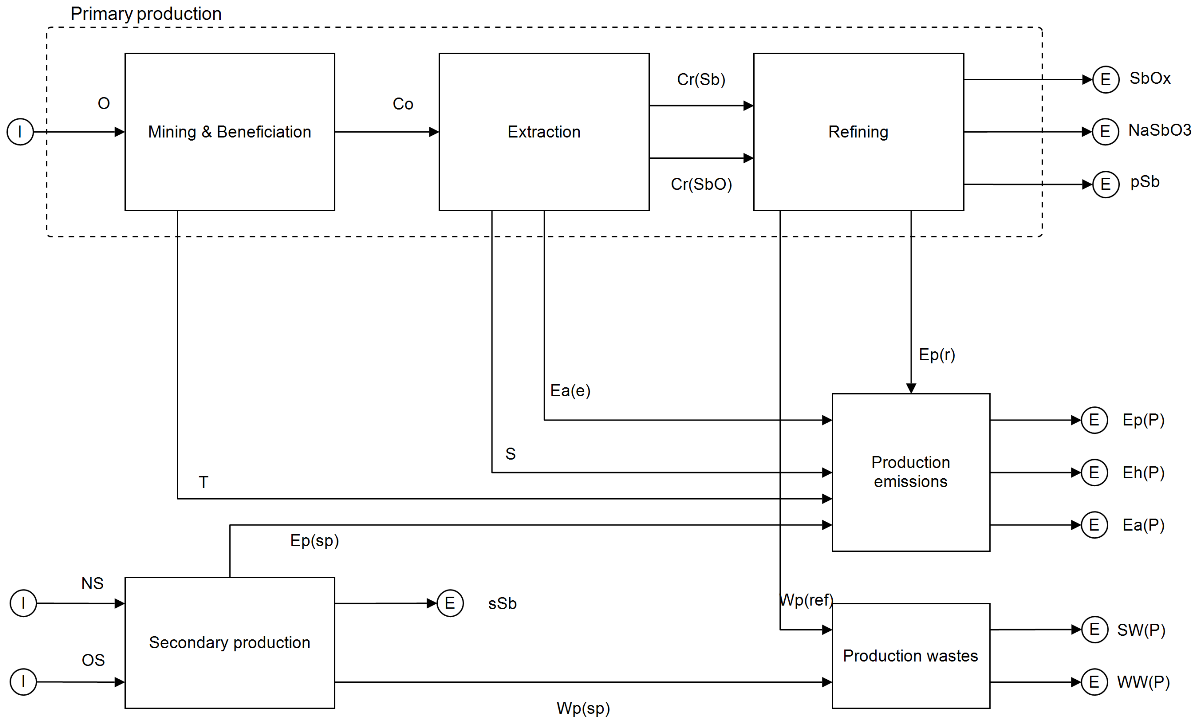


Figure 11: Production subsystem

Legend:

O	Sb from ore	OS	Sb in old metal scrap
Co	Sb concentrate to smelting	sSb	Refined secondary Sb metal and alloys
T	Sb in tailings	Ep(r)	Sb emissions from refining
Cr(Sb)	Crude Sb metal	Wp(r)	Sb in wastes from refining
Cr(SbO)	Crude Sb oxide	Ep(sp)	Sb in emissions from secondary production
S	Sb in slag	Wp(sp)	Sb in unrecovered metal scrap
Ea(e)	Sb in air emissions from extraction	SW(P)	Sb in solid waste from Production
SbOx	Refined Sb oxide	WW(P)	Sb in wastewater from Production
NaSbO3	Refined sodium antimonate	Ea(P)	Sb in emissions to atmosphere from Production
pSb	Refined primary Sb metal	Eh(P)	Sb in emissions to hydrosphere from Production
NS	Sb in new metal scrap	Ep(P)	Sb in emissions to pedosphere from Production

Overall mass balance:

$$\mathrm{O + OS + NS = SbO_x + NaSb + pSb + sSb + Ep(P) + Eh(P) + Ea(P) + SW(P) + WW(P)}$$

Primary production processes

Primary production processes transfer antimony contained in Earth's crust into refined antimony metal and compounds. Ores are first mined, through open pit or underground mining, and ore grade is then increased by concentration (beneficiation) methods such as crushing, gravity separation and flotation. Antimony contained in the ore but not transferred into the concentrate is mostly put back into the environment in the form of tailings. Tailings are usually discharged as a slurry in tailings ponds where solid particles sediment.

Extraction and refining processes transform ore concentrates into refined antimony metal, alloys and compounds. Depending on the antimony oxidation state (oxide, sulfide, or mixed) and ore grade, which range from about 5% to more than 60%, different pyro- and hydrometallurgical methods can be used to extract antimony from its ores (Table 4).

Table 4: Pyrometallurgy and hydrometallurgy of antimony (Grund and colleagues 2011; Anderson 2012)

Sb oxidation state	Sulfide				Oxide		Mixed
Ore grade	5-25%	25-45%	45-60%	>60%	~30%	~60%	
Type	Pyrometallurgical						Hydrometallurgical
Extraction method	**Roasting**	**Smelting**	**Liquation**	**Precipitation**	**Reduction (i)**	**Reduction (ii)**	**Smelting or solvent extraction and electro-winning**
Description	Heated with charcoal or coke, usually in rotary kilns; sulfide evaporates and condensed high-grade Sb2O3 is produced	Smelted at high temperatures in blast furnaces.	Melted in a reverberatory furnace with a reducing atmosphere. The molten ore liquifies and flows down from the furnace	In a crucible furnace, scrap iron is used to reduce sulfur and yield impure Sb metal	Sb oxide is reduced to crude metal in a blast furnace with charcoal	Sb oxide is reduced to crude metal in a reverbatory furnace with charcoal	Usually smelted in blast furnaces. Sometimes processed by selective leaching (with Na2S or NaOH as solvent) followed by electrolysis that yields 93-98% pure Sb at the cathode
Recovery rate	95-98%	98%	?	?	90-92%	92%	50-94%
Temperatures	1100-1300 °C	1300-1400 °C	550-600 °C	?	?	1200 °C	?
Main product	Sb2O3 (commercial grade after 2nd roasting process)	Crude sb metal (impure)	Sb sulfide (>70% Sb)	Crude Sb metal (Fe, S impurities)	Crude Sb metal	Commercial grade Sb metal	Sb metal (93-99.5% Sb)

Little information exists on the relative importance of each route for the global primary production of antimony. In the Xikuangshan mining region, which supplies about 60% of the global supply according to the U.S. Geological Survey (2012), a combination of methods is used (Yang and colleagues 2011). The concentrate is first roasted in rotary kilns where antimony trioxide is volatilized and condensed. The trioxide is then reduced with carbon to metallic antimony in reverberatory furnaces. Antimony production is done similarly in several countries (Grund and colleagues 2011).

Antimony produced by pyrometallurgical and hydrometallurgical processes must often be further refined to attain commercial purity. The principal impurities are usually, in declining order of abundance, lead, arsenic, sulfur, iron, and copper. Iron, copper and arsenic concentrations be lowered through simple chemical treatments but lead cannot be readily removed, which is not problematic since antimony metal with a high lead content can be used in the production of antimonial lead.

ATO is produced either via volatilization of refined antimony metal or via oxidation of crude stibnite followed by revolatilization of ATO. The latter predominates in the Europe (EU 2008a) and it is assumed that it is also the case worldwide. Sodium antimonate is either produced from crude antimony oxide or recovered from waste CRT glass (Hageluken 2006).

Secondary production processes

Blast furnaces, reverberatory furnaces and rotary furnaces can be used for the recovery of antimony from scrap metal alloys. Antimony is then transferred into the recycled alloys. Roskill (2012) estimates that approximately half of the global demand for antimony in metallic applications is met by secondary sources, coming mainly from the recycling of lead-acid batteries.

Data inputs

Inflows to production:

- Sb from ore (*O*) is estimated using estimates on primary production for 2011, which range between 150Gg (British Geological Survey 2015) and 185Gg (U.S. Geological Survey 2012). The flow value is set at 166.5±16.7 Gg.
- Sb from new and old scrap (*NS*; *OS*) is obtained with mass balances from the F&M and Waste Management subsystems, respectively.

Outflows from production:

- Flows of refined primary and secondary Sb metal and compounds (*SbO_x*; *NaSb*; *pSb*; *sSb*) are estimated using Roskill (2012) figures on global consumption of primary antimony products in 2011 (Table 5). This approximation is justified by the fact the antimony market was near competitive equilibrium in 2011 according to Roskill (2012), with a small supply deficit (-1.4%).

Table 5: Modeled outflows from Production (Roskill 2012)

Antimony product	Flow value, (Gg)	Share	Flow in MFA model	Uncertainty interval
Primary antimony metal	39.5	19.1%	pSb	±10%
Antimonial lead (secondary)	38.0	18.4%	sSb	±30%
Antimony oxides	125.0	60.5%	SbO_X	±10%
Sodium antimonate	4.3	2.1%	$NaSbO_3$	±10%
Total	206.8	100%		

- Emissions and wastes (Table 6):
  - Mining & Beneficiation: Ore concentration efficiency was estimated at 94% by Anderson (2012) for a stibnite deposit in Xikuangshan. Ore concentration is realized in similar ways in other mines (Grund and colleagues 2011). In the model, concentration efficiency is set at 0.94±0.02. Non-recovered Sb is usually discharged in tailing ponds and is considered as emissions to soil. A fraction of the Sb deposited in tailings may eventually leach and contaminate surrounding water bodies. Such "second-order" emissions are difficult to assess as they depend on local environmental characteristics and occur over various time frames. They are not included in the MFA model.
  - Extraction: Recovery rates are unknown for some extraction methods and vary between 90% and 98% for those for which information is available. On a global level, the relative importance of each extraction route and the extent of internal recovery processes from slag or flue gas are not well known. According to Yang and colleagues (2011b), in Xikuangshan antimony is mainly extracted through the roasting method. Roasting is also used in the South African Consolidated Murchinson mine (Grund and colleagues 2011), one of the world's largest (Schwarz-Schampera 2014). Without more information, an average smelting efficiency factor of 0.95±0.03 was assumed. Non-recovered antimony leaves as emissions to soil (slag) or

to air. An air emissions factor of 75 grams Sb per ton of primary Sb produced as estimated by Tian and colleagues (2014), was used, with a very low confidence level (±100%). As in the case of tailings, eventual leaching of Sb deposited in slag into to water bodies is not included in the model.

- Refining: Emission and waste factors for refining of antimony oxides are based on monitoring data from European production sites (EU 2008a). It is assumed to be valid for the production of sodium antimonate as well, with a very low confidence level (±100%). Because of a lack of quantified information, emissions during refining of antimony metal are not modeled.
- Secondary production: Carlin (2006) estimated at 0.89 the old scrap recycling efficiency in the USA. In the model, recycling efficiency is set at 0.89±0.09. Atmospheric emissions due to secondary production of antimony alloys are estimated using the air pollutant emission inventory guidebook published by the European Environment Agency (EEA 2013). Air emission factors for secondary antimony production are approximated with those for secondary lead production (unspecified technology), giving an emission factor of 426 grams per ton. The air emission factor is of very low confidence (±100%). Antimony scrap that is not recovered and not emitted in the air is transferred to waste management processes as solid waste.

Table 6: Emission and waste factors for Production processes (rounded to one significant digit)

Process	Emission factor			Waste factor		References
	Soil	Air	Water	Solid waste	Waste-water	
Ore concentration	6E-02	–	–	–	–	Grund and colleagues (2011); Anderson (2012)
Smelting	1E-01	8E-05	–	–	–	Grund and colleagues (2011); Anderson (2012); Tian and colleagues (2014)
Refining (ATO)	8E-05	8E-05	3E-07	5E-08	–	EU (2008)
Secondary production	–	4E-04	–	1E-01	–	Carlin (2006); EEA (2013)

4.3.3 LIFECYCLE STAGE: FABRICATION AND MANUFACTURE (F&M)

The F&M stage involves metallurgical and non-metallurgical industries that use antimony metal, alloys and compounds to produce final goods. Antimony oxides and sodium antimonate are used in the manufacture of non-metallic goods, whereas antimony metal and alloys are used in the manufacture of metallic goods. The flows of antimony entering, circulating within, and leaving the F&M stage are modeled in STAN as shown in Figure 12.

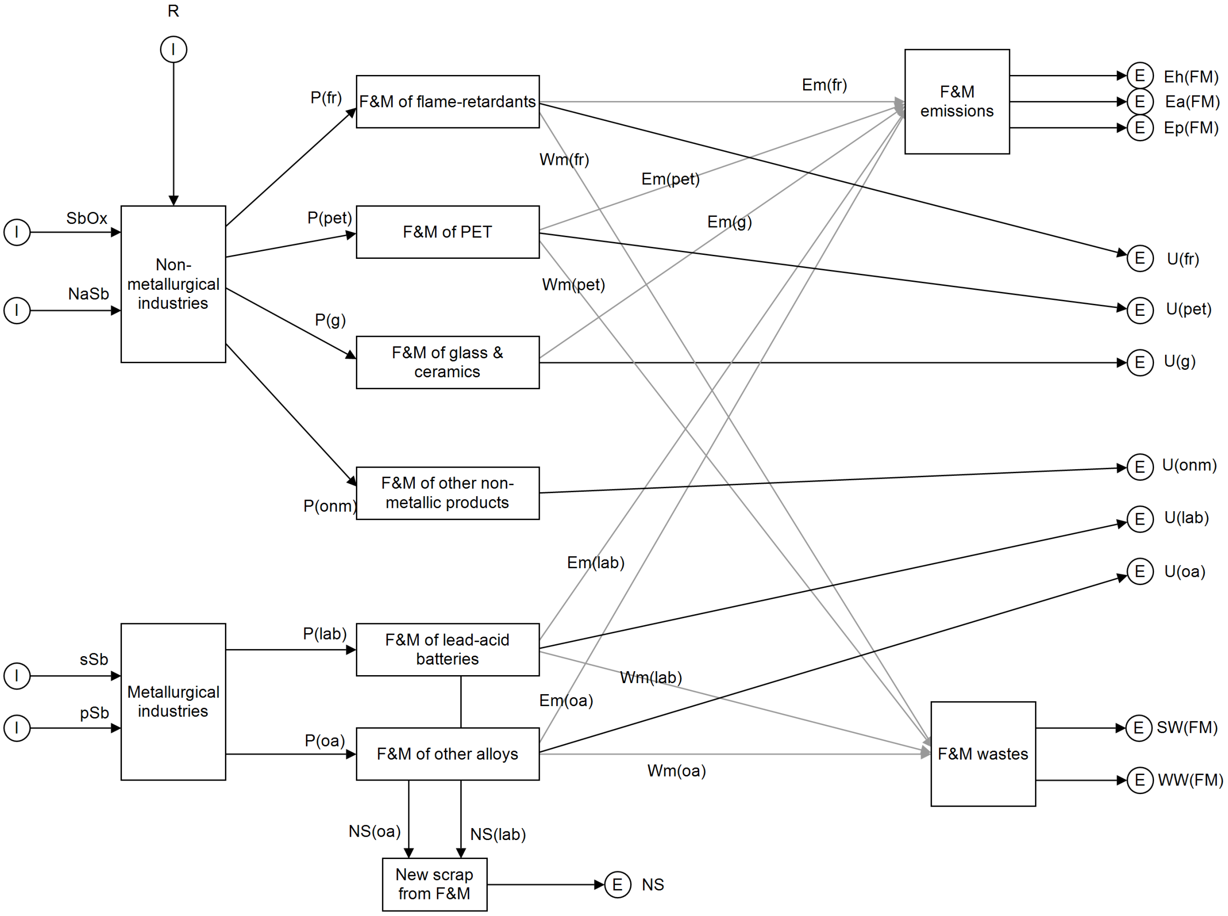


Figure 12: Fabrication & Manufacture subsystem

Legend:

R	Sb in recycled plastic and glass	Ea(FM)	Sb in emissions to atmosphere from F&M
P(*i*)	Sb used in the F&M of product *i*	Eh(FM)	Sb in emissions to hydrosphere from F&M
U(*i*)	Sb in product *i* entering Use	Ep(FM)	Sb in emissions to pedosphere from F&M
NS(*i*)	Sb in new metal scrap from F&M of product *i*	SW(FM)	Sb in solid waste from F&M
Em(*i*)	Sb in emissions from F&M of product *i*	WW(FM)	Sb in wastewater from F&M
Wm(*i*)	Sb in waste from F&M of product *i*		

Overall mass balance:

$$SbO_x + NaSb + pSb + sSb + R = \sum_{i}^{A} U(i) + \sum_{i}^{A} Em(i) + \sum_{i}^{A} Dm(i) + \sum_{i}^{A} NS(i)$$

where A is the number of different antimony end-use categories.

Inflows to F&M processes

Inflows to F&M processes are estimated based on a variety of sources (Table 7). Roskill (2012) publishes figures on global consumption of antimony by end-use category, while various sources give information on individual applications. Overall, metallic applications account for about one third of the global consumption, while non-metallic uses take up the rest. Hereafter, the main data sources and assumptions are described. An uncertainty interval of 10% is assigned to all inflows to F&M processes.

- Roskill (2012) estimates the global demand for Sb in lead-acid batteries at approximately 53.6 Gg for 2011 (i.e., about 70% of the demand for metallurgical applications and 26% of the total demand). In the same source, it is estimated that about 90% of the 450 million lead-acid batteries produced worldwide are of the SLI type.
- Non-battery antimony alloys used 23.9 Gg Sb in 2011 according to Roskill (2012). Mathys and colleagues (2007) estimate that above 80% of non-battery antimony alloys consumed globally are lead-antimony alloys. Roskill (2012) estimates that rolled and extruded lead products account for approximately 75% of metallurgical uses of antimony other than lead-acid batteries. A similar share is obtained by multiplying the global demand for lead in rolled and extruded products as estimated by Mao and colleagues (2008b) by an average antimony content of 5% as used in the MFA of antimony in Switzerland (Mathys and colleagues 2007). Considering a global demand of lead for ammunition of 300 Gg Sb as estimated by Hurley (2013), and an average antimony content in lead ammunition of 1% as given by Butterman and Carlin (2004), the demand for Sb in ammunition is estimated at 3 Gg. Minor metallic applications include cable sheathing, solder alloys, bearings, etc.
- According to Roskill (2012), demand for flame retardants amounted to 108.3 Gg Sb in 2011, mostly as ATO – it is estimated that 90% of the global Sb_2O_3 production goes to flame retardants (Roskill 2011). According to Townsend Solutions (2012), about 2 millions tons of flame retardants have been consumed in 2011, with a share of 7% for "antimony oxides", i.e. 140 Gg. Assuming that it is the trioxide form that is used, containing 83% Sb by weight, gives in a global consumption of about 116 Gg Sb. The value for this flow is therefore set at 112 Gg. Figures on global consumption of antimony for flame-retardants are only available at an aggregated level, with very little information on the relative shares of applications within this end-use category. Those were estimated for Japan and Switzerland. In their MFA of antimony in Switzerland, Mathys and colleagues (2007) estimated that EEE accounted for about 70% of the national antimony consumption in flame retardants in 2001, while passenger cars and building materials had respective shares of 19% and 8%. Tsunemi and Wada (2008) estimated that the relative shares of E&E, cars and building materials in the consumption of antimony in Japan was respectively 67%, 3% and 24%. Based on this limited information, we assume relative shares of 75% for EEE, 10% for both cars and building materials, and 5% for other applications.
- About 2.7 Gg Sb was used as heat stabilizer in PVC in 2011 according to Roskill (2011).
- Roskill (2012) estimates that demand for PET amounted to about 12.1 Gg Sb in 2011. According to Gibbs (2012), out of the 61 million tons of PET produced worldwide in 2011, 65% were used in textiles and 28% in bottles. Concentrations of 190-300 ppm Sb were measured in PET bottles and 160-240 in polyester textiles (Shotyk and colleagues 2006; Belzile and colleagues 2011). Using those figures, the global consumption of Sb in PET can be estimated to lie between 10 Gg and 15 Gg. This suggest that the value of 12.2 Gg estimated by Roskill (2012) is rather accurate, and it is used for the model.

- Demand for glass and ceramics amounted to 1.7 and 2.6 Gg, respectively, according to Roskill (2012).
- Other non-metallic applications put a total demand of 1.9 Gg according to Roskill (2012). They include pigments, brake linings, lubricants, and other minor non-metallic products (e.g. medicine, biocides, matches). As very little information is available on the amount of antimony consumed in these applications, equal shares are assumed.

Table 7: Estimated consumption of antimony by application, 2011

End-use sector	Application		End-use share, 2011	Yearly consumption (Gg Sb)	References
Metallic products	Lead-acid batteries	SLI	22.0%	48.2	Roskill (2012)
		Stationary	2.5%	5.4	Roskill (2012)
	Lead alloys	Rolled & extruded lead	7.1%	15.5	Roskill (2012)
		Ammunition	1.4%	3.0	Hurley (2013); Mao et al. (2008a); Butterman & Carlin (2004)
		Other	0.3%	0.7	Balance
	Other alloys		2.2%	4.8	Mathys et al. (2007)
		Total metal	35.3%	77.5	Roskill (2012)
Flame retardants	EEE		39.9%	84.0	Mathys et al. (2007); Tsunemi & Wada (2008); Assumption
	Cars		5.3%	11.2	Mathys et al. (2007); Tsunemi & Wada (2008); Assumption
	Building materials		5.3%	11.2	Mathys et al. (2007); Tsunemi & Wada (2008); Assumption
	Other		2.7%	5.6	Mathys et al. (2007); Tsunemi & Wada (2008); Assumption
		Total flame retardants	55.2%	112.0	Roskill (2012); Townsend Solutions (2012)
Other	PET		5.6%	12.2	Roskill (2012); Gibbs (2012); Shotyk and colleagues (2006); Belzile and colleagues (2011)
	Heat stabilizer		1.2%	2.7	Roskill (2012)
	Glass		0.8%	1.7	Roskill (2012)
	Ceramics		1.2%	2.6	Roskill (2012)
	Pigments		0.2%	0.5	Assumption
	Brake linings		0.2%	0.5	Assumption
	Lubricants		0.2%	0.5	Assumption
	Other		0.2%	0.5	Assumption
		Total other	9.5%	20.9	Roskill (2012)
		Total	100.0%	210.4	Roskill (2012)

Antimony applications were aggregated in six categories for the static model (Table 8): flame retardants (including heat stabilizers), PET, glass & ceramics, other non-metallic applications, lead-acid batteries, and other alloys (including non-battery lead alloys and other alloys). Similar categories are used in several sources (e.g. Roskill 2012; U.S. Geological Survey 2014a; Schwarz-Schampera 2014). It is considered that

F&M, Use and Waste Management processes are sufficiently homogeneous within each end-use category to justify such an aggregation.

Table 8: Modeled inflows to F&M processes

End-use category		Flow name	Flow value (Gg)	Uncertainty interval
Non-metallurgical	Flame-retardants	P(fr)	114.7	±10%
	PET	P(pet)	12.2	±10%
	Glass & ceramics	P(g)	4.3	±10%
	Other non-metal	P(onm)	1.9	±10%
Metallurgical	Lead-acid batteries	P(lab)	53.6	±10%
	Other alloys	P(oa)	23.9	±10%
Total			210.6	

Outflows from F&M processes

During the F&M processes, not all the inflow of antimony ends up in the finished good. In some cases, such as in polyester production, antimony is used as a catalyst and is therefore not intended to end up in the final product (although it may do so). In other cases, part of the antimony used is lost in the form of emissions to air, new scrap, and discards to waste management due to process inefficiencies. Very little information exists on those fabrication losses, rendering the estimation of transfer coefficients difficult. Hereafter, data sources and assumptions used to estimate those variables are given:

- For F&M processes of metallic products, emission, waste and new scrap coefficients were derived based on modeling assumptions used by Mao and colleagues (2008) in their characterization of the global anthropogenic lead cycle (Table 9). Fate of emissions and wastes is derived from the same study (Table 10).
- As regards F&M processes for non-metallurgical applications, losses of antimony as emission to air, water or soil and/or as solid waste and wastewater during F&M processes of flame retardants, polyester, and glass & ceramics were quantified for Europe in the EU Risk Assessment (EU RAR 2008) using monitoring data and the EUSES (European Union System for the Evaluation of Substances) environmental model. Emission factors were derived (Table 9) by dividing calculated emissions and wastes flows by total volumes of antimony used in those three end-use sectors in Europe, also reported in the EU report. Fate of emissions and wastes is derived from the same source (Table 10).
- No information could be found on the emissions and wastes generated during the F&M of other non-metallic antimony-containing products. Those represent however less than 2% of the global Sb consumption and emissions during F&M are probably negligible.

Table 9: Emission, waste and new scrap factors for F&M processes (rounded to one significant digit). An uncertainty interval of ±100% is assumed for each transfer coefficient

End-use category	Emission factor	Waste factor	New scrap factor	References
Flame retardants	8E-04	2E-02	–	EU RAR (2008)
PET	5E-04	2E-04	–	EU RAR (2008)
Glass & ceramics	6E-03	–	–	EU RAR (2008)
Other non-metal	–	–	–	–
Lead-acid batteries	2E-02	3E-02	5E-02	Mao et al. (2008)
Other alloys	2E-02	4E-02	6E-02	Mao et al. (2008)

Table 10: Fate of emissions and wastes for F&M processes. An uncertainty interval of ±50% is assumed for emission coefficients, and of 10% for waste coefficients.

End-use category	Fate of emissions			Fate of wastes		References
	Soil	Air	Water	Solid waste	Wastewater	
Flame retardants	9.9E-01	7.4E-03	0	8.3E-01	1.7E-01	EU RAR (2008)
PET	9.9E-01	1.0E-02	0	0	1	EU RAR (2008)
Glass & ceramics	7.4E-01	2.2E-01	4.5E-02	–	–	EU RAR (2008)
Other non-metal	–	–	–	–	–	–
Lead-acid batteries	7.1E-02	8.6E-01	7.1E-02	1	0	Mao et al. (2008)
Other alloys	7.1E-02	8.6E-01	7.1E-02	1	0	Mao et al. (2008)

4.3.4 LIFECYCLE STAGE: USE (U)

After its incorporation into final products in the F&M stage, Sb enters the Use phase and becomes part of the "in-use stock". At the end of their useful lifetime, antimony-containing products are transferred to the Waste Management stage in the form of end-of-life flows. In some applications, such as ammunition, brake linings, pigments or lead sheets for roofing, significant amounts of antimony is lost into the environment during the use of the product as a result of leaching processes (e.g. corrosion of lead sheets) or due to the inherently dissipative nature of the application (e.g. ammunition). Significant quantities of antimony are also lost in wastewater during the washing of textiles containing antimony in flame retardants or polyester (EU 2008a). It is assumed that all antimony in use eventually leaches out of the in-use stock as emissions or is transferred to the waste management stage (both as end-of-life product or as losses in wastewater).

The magnitude of in-use stocks and end-of-life flows depends on the past inflows of antimony into use and on the lifetime distribution of the products. The amount of antimony lost to the environment through corrosion and abrasive wear, and to wastewater through washing, depends on the size of the in-use stocks. The estimation of in-use stocks, end-of-life flows, and losses during use is therefore realized using a dynamic model, presented in the next chapter. In the static model, consumptive losses are not included and end-of-life flows are assumed equal to inflows to Use (i.e., a steady-state situation is assumed). This is unrealistic, but is sufficient to estimate transfer coefficient in upstream and downstream life cycle stages. Realistic emission, waste and end-of-life flows quantified using the dynamic model are entered in the static model later in this study (retrofitting). The flows of antimony entering and leaving the Use stage in the static model are modeled in STAN as in Figure 13.

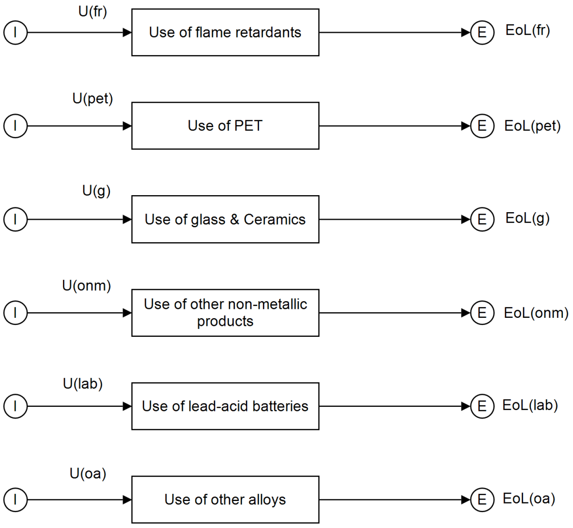


Figure 13: Use subsystem

Legend:

U(*i*)	Sb in product *i* entering Use
EoL(*i*)	Sb in End-of-life product *i*

Overall mass balance:

$$\sum_{i}^{A} U(i) = \sum_{i}^{A} EoL(i)$$

where *A* is the number of different antimony end-use categories.

4.3.5 LIFECYCLE STAGE: WASTE MANAGEMENT (WM)

End-of-life products enter the Waste Management stage through the collection subsystem, where waste fractions are sent to different waste management routes (i.e., incineration, recycling, landfilling). Some waste streams are not centrally collected but delivered directly to treatment plants from the source (e.g., solid waste and wastewater streams from Production, F&M and Use stages). The flows of antimony entering, circulating within, and leaving the F&M stage are modeled in STAN as in Figure 14.

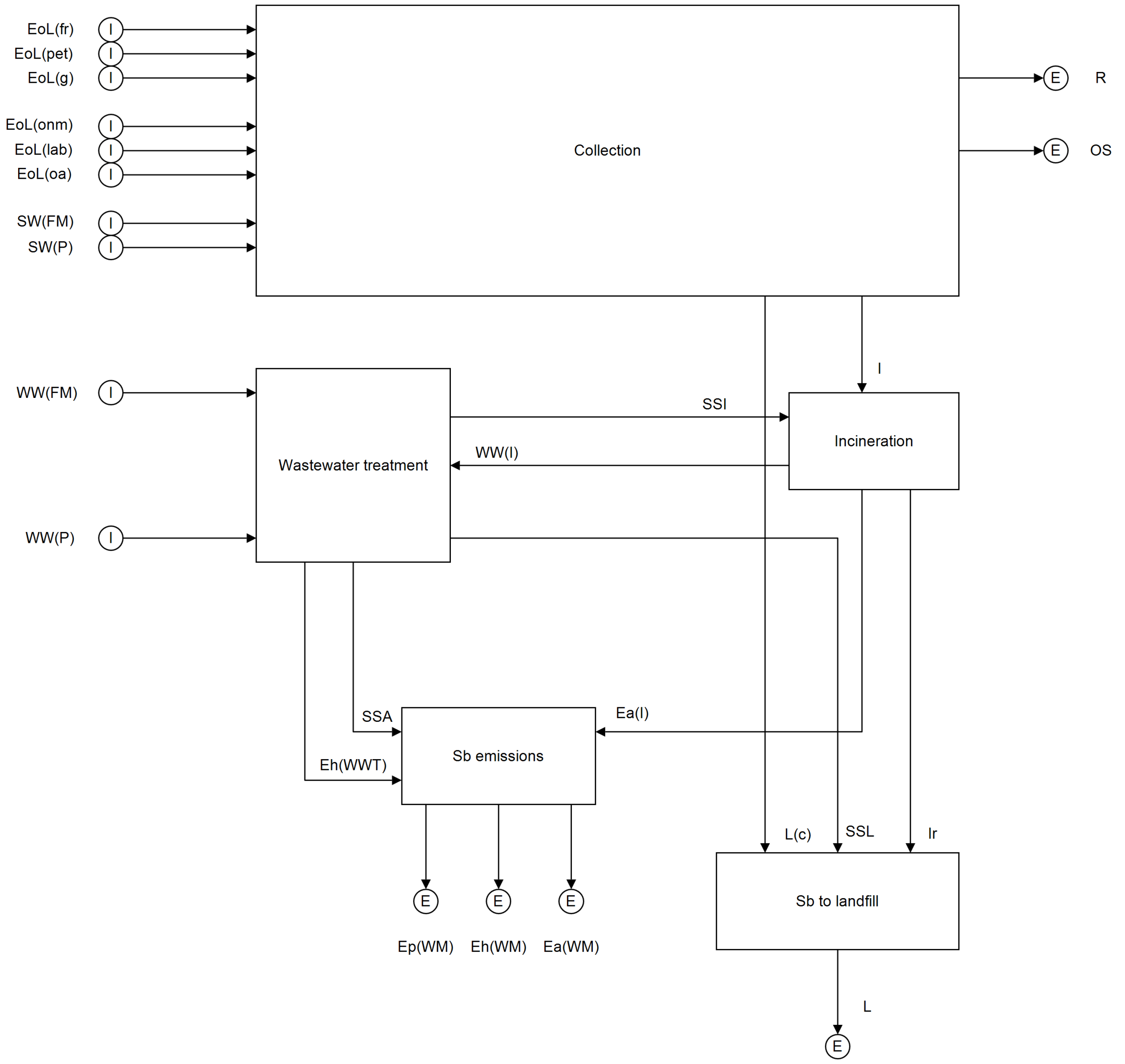


Figure 14: Waste Management subsystem.

Legend:

EoL(*i*)	Sb in end-of-life product *i*	Ea(I)	Sb in emissions from incineration
SW(*j*)	Sb in solid waste from stage *j*	SSA	Sb in sewage sludge to agriculture
WW(*j*)	Sb in wastewater from stage *j*	SSI	Sb in sewage sludge to incineration
OS	Sb in old metal scrap	SSL	Sb in sewage sludge to landfill
R	Sb in recycled plastic and glass	Eh(WWT)	Sb in purified wastewater
L(c)	Sb in non-incinerable waste	L	Sb to landfills
I	Sb in incinerated waste	Ea(WM)	Sb in emissions to atmosphere from WM
Ir	Sb in incineration residues	Eh(WM)	Sb in emissions to hydrosphere from WM
WW(I)	Sb in wastewater from waste incineration	Ep(WM)	Sb in emissions to pedosphere from WM

Overall mass balance:

$$\sum_{i}^{A} EoL(i) + \sum_{j}^{S} SW(j) + \sum_{j}^{S} WW(j) = R + OS + L + Ep(WM) + Eh(WM + Ea(WM)$$

where S is the number of lifecycle stages.

The pathway of antimony flows in the Waste Management phase depends on several factors related to waste management infrastructure and waste streams properties. Both vary considerably between countries and global figures rarely exist. Hereafter, data sources and assumptions used to estimate the share of each waste management options (Table 11) are presented:

- Flame retardants: According to van Velzen and colleagues (1998), about 40% of the antimony used in flame retardants in Europe end up in the feed for waste incinerators. Considering that approximately 85% of antimony-containing flame retardants are used in plastics and assuming global plastic recycling rates of 10% (based on figures for Europe and the United States published by PlasticsEurope (2012) and the U.S. EPA (2014)), it is estimated that about 8.5% of antimony in flame retardants is recycled. However, those figures relate to the whole plastic market, whereas antimony is mostly used in plastics for electrical and electronic equipment. Recycling rates for this specific market are unknown on a global level, but they could be lower than 10% as plastics recycling rates for WEEE are low in general, and plastics containing halogenated flame retardants are generally not recycled in industrialized countries. Overall, the recycling of antimony from WEEE plastics is poorly documented (UNEP 2012). Recycling of Sb in flame retardants textiles, rubber, paints and adhesives is assumed to be insignificant.
- PET: Thiele (2007) estimated that about 10% of the total PET production would be recycled worldwide in 2010, mainly from collected bottles. PET used to product polyester textiles – 65% of total PET use (Gibbs 2012) – is mostly incinerated. It is assumed that PET used in bottles but not recycled is also incinerated.
- Glass & ceramics: In the absence of data, it is assumed that 10% of Sb contained in end-of-life glass and ceramic products is recycled, mostly through the recycling of CRT glass, while the rest is landfilled.
- Other non-metallic products: With very little available information, it is assumed that they are incinerated and landfilled in equal shares, with no recycling.
- Lead-acid batteries: According to UNEP (2013a), recycling rates for lead-acid batteries are greater than 90% in developed countries nowadays. Worldwide, they were estimated to be about 70% in 2000 (Thornton and colleagues 2001). A recycling rate of 70% was therefore assumed for the global situation in 2011, and it is considered that the remaining fraction is landfilled.
- Other alloys: Antimony is mostly used in rolled & extruded lead products, for which recycling rates are relatively high. A recycling rate of 60% is assumed, as used by Mao et al. (2008) for the global anthropogenic lead cycle. The rest is assumed to be landfilled.

Most of the antimony in wastewater generated in upstream lifecycle stages is removed from the water in wastewater treatment plants and is transferred in sewage sludge, which can be incinerated, spread on agricultural soils or landfilled. A small portion remains in the purified water. Transfer coefficients estimated by Mathys and colleagues (2007) for Swiss wastewater treatment plants were used as a proxy for the global situation.

Antimony in the feed for waste incinerators is mostly transferred to bottom and fly ashes, assumed to be landfilled. Emissions factors for antimony emissions to air from municipal solid waste incineration (MSWI) range between 0.001 and 0.01 according to different studies reviewed in the EU Risk Assessment report (EU RAR 2008). Wastewater from incineration also contains some antimony and the emission factor was set at 0.0012, as estimated by van Velzen and colleagues (2008).

Table 11: Estimated share of waste management options

End-of-life flow	Recycling (%)	Incineration (%)	Landfill (%)	References
Flame retardants	8±4	40±30	52±34	van Velzen and colleagues (1998); PlasticsEurope (2012); US EPA (2014)
PET	10±5	90±5	0	Thiele (2007); Gibbs (2012)
Glass & ceramics	10±5	0	90±5	Assumption
Other non-metal	0	50±35	50±35	Assumption
Lead-acid batteries	70±20	0	30±20	Thornton and colleagues (2001); UNEP (2013a)
Other alloys	60±20	0	40±20	Mao and colleagues (2008b)

Table 12: Transfer coefficients for Waste Management Processes (rounded to two significant digits)

Incineration	To landfill	To air	To wastewater		References
	0.99±0.01	0.0055±0.0055	0.0012±0.0006		EU (2008a); van Velzen and colleagues (1998)
Wastewater treatment	To landfill	To incineration	To (agricultural) soil	To water	
	0.48±0.13	0.26±0.13	0.13±0.13	0.13±0.13	Mathys and colleagues (2007)

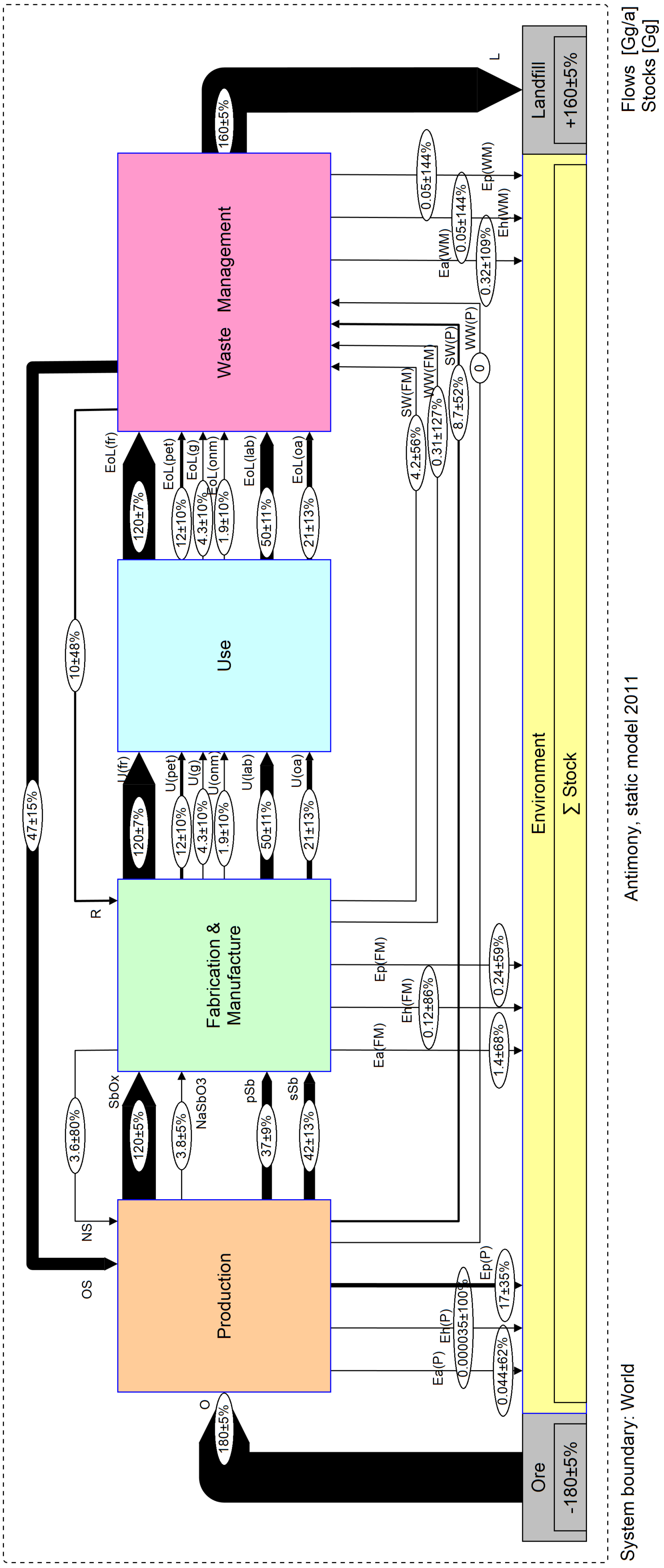
Antimony disposed in landfills may eventually leach into the surrounding environment. Such emissions are difficult to quantify since they depend on local landfill characteristics and occur over various time frames, and they are therefore not included in the MFA model.

4.4 CALCULATION

Gathered data on antimony flows and transfer coefficients as well as their assigned uncertainty were entered in the STAN software and the mass balance was performed with the “Cencic 2012” integrated calculation module that includes a data reconciliation method (Cencic and Rechberger 2008). If the system is overdetermined (i.e. there is more equations than unknown), conflicting uncertain data are reconciled in STAN by altering the mean values. The inverses of the variances of uncertain data are used as weighting factors in the reconciliation, meaning that highly uncertain values will be more strongly altered than values with low uncertainty. Uncertainties of unknown flows are calculated with the method of error propagation based on the least square method, briefly explained in Appendix A.

The results of the global antimony MFA are presented in Figure 15. Circled numbers in the arrows indicate the flow values in gigagrams of antimony per year, and the uncertainty is expressed as a percentage (standard deviation). Each blue box contains a subsystem with more detailed flowcharts that are included in Appendix B, which also includes the legend to the abbreviations. It must be stressed that the modeling of the Use phase in the static model is a simplification, as dissipation, leaching and delay mechanisms are ignored and a steady-state situation is assumed (inflow to Use=outflow from Use). In the next chapter, in-use stocks, emissions from Use and end-of-life flows for the year 2011 are quantified using the dynamic model, and the resulting material system is analyzed.

Figure 15: Global antimony MFA for the year 2011 as in STAN



5 DYNAMIC MFA

5.1 INTRODUCTION

The static model offered a characterization of the global antimony cycle for one year. While this snapshot offers valuable insights into the anthropogenic metabolism of antimony, including estimates of the quantities of antimony entering, circulating within and leaving the different stages of the global cycle, it fails to inform on the evolution of the system over time and on in-use stock dynamics. Those aspects are however crucial for assessing future requirements and availability of antimony. Due to the path dependency and inertia of socio-technological system, the future demand for antimony is highly dependent on past demand trends. Furthermore, in-use stocks of metals represent potential future emission or waste flows, and investigating their size and dynamics allows for estimating the quantity of antimony that may become available for future recycling. The combination of future demand scenarios, outlook on primary supply, and potential for future recycling gives indications on the risk of future demand-supply mismatches. In other words, dynamic MFA allows for assessing the future criticality of antimony.

The main difference between static and dynamic material flow modeling is that stocks are included in the latter case (van der Voet 1996). Production, F&M, and Waste Management processes primarily transform materials and it is assumed that no significant quantities are stored at those stages. Dynamic metal flow modeling therefore focuses on the stock changes at the Use stage. The static model built with the STAN software was transformed into a relational data model (in Microsoft Excel) to perform retrospective and prospective dynamic analyses. Only mean values from the static MFA were included in the dynamic MFA. The main inputs to the dynamic model are inflows to the Use phase (demand-driven model). Transfer coefficients from other life cycle stages are assumed to be constant over time. Past inflows to Use are reconstructed based on available data, whereas demand scenarios are used to assess future flows into Use. Past and future outflows from Use are modeled using delay and leaching models.

As some antimony-containing products can remain in use for a relatively long time (e.g. lead alloys used in roofing), the time period used for the retrospective analysis is 1900-2011. A target year of 2050 was identified as a relevant time horizon for prospective MFAs of metals (e.g., Hatayama and colleagues 2010; Nassar and colleagues 2012; Cullen and Allwood 2013), and it is used for this study.

5.2 RETROSPECTIVE DYNAMIC MFA (1900-2011)

5.2.1 PAST INFLOWS TO USE

Global antimony consumption by applications for the period 2000-2011 is estimated by Roskill (2011). Before 2000, information is scarce and scattered among various sources. The inflows of antimony into each end-use category for the period 1900-2011 were estimated using the following data sources and assumptions:

1. The sum of estimated yearly primary and secondary supply is used as a proxy for yearly consumption. Estimated end-use shares are multiplied by yearly consumption to give yearly inflows to each end-use sector.
2. Yearly primary production used as given by the U.S. Geological Survey (2014a) for the period 1900-1969 and by the British Geological Survey (2015) for the period 1970-2011.
3. As far as historical end-use shares are concerned, no database exists for the global situation before 2000. However, given that the USA and Europe accounted for respectively a half and a third of the global antimony consumption until 2000 (Butterman and Carlin 2004) and assuming that end-use

shares for both regions were comparable during that period, global end-use shares for the period 1975-2000 are approximated using U.S. figures (U.S. Geological Survey 2014a). To estimate end-use shares before 1975, a combination of quantitative extrapolation (using the most fitting function) from U.S. end-use shares and qualitative information was used. According to Carlin (2006), antimony was mostly used in lead-acid batteries and other lead alloys until the 1970s. Demand for antimony in ammunition peaked during World War I and demand for lead-acid batteries took off in the following years. The latter decreased in the 1970s with the introduction of "low-maintenance" and "maintenance-free" lead-acid batteries, containing respectively less or no antimony. The decreasing antimony content in lead-acid batteries has however been, to an extent, offset by the global growth in demand for lead-acid batteries since the 1980s. Antimony-lead alloys were widely used in rolled and extruded products until the 1970s, but their use was then increasingly reduced in several applications (e.g. plumbing, ammunition, solder) due to health and environmental concerns (Tukker and colleagues 2001; UNEP 2010b). As in the case of lead-acid batteries, the global consumption of antimony for lead alloys started to increase again in the 1980s due to an increased demand from industrializing countries. End-use shares for glass & ceramics and other non-metallic uses are assumed to be constant between 1900 and 1970.

4. Traditionally, secondary antimony has mainly come from the recycling of lead-acid batteries (European Commission 2014a). Small amounts of antimony are also recovered through the recycling of other alloys. Non-metallic applications suffer from low recycling rates, and antimony used in those products mostly ends up in landfills. In the absence of information on recycling rates of lead products throughout the 20th century, it is assumed that recycling rates increased linearly since 1900 to reach their current levels (Table 13). The initial value is set at to 10% for metallic applications, and 0% for other products. Landfill/incineration ratios for the remaining waste streams are assumed to be identical to current ones.

Table 13: Recycling rates used for the period 1900-2011

	1900	1920	1940	1960	1980	2000	2011
Lead-acid batteries	10%	19%	30%	41%	53%	64%	70%
Other alloys	10%	17%	27%	36%	46%	55%	60%
Flame retardants	0%	2%	4%	5%	7%	9%	10%
PET	0%	2%	4%	5%	7%	9%	10%
Glass & ceramics	0%	2%	4%	5%	7%	9%	10%
Other non-metal	0%	0%	0%	0%	0%	0%	0%

Based on these considerations, the evolution of the global antimony consumption for different end-use categories is reconstructed as in Figure 16. Given the number of approximations and assumptions made, this picture should not be taken as an accurate representation of the antimony consumption since 1900, especially end-use shares before 1970. However, it is believed that the level of accuracy achieved is sufficient to reveal trends in demand and estimate current in-use stocks.

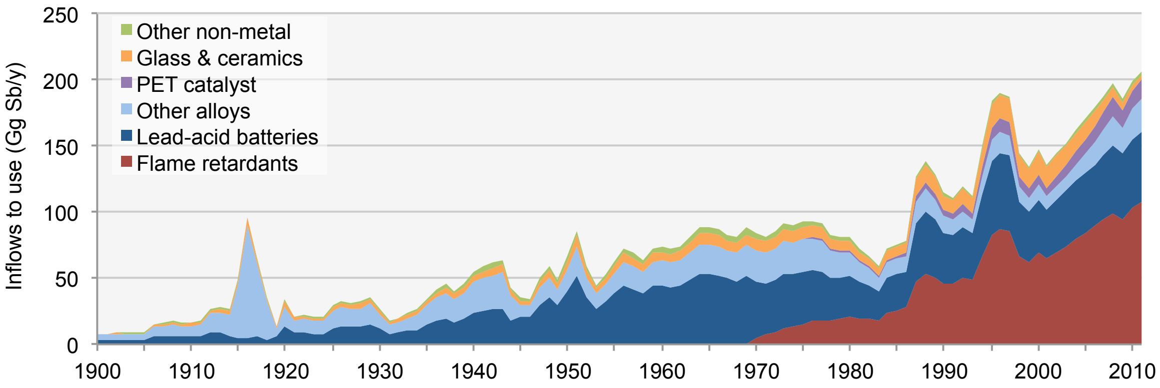


Figure 16: Estimated antimony consumption per end-use category (1900-2011)

5.2.2 PAST & CURRENT ANTHROPOGENIC ANTIMONY CYCLE

Dynamic stock model

Antimony contained in products entering service resides in the Use phase for some time, becoming part of the in-use stock, before being discarded as end-of-life flows or emitted to the environment as consumptive losses. Relations between inflows to use, residence time, in-use stocks, end-of-life flows and consumptive losses were described in Section 3.1.3. In order to fit the investigated system, Eqs. (2)-(6) were modified as follows:

$S_{i,t+1}$, the in-use stock of Sb in end-use category i at time $t + 1$, is estimated in discrete time steps as:

$$S_{i,t+1} = \sum_{t=1900}^{2011} \left((1 - d_i) \times U_{i,t} - outflow_{i,t}\right) + S_{i,0} \tag{7}$$

where T_0 is the time of the initial time step, T is the current time step, d_i is the dissipative factor for end-use category i, $U_{i,t}$ is the amount of Sb entering use in end-use category i at time t, $outflow_{i,t}$ is the amount of antimony leaving the in-use stock of end use category i at time t as a result of delay and leaching processes, and $S_{i,0}$ the stock at the initial time step. Levels of consumption before 1900 are considered as negligible, so that $S_{i,0} = 0$. As indicated by the factor "$(1 - d_i)$", it is assumed that Sb used in inherently dissipative applications is essentially lost to the environment as soon as it enters the Use phase. It does not add to in-use stocks.

Outflows from the Use phase due to dissipative applications are therefore estimated for each dissipative end-use category as:

$$dissipation_{i,t} = (1 - d_i) \times U_{i,t} \tag{8}$$

In Eq. (7), $outflow_{i,t}$ can be expressed as the result of both delay and leaching processes:

$$outflow_{i,t} = delay_{i,t} + leaching_{i,t} \tag{9}$$

with

$$delay_{i,t} = \left((1 - d_i) \times U_{i,t}\right) * f_i \tag{10}$$

where f_i is the probability density of the lifetime distribution function for end-use category i, with the symbol “*” denoting a convolution.

$$leaching_{i,t} = (l_i + w_i) \times S_{i,t} \tag{11}$$

where $S_{i,t+1}$, the in-use stock of Sb in end-use category i at time t, l_i and w_i are the leaching factors to the environment and to waste management for the end-use category i, respectively

Therefore, S_{t+1}, the total in-use stock at time $t+1$ is estimated using the following formula:

$$S_{t+1} = \sum_{i=1}^{A} \sum_{t=1900}^{2011} \left((1-d_i) \times U_{i,t} - \left(\left((1-d_i) \times U_{i,t} \right) * f_i \right) - \left((l_i + w_i) \times S_{i,t} \right) \right) + S_{i,0} \tag{12}$$

where A is the number of different end-use categories.

Estimation of parameters

Different lifetime distributions f, dissipative factors d, and leaching factors l and w were used for each end-use category, based on various sources and assumptions (Figure 17 & Table 14). Lifetime distributions are assumed to follow a Weibull distribution, as it has been shown experimentally to provide a good fit for many types of products (Melo 1999).

Figure 17: Assumed lifetime distribution of antimony end-use categories

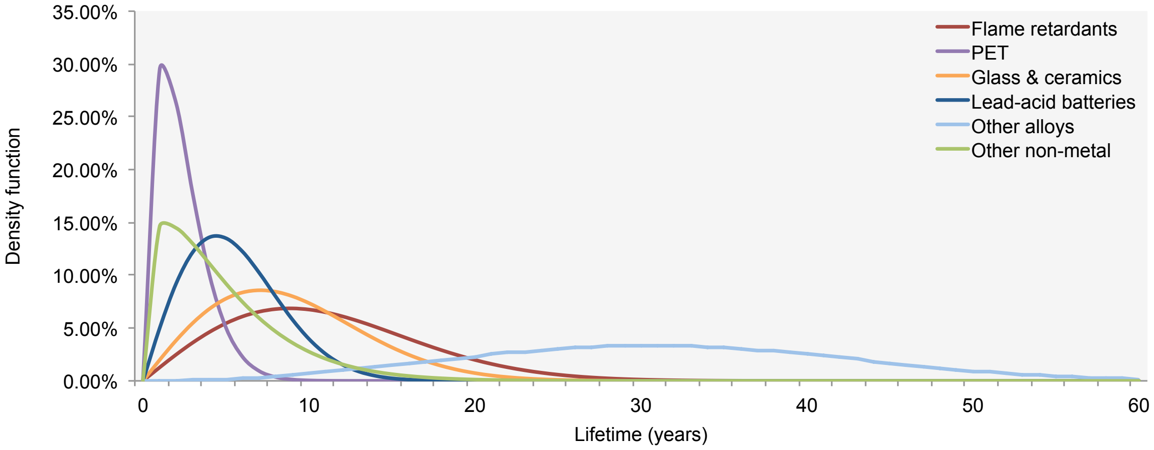


Table 14: Estimated dissipative and leaching factors for antimony applications

End-use sector	Application		Consumptive losses: Dissipative factor d_i (Fraction of the inflow)	Leaching to environment factor l_i (Fraction of the stock)	Leaching to waste factor w_i (Fraction of the stock)	References
Metallic products	Lead-acid batteries	SLI	–	0	–	Tukker et al. (2001)
		Stationary	–	0	–	Tukker et al. (2001)
	Lead alloys	Rolled & extruded lead	–	8E-05	–	Tukker et al. (2001)
		Ammunition	5E-01	–	–	Tukker et al. (2001)
		Other	–	0	–	Assumption
	Other alloys		–	0	–	Assumption
Flame retardants	EEE		–	1E-04	–	EU (2008)
	Cars		–	1E-04	–	EU (2008)
	Building materials		–	1E-04	–	EU (2008)
	Other		–	1E-04	–	EU (2008)
Other	Polymerization catalyst		–	0	4E-05	EU (2008)
	Heat stabilizer		–	0	0	EU (2008)
	Glass		–	0	0	EU (2008)
	Ceramics		–	0	0	EU (2008)
	Pigments		5E-01	–	–	Ayres & Ayres (1994)
	Brake linings		7E-01	–	–	Månsson et al. (2009)
	Lubricants		5E-01	–	–	Assumption
	Other non-metal		1E+00	–	–	Assumption

Below, data sources and assumptions used to estimate lifetime distributions, dissipative factors, and leaching coefficients are described for each end-use category:

- Flame retardants: Antimony-containing flame retardants are mostly used in electrical and electronic equipment (about 75% of the Sb use in this category, mainly in housings, cable sheathings and printed circuit boards), passenger cars (about 10%, mainly in seat housings) and building materials (about 10%, mainly in insulation and lining). In their dynamic MFA of brominated flame retardants in Switzerland, Buser and colleagues (2007) used average lifetimes of 7, 12 and 30 years for EEE, cars and building materials, respectively. Using the relative share of each product type as weighting factor results in an average lifetime of about 9 years. For this study, it is assumed that the lifetime distribution for this end-use category fits a Weibull distribution with the scale parameter $\alpha=2$ and the shape parameter $\beta=3$. Most of the products in which antimony is used as a flame retardant are not normally subject to weathering. Furthermore, ATO has a low volatility and low water solubility, so that consumptive losses for this application sector are likely small. An environmental leaching factor of 0.01% as assumed in the EU risk assessment (EU 2008), is used. No leaching in wastewater was documented.
- Lead-acid batteries: About 90% of the lead-acid batteries produced worldwide are of the SLI type, for which an average lifetime of 3-5 years is usually assumed (Mathys and colleagues 2007; Mao and colleagues 2008b; Harper and colleagues 2014). Stationary batteries account for the rest and usually stay in use for 8-15 years (Mao and colleagues 2008b). A Weibull distribution with $\alpha=2$ and $\beta=1.3$ is used for the dynamic stock model. No emissions of lead during the use of lead-acid batteries are reported in the literature (Tukker and colleagues 2001), and it is assumed that this is also the case for antimony. Therefore, all antimony used in this category will eventually be transferred to the Waste Management phase.
- Other alloys: It is estimated that rolled and extruded lead products account for three fourths of the antimony consumption in this category, primarily as lead sheets in buildings. Ammunition comes second, with about 10% of the Sb use in non-battery alloys. The remained is used in solders, bearings, type metal, pewter, etc. Tukker and colleagues (2001) consider an average lifetime of 25 years for rolled and extruded lead products, while Mathys and colleagues (2007) assume it to be 40 years. Mao and colleagues (2008) use a lifespan range of 10-50 years for lead pipes and 20-100 years for lead sheets. Ammunition often remains in the Use phase for less than a year. Products belonging to this category therefore have very different lifetimes. It is assumed that a Weibull curve with $\alpha=2.75$ and $\beta=1.3$ fits the lifetime distribution of antimony used in other alloys. Significant consumptive losses occur in this category. Ammunition is an inherently dissipative application when it is used outdoors, but bullets may be collected and enter the Waste Management stage when they are used in indoor shooting ranges. Furthermore, it is likely that a significant portion of the ammunition produced will in fact not be used and will be recycled. For these reasons, it is assumed that only half of the antimony used in ammunition will be dissipated. Similar assumptions were used by Tukker and colleagues (2001). Also, rolled & extruded lead products are often exposed to weathering and antimony may therefore leach into the environment. As estimated for lead by Tukker and colleagues (2001), it is assumed that 0.008% of the in-use stock of antimony in rolled & extruded lead products leaches into the environment each year. It is considered that other applications using antimony alloys are not dissipative and not subject to corrosion. Lacking information on the evolution of relative end-use shares since 1900 within this category, they are assumed to have remained the same until now, with an exception for the period 1912-1918, where the surge in Sb production reflects the dramatic increase in ammunition production before and

during wartime. The total amount of antimony above the 'baseline' demand for this sector is assumed to have been used in ammunition and lost into the environment.

- PET: An average lifetime of 1 year for PET bottles and 3 years for polyester textiles is assumed by Mathys and colleagues (2007). Using the relative share of both applications as a weighting factor gives an average lifetime of 2 years. It is assumed that the lifetime distribution for this end-use category fits a Weibull distribution with α=1.5 and β=0.5. Consumptive losses from PET mainly occur to wastewater during the washing of polyester textiles (65% of the Sb use in this category). A waste leaching factor of 0.0036% as assumed for the EU Risk Assessment is used (EU 2008a).
- Glass & ceramics: According to Mathys and colleagues (2007), antimony-containing glass and ceramics products have an average lifetime of 7 years. The lifetime distribution for this category is assumed to fit a Weibull curve with α=2 and β=2. Consumptive losses from this glass & ceramics were considered as non-significant in the EU Risk Assessment (2008).
- Other non-metallic uses are mainly pigments, brake linings, lubricants, pharmaceuticals, pesticides, safety matches and fireworks. Those are mostly dissipative applications. Particularly, several studies have showed that brake linings were an important source of antimony in urban environments (von Uexküll and colleagues 2005; Mathys and colleagues 2007; Månsson and colleagues 2009). A dissipation factor of 50% is derived from Ayres and Ayres (1994) for pigments, while Månsson and colleagues (2009) estimate that 70% of Sb used in brake pads will be lost into the environment. It is assumed that half of the Sb used in lubricants will be dissipated. For others applications belonging to this category, dissipation is considered to be complete. A Weibull distribution with α=1.25 and β=1 is assumed, as most application within this category have an average lifetime between 1 and 7 years (Mathys and colleagues 2007).

Past and current end-of-life flows, in-use stock, and emissions

Estimated historical inflows to use, assumed lifetime distributions, and chosen dissipative and leaching factors can be used as in Eq. 11 to estimate the yearly in-use stocks, end-of-life flows, and losses into the environment since 1900 (Figure 18).

Due to the twentyfold increase in antimony consumption since 1900, in-use stocks have considerably increased. Interestingly, non-battery alloys (mainly Sb used in rolled and extruded lead products) dominated the in-use stock for most of the last century although less Sb is used in this application than in lead-acid batteries. This can be explained by the fact that antimony in rolled and extruded lead products remains in use for a much longer time than in batteries. With the decrease in the use of lead alloys for several applications since the 1980s and the discard of products that entered Use one lifetime ago, the stock of antimony used in other alloy products has decreased since 1980. On the other hand, the steep rise in Sb demand for flame retardants caused an equally steep increase in the societal stock of Sb in this application. As a result, flame retardants account for about half of the stock of antimony currently in use, followed by other alloys (25%) and lead-acid batteries (16%). In total, approximately 1800 Gg of antimony is currently in use, which represents about 23% of the cumulative primary production since 1900 (i.e., 7700 Gg), and is equal to the size of reserves estimated by the U.S. Geological Survey (2015).

Eventually, antimony flows out of the in-use stock as end-of-life products or as emissions. The distribution of end-of-life products over time follows that of inflows to use, with a time lag and a smoothened curve resulting from the buffering effect of in-use stocks. Due to the relatively high recycling rates for metallic applications, a significant portion of antimony in those end-of-life flows has been recycled. It is interesting to note that the overall end-of-life recycling rate (percentage of antimony in all discards that is recycled) has increased until the mid-1970s before decreasing as a result of the increasing share of non-metallic applications, for which recycling rates are much lower. Thus, the amount of antimony being landfilled is growing rapidly since the 1990s. Overall, most antimony used by anthropogenic activities flows linearly and rapidly through the economy, from cradle (ore) to grave (landfill). Between 1900 and 2011, a cumulative sum of 4600 Gg Sb has been deposited in landfills globally.

Significant amounts are also emitted into soil (not including landfills), air and water during the production, use and disposal of antimony. The use of huge amounts of antimonial lead ammunition during the Great War resulted in emissions into soils peaking at 80 Gg Sb per year. Currently, about 20 Gg Sb is emitted into the biosphere each year, mostly in soils (83%) but also in the atmosphere (15%). In total, approximately 1300 Gg Sb has been released into the environment as emissions over the period 1900-2011, mainly in soils (76%).

In sum, about 7700 Gg Sb was mined since 1900, a quarter of which (1800 Gg) still remains in use. The rest (5900 Gg) has been lost into the environment over time, mainly in landfills (78%) but also as emissions (22%).

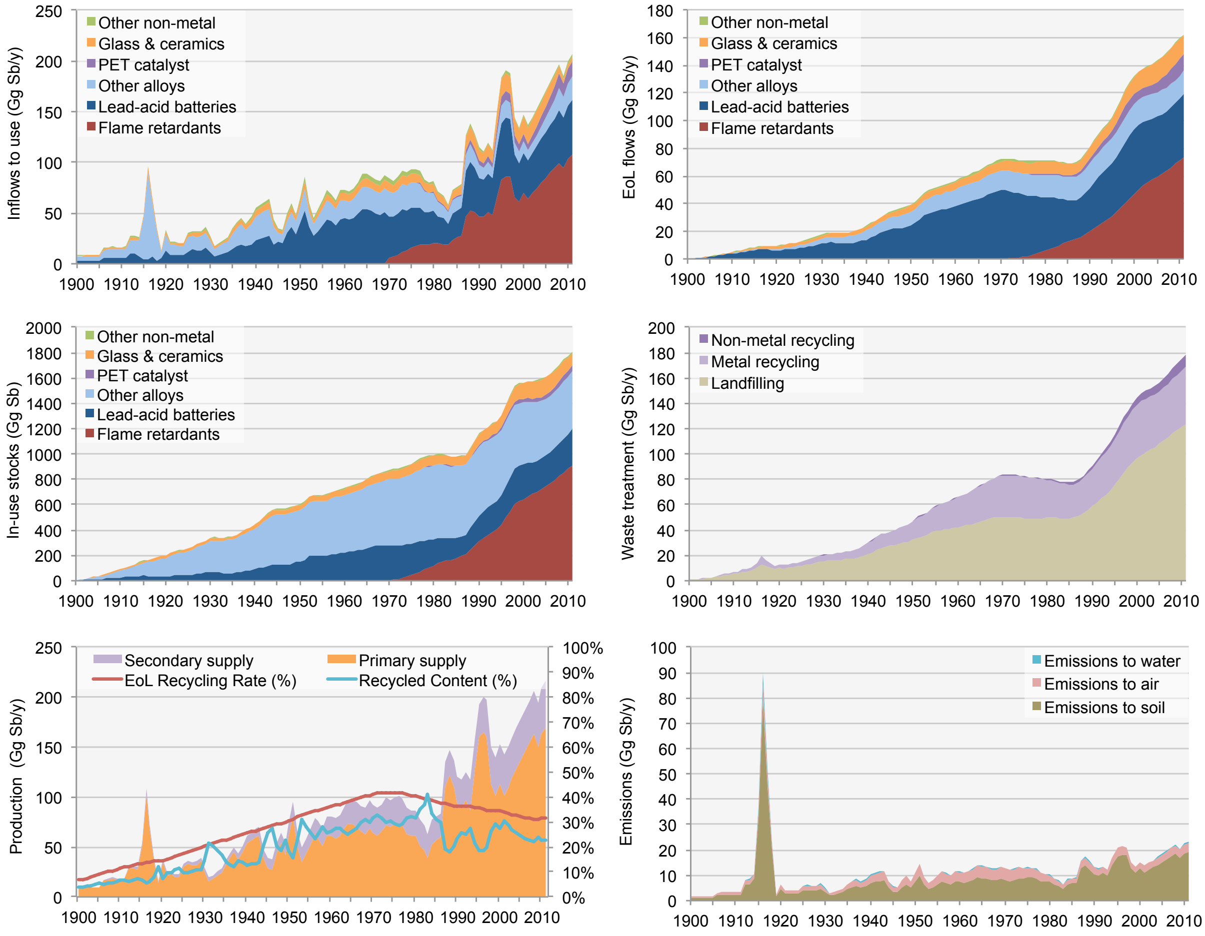


Figure 18: Inflows to use, end-of-life flows, in-use stocks, waste generation, Sb production, and emissions since 1900 according to the dynamic MFA model

5.2.3 COMPARISON WITH PREVIOUS STUDIES

No study on the global flows and stocks of antimony has previously been published. Studies at the country- and city-level have however been conducted; for the USA (Carlin 2006), Switzerland (Mathys and colleagues 2007), Japan (Tsunemi and Wada 2008), and Stockholm (Månsson and colleagues 2009). Those are all high-income regions. The purpose, approach and main findings of those four studies are summarized in Table 15. While a detailed overview of the methodology and data sources used was easily accessible in the MFA studies for Switzerland and Stockholm, they were not described in the U.S. study and only in Japanese in the MFA for Japan.

Table 15: Review of existing antimony MFA studies

Study	Purpose	Approach	Main findings
Carlin 2006: *Antimony Recycling in the USA in 2000*	Assess the flows of antimony in the US in 2000, from mining through its uses and disposal with emphasis on recycling	Static modeling using a top-down approach to identify the main source of recycled antimony, calculate the old scrap ratio (share of old scrap in the total scrap flow), and estimate the old scrap recycling efficiency for the year 2000	About 95% of old antimony scrap was generated from used lead-acid batteries in 2000 The old scrap ratio was of approximately 80% The old scrap recycling efficiency was about 89%
Mathys and colleagues 2007: *Antimony in Switzerland: A Substance Flow Analysis*	Identify the most important areas of application for antimony, and determine the source and quantities of antimony released into the environment	Static modeling using a bottom-up approach to quantify the inflows, stocks and outflows of antimony for each application for the year 2001	About 90% of antimony that is imported into Switzerland is subsequently exported as products and wastes. About 74% of the antimony remaining in Switzerland is landfilled, 20% is dissipated to the environment and 10% increases the in-use stock (consisting of 73% of flame-retarded products) The main sources of emissions to the environment were brake linings (17 tons) and shooting ranges (16.5 tons)
Tsunemi and Wada 2008: *Substance Flow Analysis of Antimony for Risk Assessment of Antimony and Antimony Compounds in Japan*	Quantify inflows, stocks and outflows of antimony in order to perform a risk assessment of antimony and antimony compounds	Dynamic modeling using a top-down approach to estimate the amounts of domestically supplied antimony, stocked antimony, and generated outflows in the form of air emissions, for the period 1970-2015 Sensitivity analysis to identify how the uncertain parameters affect the model outputs	Estimated amount of domestic waste generated for 2015 was nearly equal to the amount of domestic supply for the same year Amount of recovered antimony in 2008 estimated to be over 3 times that amount in 2001, and it is strongly affected by waste management policies Main source of emission into the air is wear of brake linings
Månsson and colleagues 2009: *Sources of antimony in an urban area*	Analyze the urban sources of antimony in Stockholm in 2005, by estimating the stock of antimony in use and related flows and emissions	Static modeling using a bottom-up approach to quantify the inflows, stocks and outflows of antimony for each application for the year 2005	In-use stock is dominated by flame-retarded goods, cable shielding, glass and ceramics, and batteries Major source of emission identified is wear of brake linings

Similarities and differences between the four studies can be identified, in terms of purpose, approach and main findings. Carlin's main focus is the resource efficiency of the U.S. anthropogenic antimony cycle, while the three other studies put more emphasis on the emissions of antimony to the environment generated during use of antimony-containing products. It can be argued that Carlin's methodology is the least sophisticated, consisting of a simple, steady-state model based on national statistics on antimony supply and demand and ignoring stock, trade and losses. Nevertheless, it still provides added value compared to the other studies, in terms of the insights it provides on sources of recycled antimony, ratio of new scrap to old scrap, and old scrap recovery efficiency. The other studies highlight and quantify the dissipative uses of antimony, identifying brake linings wear as the main source of antimony emissions. In the study for Switzerland, emissions from ammunition are almost equal to those from brake linings, while this end-use results in much lower emissions in the study on Stockholm (possibly due to the fact that shooting ranges are generally located outside of cities) and is not included in the Japanese analysis.

In order to be able to quantitatively compare the results from previous studies with those of the current study for the year 2011, six key mass flow indicators – inflows to use, end-of-life flows, in-use stock, consumptive losses (emissions from use), secondary production, landfilling – are normalized with population (Figure 19) and with GDP of the year of estimation, expressed in constant US dollars (PPP 1990$), i.e. adjusted to inflation (Figure 20). U.S., Swiss, and Japanese studies give single scores for each indicator, while results for Stockholm are accompanied by uncertainty ranges ("*/ 1.7" for inflows to use, EoL flows, consumptive losses, and landfilling; "*/ 4" for in-use stock; and "*/ 10" for secondary production). The uncertainty range is not included in the quantitative comparison with other studies. Besides indicators from those four studies, an additional Sb in-use stock estimation for Japan in 2000 (Murakami 2006) is included.

Comparison of per capita flows/stocks reveals considerable variations between estimates, up to a factor 7 for inflows into use, 6 for end-of-life flows, 4 for in-use stocks, 10 for emissions from use, 5.5 for secondary production, and 3.5 for landfilling. Results from the MFA model are systematically below those from previous studies with one exception, i.e., per capita end-of-life flows estimated for Stockholm. On the other hand, Switzerland has the highest score for three out of four indicators for which a Swiss estimation exist (and the second highest score for the fourth indicator). This can be explained by the fact that material use is usually higher in wealthy regions than in poor ones. Gerst and Graedel (2008) indeed observed that estimated per capita in-use stocks of aluminum, copper, iron, lead, and zinc are five to ten times higher in more-developed countries (Australia, Canada, EU-15, New Zealand Sweden, Switzerland, the USA and Japan) than in less-developed ones. Considering that the poor are much more numerous than the rich on a global level, it seems logical that world average per capita material use is much lower than per capita material use in highly developed areas. It is therefore not a surprise that indicators of global Sb use estimated in this study are lower than those estimated for the USA, Japan, Switzerland, and Stockholm, all being highly developed regions. For instance, the global per capita in-use Sb stock (0.3 kg/cap) is two to five times lower than that estimated for the USA, Japan, Switzerland and Stockholm, which is in line with the findings of Gerst and Graedel (2008).

Much less variation is observed in per unit GDP flows/stocks, with differences of less than a factor two for all indicators except consumptive losses, which is acknowledged as a very uncertain indicator. This tends to confirm the relation between wealth and Sb use raised in the previous paragraph. However, values estimated for Stockholm contradict this relation, as per GDP inflows to use, EoL flows, in-use stocks, emissions from use and secondary production are considerably lower than values for both wealthy areas, previously estimated, and for the world, estimated in this study. This suggests a systematic underestimation in results of the study by Månsson and colleagues (2009). Overall, per GDP Sb flows quantified in this study are very similar to that of Tsunemi and Wada (2008) for all indicators except emissions from use. For this particular metric, the estimated value lies between previous estimates. Per GDP in-use Sb stock estimates are remarkably similar, and the value for Stockholm diverges the most. When plotted together, the correlation between Sb in-use stocks and GDP is very high (0.99) (Figure 21). Such a high correlation between GDP and in-use stocks was previously observed by Rauch (2009) for aluminum (R^2=0.99, n=8), copper (R^2=0.94, n=18), zinc (R^2=0.81, n=6), and iron (R^2=0.85, n=7).

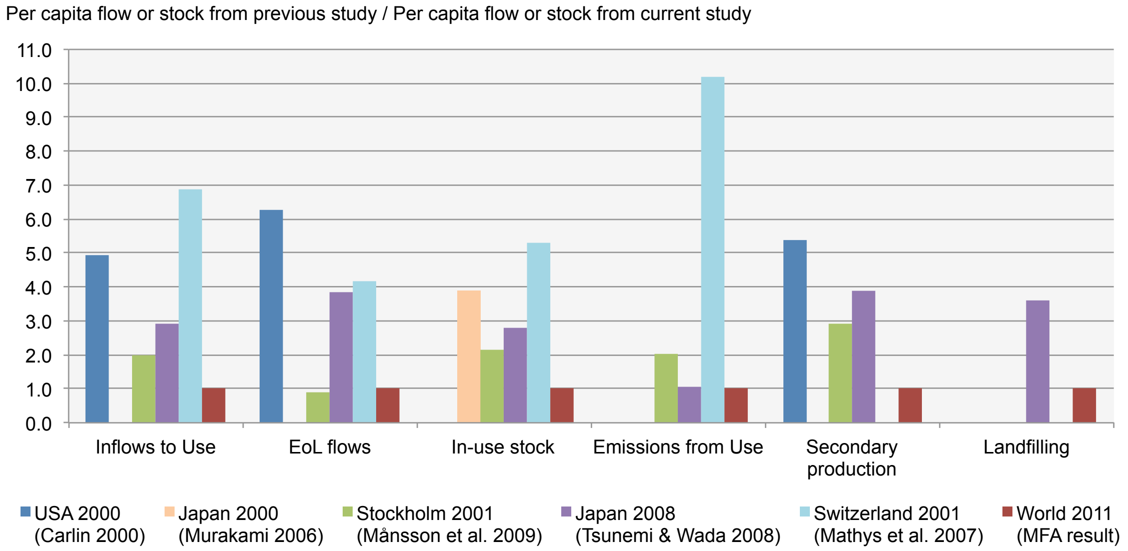


Figure 19: Comparison of estimated Sb flows and stocks with results from previous studies, using population as a normalization basis. Population of respective cities/countries were taken from OECD (2005), World Bank (2014), and UN (2014)

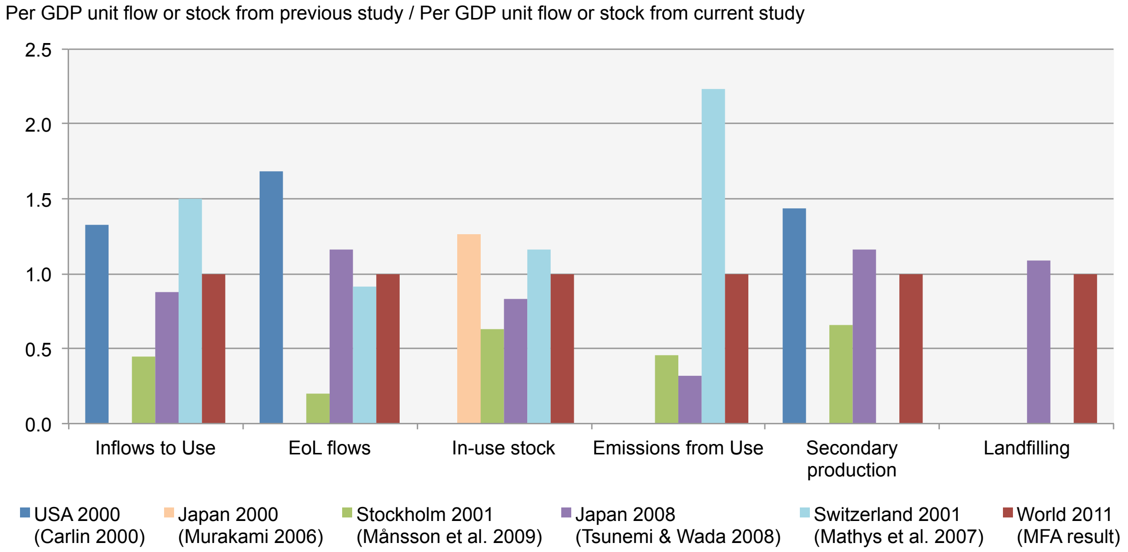


Figure 20: Comparison of estimated Sb flows and stocks with results from previous studies, using GDP as a normalization basis. GDP of respective cities/countries in US$ were taken from OECD (2005), World Bank (2014), and UN (2014) and converted into 1990 US$ using an online converter (Areppim 2015)

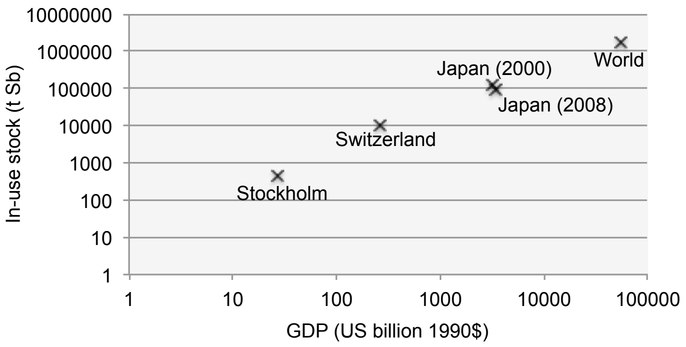


Figure 21: Relation between GDP and estimated in-use Sb stocks. The value for the world was estimated in this study, while values for Stockholm, Switzerland, and Japan were estimated in previous studies (Månsson and colleagues 2009; Mathys and colleagues 2007; Murakami 2006; Tsunemi and Wada 2008)

Based on the comparison of this study's results with those of previous antimony MFA studies, the following conclusions can be drawn:

- There is a much greater similarity in results normalized with GDP than with population, indicating that a region's wealth contributes more to its antimony consumption than the size of that region's population. A corollary of this observation is that GDP projections are a better indicator than population projections to develop scenarios on future antimony demand;
- In particular, a very high correlation is observed between per capita in-use Sb stock and GDP. Among other implications, this could be used to quickly estimate the size of a region's in-use Sb stocks based on that region's GDP;
- Among the six indicators included in the comparison, highest variations between estimates exist for Sb emissions during use. This confirms that a high uncertainty accompanies the estimation of those flows;
- Overall, results from the current study are in the same magnitude as those of previous studies, when compared on a GDP basis. This suggests that the MFA model is robust and its results reliable.

5.3 PROSPECTIVE DYNAMIC MFA (2012-2050)

The aim of the prospective dynamic MFA is to model the future anthropogenic antimony cycle according to different demand scenarios and analyze its results from the perspectives of circularity, permeability, and supply outlook. Based on a review of demand trends for each end-use, three demand scenarios are developed: (i) extrapolation based historical relationship between world GDP and Sb consumption; (ii) assumption that the global demand trends will follow those observed in developed countries since the 1990s; (iii) substitution of antimony where and when it is considered possible.

5.3.1 DEMAND TRENDS

Without the emergence of a disruptive technology requiring the use of large amounts of antimony, the future global demand for antimony will remain very dependent on trends in flame retardants and lead-acid batteries as those two end-use categories together account for almost 80% of the total consumption. Therefore, it is particularly important to understand historic demand patterns and assess possible future developments for those two applications, as well as to identify potentially disruptive antimony-consuming technologies. Figure 22 depicts the evolution of the Sb consumption by end-use category over the period 2000-2011, taken as a basis to assess demand trends.

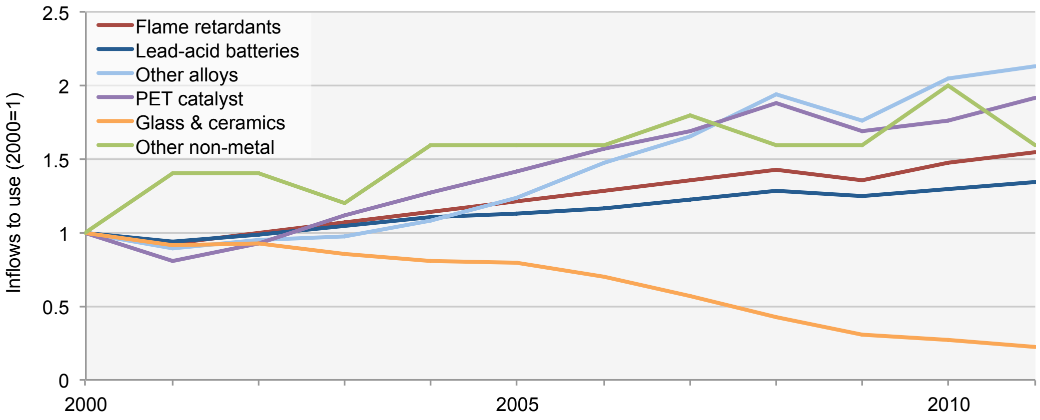


Figure 22: Relative evolution of Sb demand by end-use category, 2000-2011 (Roskill 2012)

Flame retardants

Demand for antimony in flame retardants has been increasing rapidly since the 1970s and it has grown by 55% between 2000 and 2011, representing an average annual growth rate of 5% over this period (Roskill 2012). Most of this growth has taken place in Asia (mainly China, Japan and South Korea), and the region accounted for about 65% of the global Sb demand in flame retardants in 2011 (Roskill 2012). Electrical and electronic equipment – the main end-use for antimony-containing flame retardants – are mostly manufactured in Asia, so that antimony consumed as flame retardant in this region will often end up as waste or emissions in other continents.

The future demand for antimony in flame retardants depends on several factors, including the global demand for flame retardants, the competition between different compounds in terms of price and performance, and industrial and environmental regulations. The global demand for flame retardants amounted to almost two million tons in 2011, with a share of about 7% for antimony oxides used in synergy with halogenated compounds (Townsend Solutions 2012), increased from 6% in 2004 (BRGM 2012). Market specialists forecast an average annual growth rate of 5% until 2016 for the total consumption of flame retardants, mainly as a result of increasing substitution of less-flammable materials by plastic products in several applications, and of more stringent safety and flammability standards in Asia, Latin America, and Eastern Europe (Freedonia 2013). Above average growth is anticipated for non-halogenated chemicals such as alumina trihydrate (currently the market leader, with a share of about 40%), boron compounds and magnesium hydroxide (Freedonia 2013). Below average growth is forecasted for brominated flame retardants (BFRs), which have already been phased out of several applications for economic, health, and environmental reasons. Empirical analysis suggests that antimony content in WEEE plastic has decreased in the past years due to the decreased use of BFRs (Wäger and colleagues 2010a). The U.S. Geological Survey (2015) reports that the flame retardant industry began substituting ATO with less expensive compounds in 2011 following the 2010 price peak and notes that, although prices have since been decreasing, it is 'unclear if consumers that had substituted other materials for antimony trioxide would switch back' (U.S. Geological Survey 2015). Furthermore, a trend towards using reactive instead of additive BFRs has been observed in the EEE industry (Groß and colleagues 2008), which could further reduce the demand for antimony in this sector as it is mostly applied in additive uses (Morf and colleagues 2003). On the other hand, the addition of antimony compounds in halogenated flame retardants (HFRs) greatly enhances their efficiency, which allows for using two to three times less HFRs for an equivalent performance (Dufton 2003). Also, more environmentally friendly BFR formulations are being developed and could gain market share in the future (Herzke and colleagues 2010). Lastly, the European Flame Retardants Association affirms that they 'see no major trend in replacing BFR-ATO' (EFRA 2014).

Contrasting trends can therefore be observed in the consumption of antimony in flame retardants, and it is difficult to assess the future demand for this end-use category. Ongoing substitution of BFRs in several applications suggests that the relative share of antimony oxides in the total flame retardants consumption will decrease in the future. However, the strong growth of the world demand for flame retardant could result in an increasing demand for antimony in absolute terms.

Metallic applications

As regards lead-acid batteries – the second largest application for antimony – trends are also contrasted. On the one hand, the increased need for maintenance due to the presence of antimony in the plate grids fostered its substitution with calcium. As a result, the average Sb content in lead alloys used for lead-acid batteries has decreased from 8-12% in the 1960s to 0.5-3% nowadays (Linden and Reddy 2002; Grund and colleagues 2011) in industrialized countries. In emerging countries, lead-acid batteries containing on average 10% Sb are still used (BRGM 2012). According to Carlin (2006), 'industry sources [in the USA] believe the antimony level in lead-acid batteries will reach zero by 2020'. However, antimony-containing batteries have a significantly longer lifetime than those containing calcium and are therefore preferred for some industrial uses (Butterman and Carlin 2004). Despite the reducing Sb content in lead-acid batteries used in industrialized nations, the global consumption for this end-use has been increasing over the last decades (35% between 2000 and 2011), primarily due to the global growth of the automotive sector in non-OECD countries. Rates of vehicle ownership are still growing almost everywhere and are predicted to rise very rapidly in countries such as China and India. For instance, the in-use stock of cars in China is forecasted to reach 650 million tons in 2050, as compared to about 200 million tons nowadays (Huo and colleagues 2006). Furthermore, lead-acid batteries are the most used battery system in electric and hybrid vehicles as it is a mature and low cost technology (ALABC 2013), and they are also widely used to store energy produced with renewable sources (BRGM 2012). A low carbon economy could therefore have high needs for lead-acid batteries and thus antimony. The future demand for antimony in lead-acid battery therefore depends on the extent to which antimony is substituted in lead-acid batteries, as well as on the global demand for lead-acid batteries.

The demand for antimony in other alloys has more than doubled between 2000 and 2011, mainly due to the build-up of infrastructure in Asia (Sb-Pb alloys used in rolled and extruded lead products for buildings). In industrialized countries, the use of lead alloys has been reduced in several applications (e.g. plumbing, ammunition) due to environmental regulations. In the future, demand for antimony in this end-use category will likely increase, unless more stringent environmental regulations are implemented in industrializing countries.

Other applications

Concerns over potential health hazards due to leaching of antimony from polyester products (especially food and water containers) have stimulated the research for antimony-free PET catalysts based on germanium, titanium, aluminum, magnesium or phosphorus. Several of such antimony-free polymerization catalysts have been on the market for more than a decade but have struggled to gain market acceptance due to concerns over the impacts that these catalysts may have on PET resin color, line yield and quality (Weissman 2014). Furthermore, Sb levels measured in foodstuff and water contained in PET containers are considered too low to represent a health hazard (Tylenda and Fowler 2007). As a result, demand for Sb in this end-use has doubled between 2000 and 2011 and will likely follow the growth of the PET market in the future.

The use of antimony in the glass industry has been greatly reduced in the last decade (-90% between 2000 and 2011), mainly due to the phasing out of CRT monitors. Its use in ceramics has increased (+50% for 2000-2011), but with a limited impact on the total Sb demand due to the relatively low volumes used in this end-use. Overall, glass and ceramics will most likely remain a minor end-use in the future.

The share of other non-metallic applications (pigments, lubricants, brake linings, safety matches, pharmaceuticals, pesticides, etc.) in the total Sb demand should remain small. The use of antimony in semiconductors could increase significantly, but with little impact on the total demand as only 25 tons were used worldwide for this applications in 2005 (Mathys and colleagues 2007).

Future applications

In their study on raw materials for emerging technologies, researchers from the Fraunhofer Institute (Angerer and colleagues 2009) considered as low the requirements for antimony in emerging technologies at the horizon 2030. Only two were considered relevant for antimony:

- Micro-capacitors: The trend towards miniaturization of electronics has boosted the research for micro-capacitors to store energy. Tantalum has so far been the metal of choice for such applications, but the resulting high demand and high prices, as well as its status as a conflict mineral, have pushed the need for alternative solutions. Antimony-based micro capacitors provide a potential alternative and about 28 tons of antimony was consumed for this application in 2006. Angerer and colleagues (2009) forecast a modest growth in demand, reaching about 70 tons in 2030.
- Antimony tin oxide for transparent conducting films used as a substitute for indium tin oxide, with similar properties but lower prices and used in liquid crystal displays, plasma display, organic light-emitting diodes or thin-film photovoltaic cells. This is however a marginal technology and other substitutes such as aluminum-doped zinc oxide are used in mass applications.

Furthermore, antimony nanocrystals are a promising anode material for high-rate lithium and sodium ion batteries needed for a low-carbon society according to researchers from ETH Zurich and Empa (He and colleagues 2014; Walter and colleagues 2015). The technology is still at the fundamental research stage, and it should take another decade or so before it can enter the markets according to the head of research group (Rüegg 2014). It is roughly estimated that about 0.5 kilogram Sb would be needed per kilowatt hour in both Li- and Na-ion batteries (Walter 2014). Thus, about 12 kilograms Sb would be needed in a typical 24 kWh battery pack for a plug-in vehicle (e.g. Nissan Leaf), and about 43 kilograms for a 85 kWh battery pack such as used in the Tesla Model S. If all electric vehicles produced in 2015 – about 500000 electric vehicles according to Frost & Sullivan (2015) – were equipped with a 24 kWh battery pack using antimony nanocrystals as an anode material, about 6000 tons Sb would be needed. This represents about 3% of the yearly Sb consumption, which is significant but could likely be met by an increased supply without any great difficulty. On the other hand, if all 2 billion light duty vehicles forecasted to be in circulation in 2050 by the International Energy Agency (IEA 2015) used such a battery system, about 24 million tons Sb would be needed. This represents almost six times the reserve base as estimated by the U.S. Geological Survey (2009), suggesting that this technology could not power the entire fleet of vehicles in a highly electrical transport system due to resources constraints. This is however a static figure, not taking into account the potential expansion of the reserve base due to technological advances in mining and refining, the potential for increased recycling, nor the potential reductions in Sb content of the battery system due to technological developments.

5.3.2 DEMAND SCENARIOS

Scenario 1: "Business-As-Usual" (BAU)

This scenario is based on regression analysis on the historical relationship between Gross World Product (GWB, i.e. sum of gross national product of all countries) and Sb demand. The inflow of antimony into each end-use during the last 30 years is plotted against the GWP, expressed in constant 2014 US$. Parameters of best fitting curves are then used to extrapolate future inflows based on GWP projections. GWP for the period 1980-2011 is given by the International Monetary Fund (IMF 2014), and GWP projections from the consultancy PricewaterhouseCoopers (PwC 2015) are used. The regression model for each end-use category can be found in Appendix C.

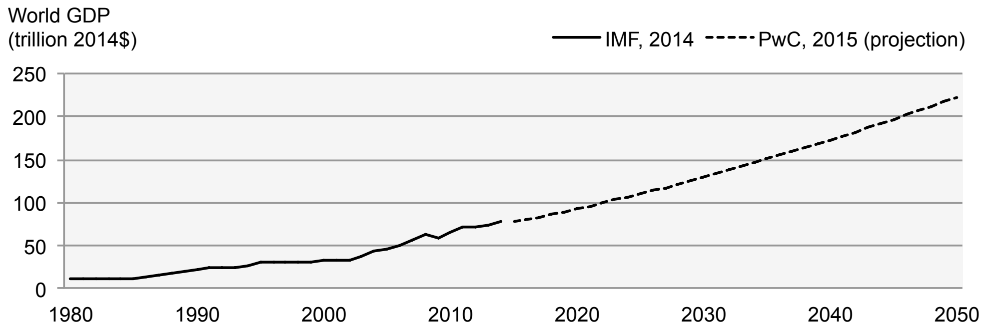


Figure 23: Historical and projected GWP used for the regression model in the BAU scenario

Scenario 2: "American World" (AW)

In this scenario, it is assumed that global demand will follow the trends observed in the USA since the 1990s, taken as proxy for demand patterns in Western countries in the absence of data for other nations (Figure 24).

A dichotomy in demand trends can be observed between emerging and industrialized regions since the 1980s. On the one hand, antimony consumption has strongly increased in emerging countries, and particularly in Asia where a large portion of the world polymer production takes places. On the other, antimony consumption tends to decrease in Western countries and a shift is observed in relative end-use shares, with those of flame retardants and, to a lesser degree, metallic products decreasing, and that of other applications increasing. In Europe, the USA, and Japan, concerns over the health and environmental impacts of lead, brominated flame retardants, and antimony have driven the development and implementation of substitutes for several applications: "maintenance-free" and "low-maintenance" lead-acid batteries, phase-out of several halogenated flame retardants, alternative PET catalysts and heat stabilizers, reduced use of lead alloys in several applications, etc. (BRGM 2012). The relocation of production capacity to Asia is also an important factor explaining the consumption reduction in Western countries and the decreasing share of flame retardants. The relative importance of delocalization or substitution effects in explaining Western demand patterns is difficult to assess.

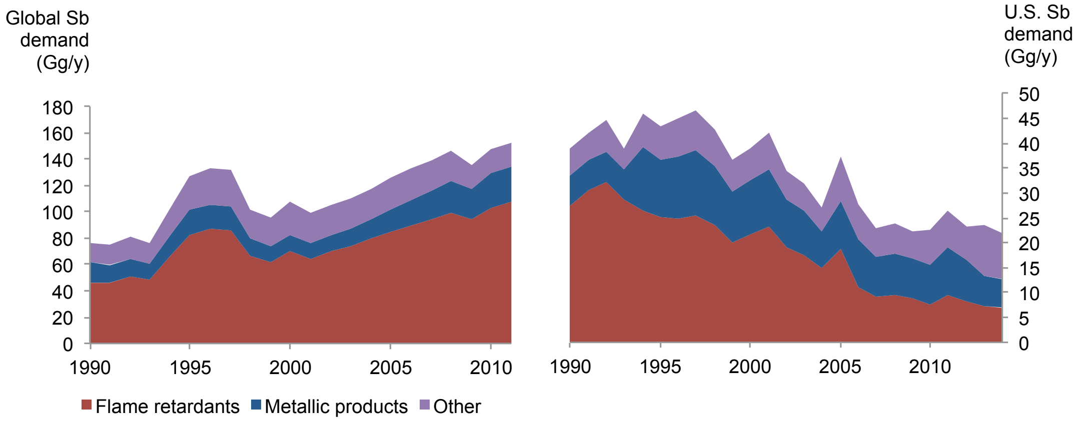


Figure 24: Estimated global Sb consumption 1990-2010 (left) & U.S. consumption 1990-2014 (U.S. Geological Survey 2014b) (right)

Scenario 3: "Maximum Substitution" (MS)

Material substitution of antimony compounds by alternative substances is possible for almost all applications without a significant decrease in the cost/performance ratio. It has already partly occurred for several end-uses, as a result of health and environmental concerns and volatile price levels. Similarly, functional substitution, i.e. the substitution of a product or a technology by another which fulfills the same function (Wäger and colleagues 2011b), has been observed in some applications. So far, global economic growth and rapidly increasing demand for antimony-containing products in emerging countries have offset substitution effects, so that global antimony consumption is still growing. With increasing substitution in the developing world and stabilization of the demand, the global consumption of antimony could be considerably reduced the future. Based on considerations of "when" and "where" (i.e., in which application) antimony can be substituted, a scenario assuming "maximum substitution" is developed.

In metallic applications various combinations of calcium, copper, tin, selenium and sulfur can be used as hardeners in lead alloys instead of antimony (U.S. Geological Survey 2015). The material substitution of antimony with calcium and tin in lead-acid batteries has begun in the 1970s, and alloys with very little Sb are nowadays used to produce lead-acid batteries in industrialized countries (typically less than 1%, as compared to 8-12% in the 1960s). Although alloys with about 10% Sb are reportedly still used in emerging countries, it can be assumed that levels will eventually also decrease due to the drawbacks of using Sb as an alloying element for this application. In the USA, lead-acid battery manufacturers believe that the antimony level in lead-acid batteries will reach zero by 2020 (Carlin 2006). Furthermore, an increasing share of alternative battery technologies (e.g. Li-ion, Ni-MH, Ni-Cd) will reduce the demand for antimony in this application (functional substitution). With regard to other metallic applications, tungsten is an alternative to antimony in ammunition, aluminum and organic polymers substitute for antimonial lead for cable covering, and tin-silver-copper solder can replace tin-antimony solder (Butterman and Carlin 2004; Schwarz-Schampera 2014). The substitution of antimony-lead alloys in several rolled and extruded products has occurred in the 1970s in industrialized countries. Overall, it is believed that antimony can be completely substituted in metallic applications in a relatively short time frame. For this scenario, a complete phase-out of antimony use in metallic applications by 2030 is assumed.

As far as the use of antimony compounds in flame retardants is concerned, several organic (mostly phosphorus- and nitrogen- based) and mineral (mainly aluminum hydroxide and magnesium hydroxide) compounds are widely accepted material substitutes (U.S. Geological Survey 2015). Some halogenated flame retardants using ATO as a synergist have been banned or voluntarily phased out and effectively replaced for environmental but also economic reasons. However, those substitutes have often an inferior performance and/or higher price compared to antimony-containing flame retardants (Schwarz-Schampera 2014). In particular, the BFR-ATO combination is still one the most cost-effective flame retardant system for ABS and HIPS polymers (widely used in EEE) according to the European Flame Retardants Association (EFRA 2014), which further states that 'alternatives often do not fulfill the same combination of functionalities as the BFR-ATO system'. It is therefore considered that antimony cannot yet be completely substituted in flame retardants, especially in EEE. However, with the continuous improvement of alternative systems pushed by environmental regulations and price volatility, the complete substitution of antimony appears feasible within a decade or two. In this scenario, a phase-out by 2040 is considered.

For most other non-metallic applications, material substitutes are also available and increasingly used. Compounds of chromium, tin, titanium, zinc, and zirconium substitute for antimony chemicals in enamels, paint, and pigments (U.S. Geological Survey 2015). Alternative compounds for heat stabilization in PVC contain barium, cadmium, calcium, lead, tin and zinc in various combinations (Butterman and Carlin 2004). Alternative PET catalysts have been developed and are increasingly used in some countries, such as germanium dioxide in Japan and East Asia and titanium in Japan. However antimony-free PET catalysts struggle to gain market acceptance due to concerns over the impacts that these catalysts may have on PET resin color, line yield and quality (Weissman 2014), so that antimony compounds should continue to dominate the market. No information was found on substitutes for antimony in the manufacture of glass and ceramic products. However, the consumption of Sb in those sectors has been decreasing over the last decades, mainly as a result of the functional substitution of CRT displays with LCD, and could reach negligible levels in coming years. With limited information over the substitution potential for non-metallic applications other than flame retardants, it is assumed here that the demand will remain constant, with the exception of the use of ATO as PET catalyst which follows the growth in demand for PET anticipated in the BAU scenario, and the use of antimony compounds in the glass and ceramics sector which is phased-out in 2020.

5.3.3 WASTE MANAGEMENT PARAMETERS

In all scenarios for the prospective MFA, recycling rate are assumed to develop linearly until 2050 to reach very high levels for metallic applications, and medium levels for flame retardants, PET, glass and ceramics (Table 16). For other non-metallic applications, mostly dissipative, recycling is assumed to be nonexistent. Landfill/incineration ratios for the remaining waste streams are assumed to be identical to current ones.

Table 16: Recycling rates used for the period 2011-2050

	2011	2020	2030	2040	2050
Lead-acid batteries	70%	75%	80%	85%	90%
Other alloys	60%	67%	75%	82%	90%
Flame retardants	10%	19%	30%	40%	50%
PET	10%	19%	30%	40%	50%
Glass & ceramics	10%	19%	30%	40%	50%
Other non-metal	0%	0%	0%	0%	0%

5.3.4 MODEL RESULTS

Scenario 1: "Business-As-Usual" (BAU)

In this scenario, based on regression between GDP and Sb demand, it is modeled that the inflow of antimony into all end-uses grows until 2050, except for glass and ceramics for which antimony consumption reaches zero in 2012. The largest growth is observed in the demand for other alloys, which rises more than tenfold between 2011 and 2050. A high increase is also seen in the demand for other non-metallic applications (+600%). During the same period, the consumption of antimony in flame retardants and PET triples, while it doubles in the case of lead-acid batteries. Overall, the consumption of antimony increases by 360% until 2050 to reach about 750 Gg. By mid-century, flame retardants account for 46% of the demand, followed by other alloys (34%), lead-acid batteries (12%), PET (7%) and other non-metallic products (2%).

Due to the great increase in demand for other alloys and the long lifetime of products belonging to this category, the stock of antimony in use increases even more steeply than the inflows into use (+390%). It reaches about 7000 Gg in 2050, with an equal share of 45% for both flame retardants and other alloys.

End-of-life flows become increasingly dominated by antimony in discarded flame-retarded products. Due to the relatively long lifetime of products belonging to the "other alloys" category, the sharp increase in demand for this end-use does not translate in an equally sharp increase in end-of-life other alloys. Most of the antimony used in this category will become end-of-life flows 30 years after its entry in use. With increasing recycling rates, and especially that of non-metallic products, secondary production sees a robust growth between 2011 and 2050 (+540%). The overall end-of-life recycling rate exceeds 60% in mid-century, and about a third of the total supply is met by secondary sources. Furthermore, the amount of Sb being landfilled in this scenario "only" increases by 70% in this scenario, although the rise in demand is five times higher. Nevertheless, in the BAU scenario primary production still needs to triple in order to meet the global demand, and emissions into the environment almost quadruple between 2011 and 2050.

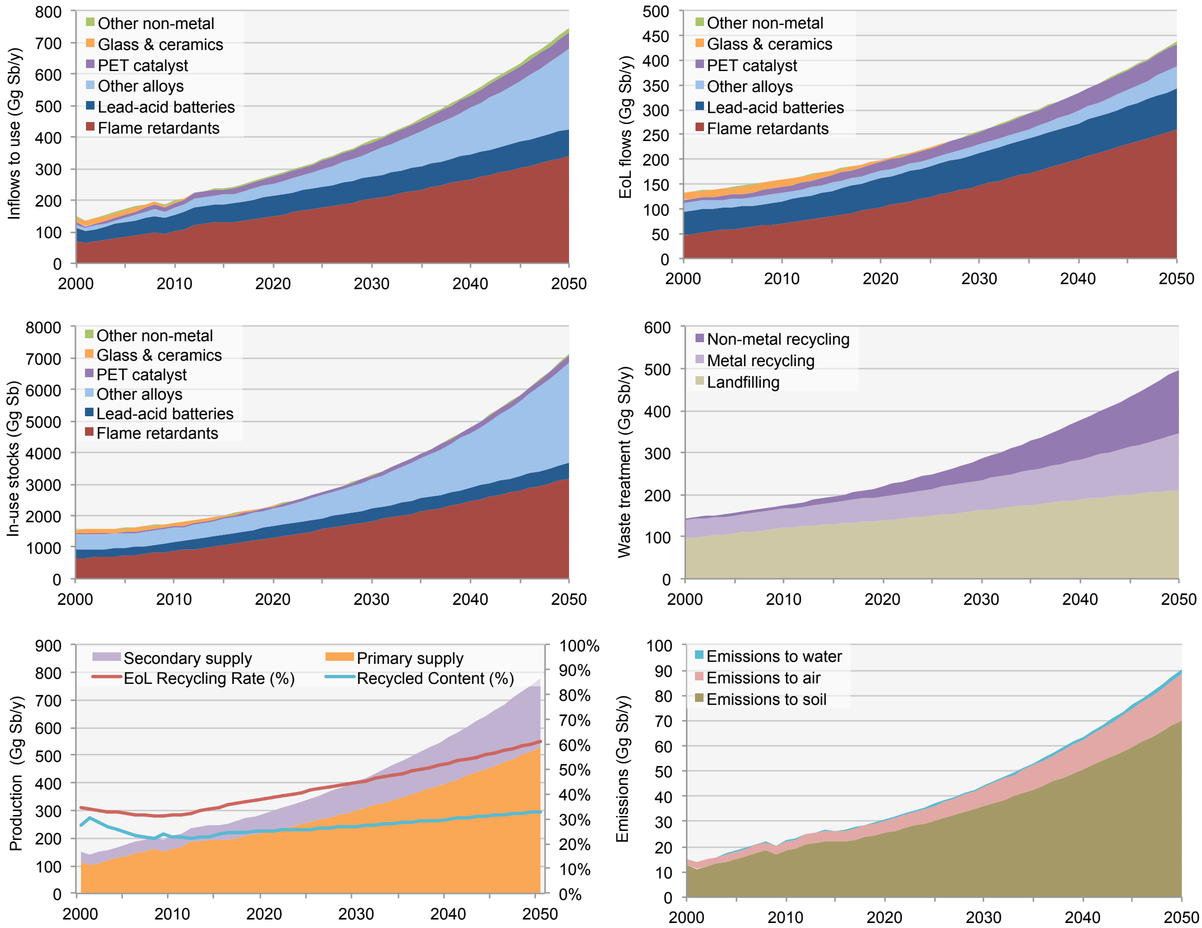


Figure 25: Inflows to use, end-of-life flows, in-use stocks, waste generation, Sb production, and emissions for the period 2000-2050 according in the BAU scenario

Scenario 2: "American World" (AW)

In the AW scenario (Figure 26), where global demand trends are assumed to follow those observed in the USA since between 1990 and 2014, Sb demand for flame retardants and other alloys decreases rapidly, whereas that of other applications remains stable or slightly changes. By 2050, the global demand for Sb drops to about 70 Gg, a third of its 2011 level.

Under this development, the in-use stock peaks in 2015 and then decreases, with a growing share of metallic applications. In 2050, about 750 Gg Sb are in use (-60% compared with 2011), with lead-acid batteries and other alloys accounting for about 40% and 30% of the total, respectively.

End-of-life flows peak in 2017, after which the share of metallic applications in total discards increases. Due to the very high recycling rates reached for those applications, the overall end-of-life recycling rate rises considerably and reaches about 80% in 2050, and so does the recycled content (i.e., fraction of secondary antimony in the total supply). As a result, the amount of antimony being disposed of in landfills decreases by 70% in 2050 as compared to its 2011 level, and the needed supply from primary sources drops below 15 Gg, less than a tenth of the present production. Furthermore, less than three tons Sb is released into the environment as emissions in 2050 (-90%).

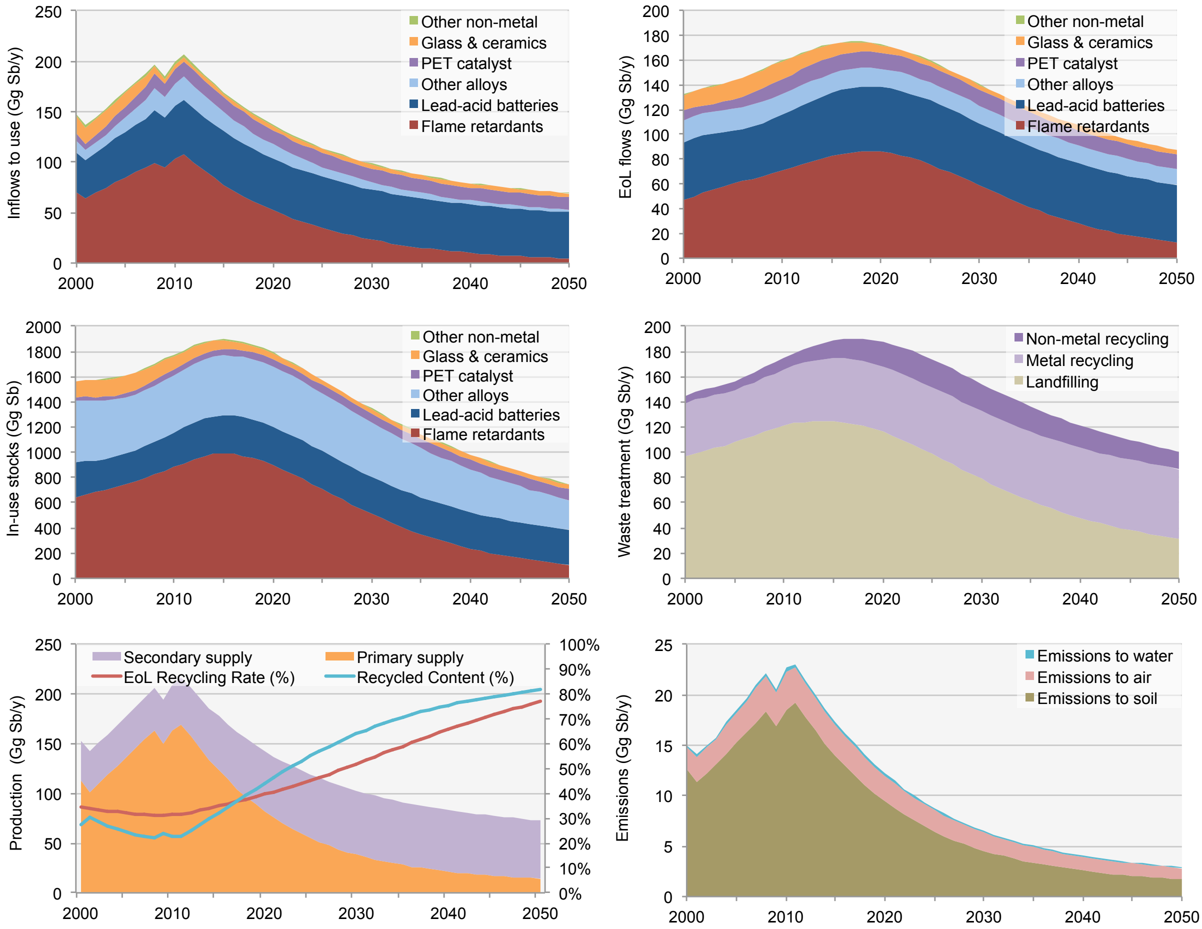


Figure 26: Inflows to use, end-of-life flows, in-use stocks, waste generation, Sb production, and emissions for the period 2000-2050 according in the AW scenario

Scenario 3: "Maximum Substitution" (MS)

In the MS scenario (Figure 27), based on considerations of "when" and "where" (i.e., in which application) antimony can be substituted, Sb demand stabilizes starts to decline in 2012 and falls below 50 Gg in 2040, before rising slightly again until 2050 as a result of the increasing demand for antimony as a polymerization catalyst in the manufacture of PET, for which it is assumed that no satisfying substitute will be developed.

The Sb in-stock peaks in 2021, and declines from that point upwards to reach about 530 Gg in 2050 (30% of 2011 level). The share of all end-uses except PET decreases during that time. At the horizon 2050, about 40% of the in-use stock consists of PET products, and the remainder is mostly contained in other alloys (ca. 30%) and flame retardants (ca. 20%).

In absolute terms, secondary supply peaks in 2024 and then decreases as the magnitude of end-of-life flows and the share of metallic products in this outflow reduces. Secondary production of antimony from non-metallic products increases until 2038 and then decreases again, as a result of the decreasing amounts of antimony in end-of-life flame retardants, glass and ceramic products. The overall end-of-life recycling rate steadily increases to reach 55% in 2050. The fraction of secondary antimony in the total supply (i.e., recycled content) grows linearly until 2035, and then exponentially until 2040 as the demand for primary supply reaches zero. At that point, secondary production equals the total demand, and the anthropogenic antimony cycle is circular. After this, demand for antimony starts to rise again, whereas secondary supply weakens due to diminishing end-of-life flows. Under this scenario, emissions to environmental compartments decrease by 80% between 2011 and 2050, mostly as a result of the reducing need for primary production. Emissions to soils (mainly tailings and slag) are reduced by almost 90%, whereas emissions to air are halved (mainly from manufacture and use of antimony-containing products).

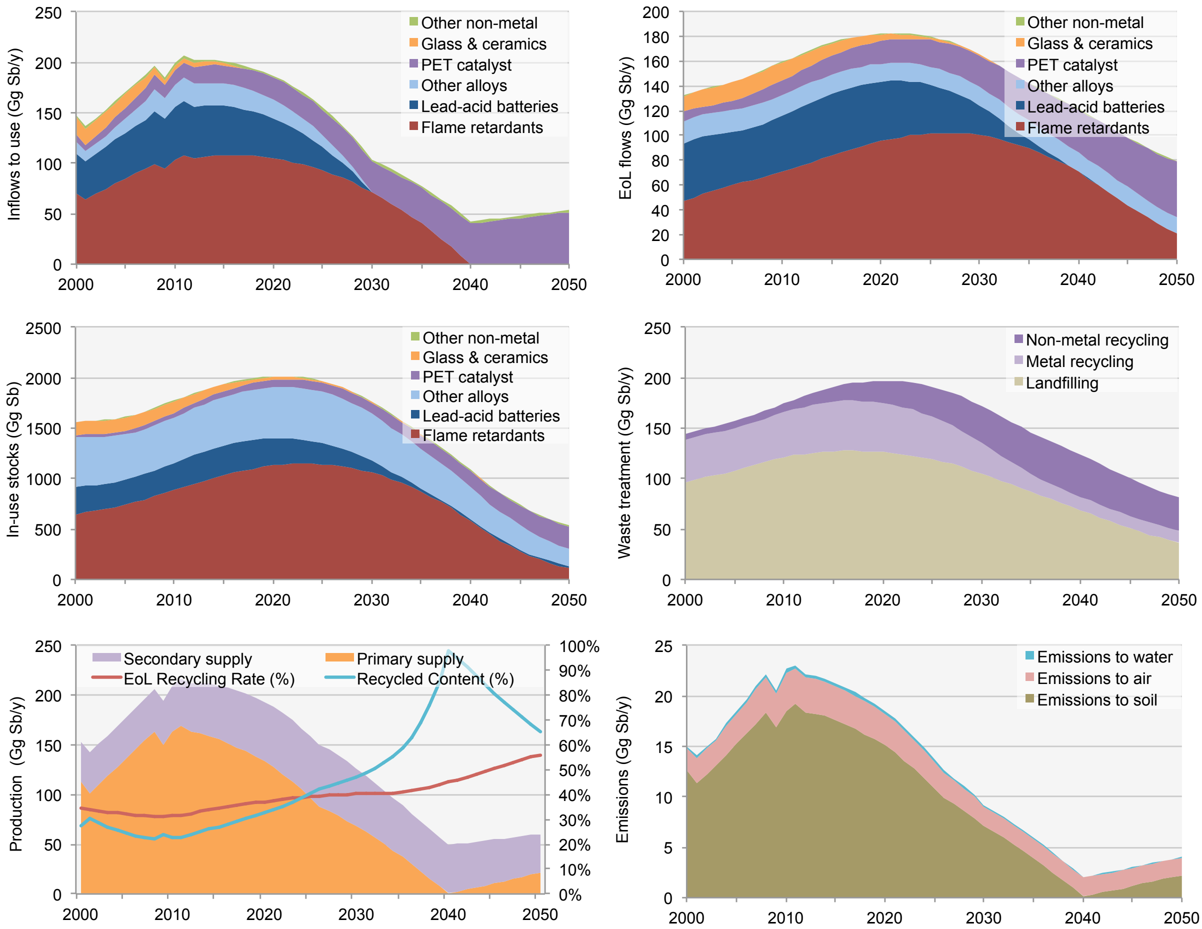


Figure 27: Inflows to use, end-of-life flows, in-use stocks, waste generation, Sb production, and emissions for the period 2000-2050 according in the MS scenario

Comparisons

In order to discuss their contribution to areas of concerns such as resource depletion, system-wide material efficiency (circularity), and environmental emissions (permeability), the three scenarios developed can be compared on the basis of total demand for primary Sb (extraction from ore), size of in-use stocks, recycling rates, ant the amount of antimony being lost to the environment and in landfills (Figure 28). Overall, it appears that the BAU scenario strongly differs from the other two projections in all indicators except end-of-life recycling rates. Between the AW and MS scenarios, differences are small compared to the deviation with values for the BAU projection.

With regard to yearly ore extraction, an increase of 312% is observed for the period 2011-2050 in the BAU scenario, while a decrease of 92% and 88% is witnessed in the AW and MS projections, respectively. Cumulatively, the sum of antimony extracted from its ores between 2011 and 2050 amounts to 14200 Gg in the BAU case, to 2500 Gg in the AW projection, and to 3200 Gg if the MS trends are followed.

As far as the in-use stock is concerned, a growth of almost 400% until 2050 occurs in the BAU scenario, whereas its size diminishes by 60% and 70% in the AW and MS cases. It reaches 7100 Gg in the BAU projection, and drops to 750 Gg and 530 Gg in the AW and MS scenarios, respectively.

End-of-life recycling rates considerably increase in all scenarios, with the greatest growth in the AW case (+250% over 2011-2050), followed by the BAU scenario (+190%) and the MS projection (+180%). The magnitude of increase in recycling rate is inversely proportional to the share of non-metallic applications in end-of-life flows. At the horizon 2050, EoL-RR amount to 61%, 77% and 56% in the BAU, AW and MS scenarios, respectively.

Annual emissions to the environment are greatly reduced in the AW and MS scenarios (-87% and -83% between 2011 and 2050). In the particular case of atmospheric emissions, the AW projection results in a diminution of 50%, while it reaches 90% in the MS scenario. Diminutions in emissions to other compartments are rather similar in both cases. In total, respectively 340 Gg and 430 Gg of antimony are emitted to the environment between 2011 and 2050 in the AW and MS projections. In the BAU scenario, yearly emissions are increased four-fold, and almost 2000 Gg of antimony is released into the environment between 2011 and 2050.

As regards amounts of antimony ending up yearly in landfills, an increase of 170% is predicted in the BAU projection, while it is reduced by 75% and 70% under the AW and MS scenarios. Between 2011 and 2050, a cumulative sum of about 6600 Gg Sb will be landfilled in the BAU scenario, which is equivalent to approximately 85% of the total amount of antimony that has been mined between 1900 and 2011. In the AW projection, the cumulative sum of landfilling for this period amounts to 3200 Gg, and it reaches 3800 Gg in the MS case.

Overall, AW can be considered as the most sustainable scenario, as it results in the lowest cumulative demand for primary antimony, and generates fewer losses to the environment and to landfills. This can be explained by the decrease in the total demand for antimony, and the increase of the share of metallic applications within this demand. Differences with the MS projection are however relatively small in regards to the indicators considered. On the other hand, the BAU scenario leads to a considerable increase of the "ecological footprint" of human activities.

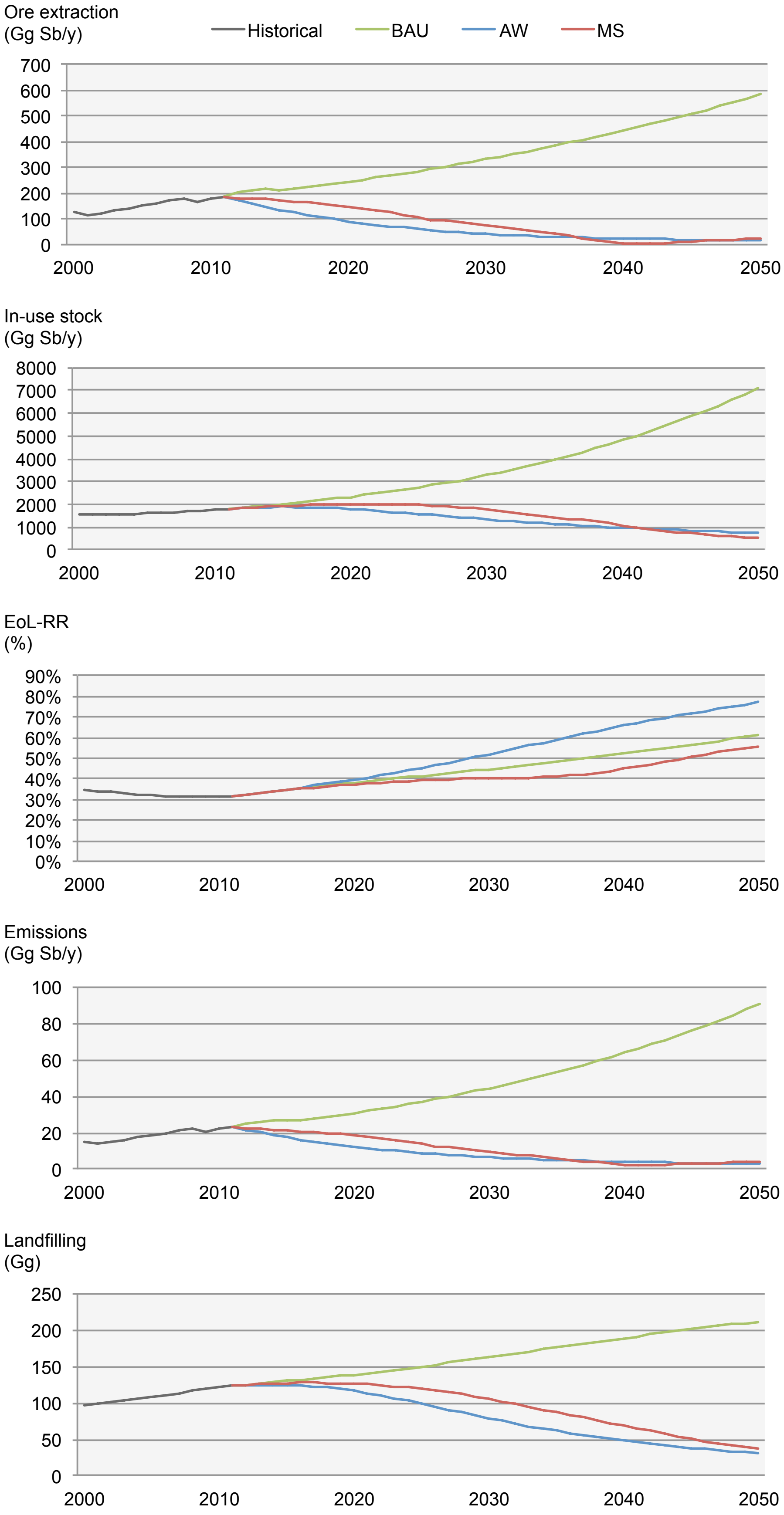


Figure 28: Comparison of scenarios as regards ore extraction, in-use stocks, end-of-life recycling rates, emissions and landfilling

5.3.5 SUPPLY OUTLOOK

Geological Stocks

Geological stocks can be measured differently depending on how they are defined. A typical classification is the JORC code (JORC 2012), distinguishing resources, reserves and reserve base. It is notably used by the U.S. Geological Survey (2015), which gives the following definitions:

1. A resource is 'a concentration of naturally occurring solid, liquid, or gaseous material in or on the Earth's crust in such form and amount that economic extraction of a commodity from the concentration is currently or potentially feasible'. Resources can be "identified" ("demonstrated" or "inferred") or "undiscovered", indicating different levels of confidence;
2. The reserve base is 'that part of an identified resource that meets specified minimum physical and chemical criteria related to current mining and production practices, including those for grade, quality, thickness, and depth. The reserve base is the inplace demonstrated (measured plus indicated) resource from which reserves are estimated. It may encompass those parts of the resources that have a reasonable potential for becoming economically available within planning horizons beyond those that assume proven technology and current economics. The reserve base includes those resources that are currently economic (reserves), marginally economic (marginal reserves), and some of those that are currently subeconomic (subeconomic resources)';
3. Reserves are 'that part of the reserve base which could be economically extracted or produced at the time of determination. The term reserves need not signify that extraction facilities are in place and operative'.

The relation between resources and reserves as well as their relative size are schematized in Figure 29.

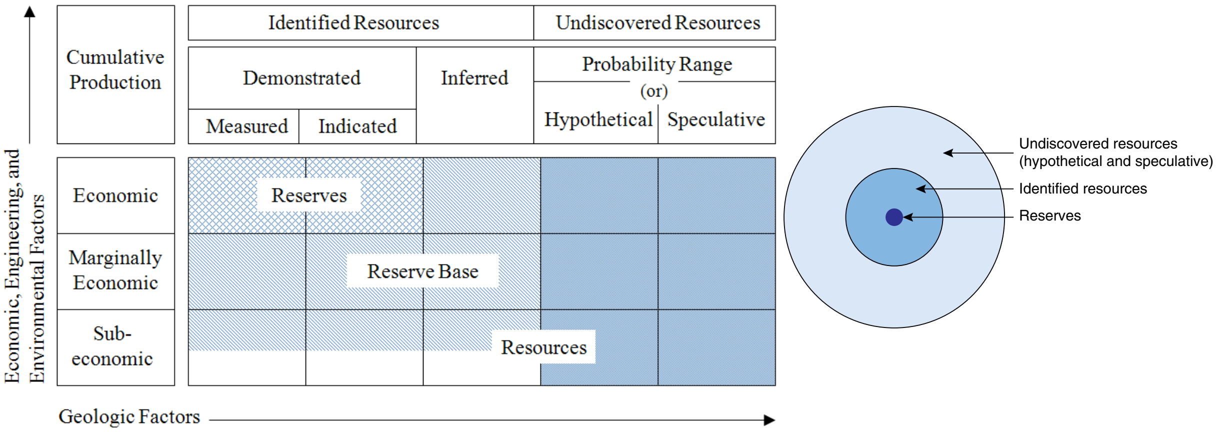


Figure 29: McKelvey (1952) diagram of geological availability (UNEP 2011b) & Schematic representation of the relative size of resources and reserves (Graedel and colleagues 2014)

Reserves therefore constitute identified deposits which are recoverable under current technical and economic constraints, whereas resources are the deposits that could be accessible later given advances in mining technology and increasing prices. World metal reserves are annually reported by the U.S. Geological Survey in its "Mineral Commodity Summaries". Reserve base estimates were published for some metals by the U.S. Geological Survey until 2009 and later abandoned, because they were mostly based on expert opinion rather than on data and were therefore not readily defensible, according to Graedel and colleagues (2014). An upper limit to the reserve base can also be approximated with the ultimately Extractable Global Resource (EGR) metric developped by the UNEP IRP Working Group on Geological Stocks of Metals (UNEP 2011b). The EGR is defined as 'the quantity of a given resource that is judged to be worthy of extraction over the long term given anticipated improvements in exploration and technology', and it is calculated as 0.01% of the amount of a metal theoretically contained in top 1 km of crust based on the estimated upper crustal concentration. It results in allegedly 'unrealistically high' estimates because much of the material covered by the definition is unsuitable for mining, but it can nevertheless give an idea of the extent to which the reserves could expand in the future.

Identified reserves & estimated reserve base

Several estimates of global antimony reserves can be found in the literature, with considerable discrepancies (Figure 30). The U.S. Geological Survey (2015) estimates global reserves at 1800 Gg for 2015, an unchanged value since 2011 (U.S. Geological Survey 2011), with China accounting for 52% of the total (950 Gg), Russia for 19% (350 Gg) and Bolivia for 17% (310 Gg). On the other hand, Schwarz-Schampera (2014) from the German Geological Survey estimated global Sb reserves at 3400 Gg in 2011, using data from Roskill (2011), the U.S. Geological Survey (2012), and information from mining companies' annual reports. Within this total, China represents 36% (1200 Gg), Thailand 16% (530 Gg), Russia 13% (460 Gg), and Bolivia 12% (420 Gg). Significant deposits are also believed to exist in Kazakhstan and Myanmar, but their size have not been estimated (BRGM 2012).

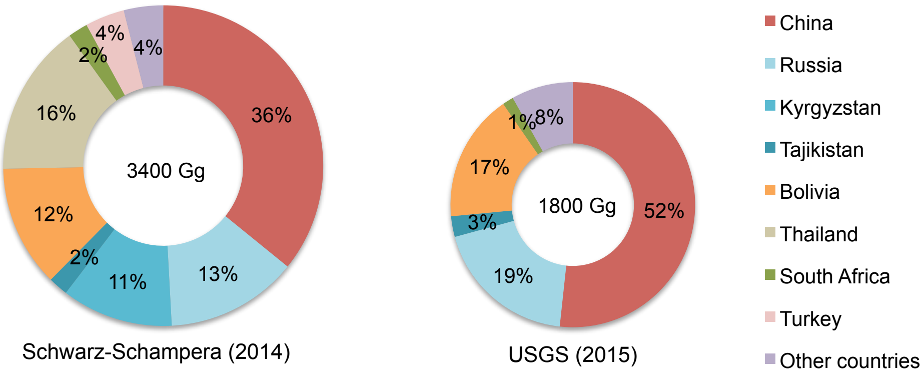


Figure 30: Reserve estimates according to different sources

Reasons for discrepancies between reserve estimates are unclear, as both sources do not include a detailed description of data sources and assumptions used to estimate global Sb reserves. As regards estimate for Thailand, the U.S. Geological Survey reported significant reserves until 2010 with 420 Gg for that year, which was then the second largest national reserve after China (U.S. Geological Survey 2010). Since 2011, Thailand does not appear in the Mineral Commodity Summaries, but China's reserves have increased in the same year, possibly indicating that the USGS includes Thailand's reserves in the Chinese figures. This could be justified by the fact that almost all production from Thailand is refined in China (BGR 2013), although no justification is given. Regardless of these differences, it appears clear that China has the largest antimony reserves, followed by Thailand, Russia and Bolivia. Together, these four countries accounts for about 80-90% of global Sb reserves.

As far as the reserve base is concerned, the last estimate reported by U.S. Geological Survey (2009) was at 4300 Gg, with China representing a little more than half of the total, followed by Thailand, Russia, and Bolivia (Figure 31). Furthermore, the IRP Working Group on Geological Stocks of Metals (UNEP 2011b) estimated the quantities of ultimately extractable global resources (EGR) to be 8000 Gg (i.e., 0.01% of amount theoretically contained in top 1 km of crust, itself derived from the estimated upper crustal concentration).

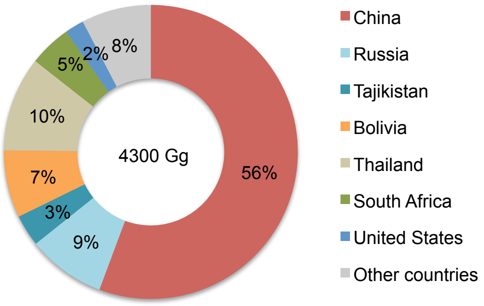


Figure 31: Reserve base according to the U.S. Geological Survey (2009)

Having the largest reserve base and reserves, China plays a crucial role in the global primary antimony supply. Hereafter, the evolution of the Chinese supply is investigated.

The China Factor

China dominates the world antimony production since the mid-1980s. The country's annual primary production has increased six-fold between 1985 and 2010, whereas the combined production of other countries decreased by a third over the same period (British Geological Survey 2015). China's near monopoly was at its peak in 2007, when the country's share in the global production reached 90% (Figure 32). Over the last decade, China has also emerged as the main producer and exporter of antimony metal, compounds and intermediate products (Schwarz-Schampera 2014). In 2011, China had shares of 78% and 53% in global exports of antimony metal and antimony trioxide, respectively (BGR 2013).

China's antimony mining industry has therefore an overbearing role on the global market, and changes in the country's production and exports volumes heavily affect world prices. In this authoritarian state, the Government plays also a crucial part and effectively exercises a tight control over the quantities of antimony being mined, refined, exported and imported. Understandably, the Chinese central power aims at securing its domestic supply and developing more value-added downstream activities.

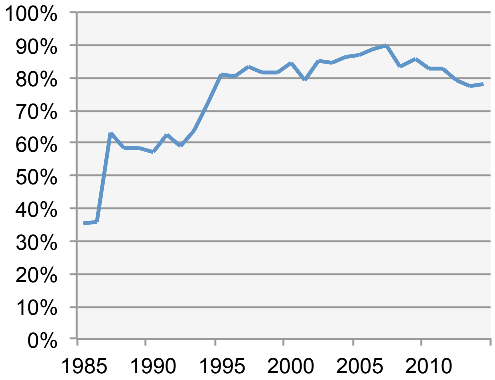


Figure 32: Share of China in the global primary Sb production (British Geological Survey 2015)

As shown in Figure 32, China's share in the global production has been decreasing over the past few years, revealing the increasing difficulties faced by the Chinese antimony industry. Reasons for its failure to increase primary production levels are complex and interwoven. In 2009, as a result of the rapid depletion of some of the largest antimony-producing mines and the lack of new mines (Li 2013), the Government tightened its grip on the antimony market and added antimony to its list of protected and strategic minerals along with tungsten and the rare earth elements. Antimony production and export was thus brought under strict control of the Ministry of Land and Resources (MLR), which introduced quotas on antimony mining, tightened the granting of exploration and mining licenses and discouraged the export of antimony products via higher export taxes and quotas, and stricter requirements for the granting of export licenses. The Government also launched a crackdown on small mining and smelting operations, for environmental and safety reasons. This resulted in the shut-down of about a hundred antimony mines and smelters in 2010 only, often because the costs of upgrading the facilities to the safety and environmental standards were too high (U.S. Geological Survey 2011). In 2011, almost all mines and smelters were closed in the Xikuangshan mining region (about 60% of the world antimony supply (U.S. Geological Survey 2012)). Between 2003 and 2011, the number of companies qualified to produce and export antimony products was reduced from about 400 to 14, among which the six largest account for 90% of the supply (Roskill 2012). Since 2009, the MLR has refused any exploration or new mining applications (U.S. Geological Survey 2015).

With the constraints on domestic primary production and lack of new mines, increasingly large quantities of antimony concentrates were imported in the last years to sustain domestic refined production, mainly from Myanmar, Russia, Canada, Thailand and Australia. In 2011, China was the largest importer of antimony concentrates with 77% of the global trade (BGR 2013). In 2014, the MLR announced the cancellation of production quotas (Smith 2014) and set export quotas of 59400 tons of antimony metal and trioxide for 2015, the same as for 2014 and 2013 (U.S. Geological Survey 2014c).

Antimony prices

Antimony is not traded on international metal exchanges and its prices are agreed between producers (and/or traders) and consumers, depending on the quality and the form (e.g. metal ingot, trioxide power) of the product (Schwarz-Schampera 2014). Antimony metal and trioxide are traded with purity ranging between 99.5 and 99.6%, and at relatively low prices compared to more abundant metals such as molybdenum (Mo), tungsten (W) and tin (Sn), whose abundance in Earth's crust and prices as of February 1st 2015 were respectively 1.1 ppm and 22$/kg Mo, 1.1 ppm and 28$/kg W, and 2.2 ppm and 22$/kg Sn, compared to 0.2 ppm and 10$/kg for antimony (Wikipedia 2015c; Metalprices.com 2015). This can be to an extent explained by the relatively low cost of antimony mining as it generally occur in highly concentrated, almost pure stibnite deposits and often with gold as a by-product.

Antimony prices have varied considerably during the last decade (Figure 33). Antimony metal and antimony trioxide prices are tightly coupled and follow the same evolution, as one is generally produced from the other. Therefore, the discussion is limited to the evolution of metal prices.

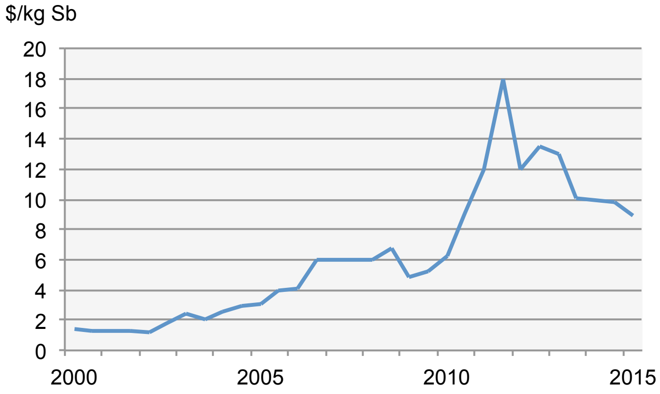


Figure 33: Antimony ingot prices (Metalprices.com, 2015)

Relatively high antimony prices in the 1990s (peak at 5.4$/kg Sb in 1995, see Figure 3) resulted in the multiplication of illegal exploitations in China, at a low cost due to the high grade and low depth of deposits (BRGM 2012). This led to an oversupply situation which drove down the prices to levels below 2$/kg Sb. Prices started to increase again in 2002, after the closure of several small and illegal exploitations in the Guangxi province following fatal flooding accidents in the Nandan mining region, where more than 80 people have died (Masters 2005). Between 2004 and 2008, antimony prices increased due to a growing global demand and the rapid depletion of high-quality deposits (Li 2013). Demand dropped with the Global Financial Crisis, leading to a decrease in prices in 2009. In March of the same year, the Government announced the introduction of production and export quotas and a crackdown on small miners and smelters. This provoked the tripling of antimony prices within a year, peaking at 18$/kg in March 2011. With the outbreak of the European debt crisis in June-July, antimony prices started a decline that is still ongoing. At the end of February 2015, antimony prices were down to 7.7$/kg Sb, close to their 2008 levels. Decreasing prices have caused the closure of many mining and smelting operations (Smith 2014). In an effort to stabilize antimony prices, the Chinese Government purchased 4,500 tons Sb in 2012 and 10,500 tons in 2013 (U.S. Geological Survey 2014d). It also cancelled production quotas in 2014 in the hope that this would encourage an increase in domestic supply (U.S. Geological Survey 2015). However, prices are currently too low for it to be profitable for producers to increase their output, and many have already suspended production or closed down (Smith 2014).

Future supply

In 2011, local authorities in Xikuangshan announced that the region had only five years of antimony mining life left, after more than 110 years of continuous production (U.S. Geological Survey 2012). If true, this would have dramatic consequences on the global market as the region accounts for about 75% of the Chinese supply (Guo and colleagues 2014) and thus 60% of the global production. Chinese production has effectively decreased since 2011, from 150 Gg to 125 Gg in 2014 (U.S. Geological Survey 2015), but not to the extent that can be expected after such an announcement. This suggests that the claims of depletion were needlessly alarmist, maybe in an effort to boost up prices. Nevertheless, evidence suggest that high grade and low cost Chinese deposits are running low (BRGM 2012). Since 2009, the MLR has refused any exploration or new mining applications (U.S. Geological Survey 2015), with the result that reserves are stagnating. With decreasing prices, many miners and smelters have been forced to halt or close their operations. For these reasons, it is unlikely that Chinese antimony supply will increase in the near future, and it could even decrease if prices continue to plummet.

With the surge in prices until 2011 and the diminishing Chinese output, mining capacity has increased in several countries. Between 2009 and 2013, Bolivia increased its primary production by 70%, Australia by 80%, Canada by 40%, Kazakhstan by 50%, Laos by 25%, Mexico by 300%, Russia by 115%, Tajikistan by 60%, and Turkey by 460%. During the same period, China's output decreased by 16%, and the total production increased by 19% (British Geological Survey 2015; U.S. Geological Survey 2015).

The putting of new antimony mines into operation and the rehabilitation of old mines could increase the global primary supply in the coming years. Several of such projects have been announced by mining companies following antimony price increases, reviewed by Roskill as well as the German and French Geological Surveys between 2011 and 2013 (Table 17). Many of the projects were at the very early planning phases with little or no information on reserves, resources, and potential annual production. Taking quantified figures into account gives an additional production of about 18 Gg Sb per year and expands the reserve base by about 600 Gg Sb, representing respectively an increase of about 11% to the current global supply and of about 14% to the reserve base estimated by the U.S. Geological Survey (2009). It is however not sure whether all projects will be realized, but it is likely that many have been cancelled or put on hold as prices have well decreased since the projects were announced.

Table 17: Potential Sb mining projects as of 2013 (Roskill 2011; BRGM 2012; BGR 2013).

Country	Project	Company	Status	Expected capacity (Gg Sb/y)	Expected start of production	Reserves/ resources (Gg Sb)
Australia	Hillgrove	Bracken Resources Pty. Ltd.	Construction	5	2014	46/102
	Blue Spec Shear/Gold Spec Shear	Northwest Resources Inc.	Rehabilitation	1.5	2013	?/9
	Bielsdown (Wild Cattle Creek)	Anchor Resources Ltd.	Exploration	?	?	?/19
	Northcote	Territory Minerals Pty. Ltd.	Exploration	?	?	?/11
Bolivia	Lipichi Gold	Luzon Minerals Ltd.	?	?	?	?/54
Canada	Bald Hill	Portage Minerals Inc.	Exploration	?	?	?/30-50
	Little River	Mountain Lake Minerals Inc.	Exploration	?	?	?/?
	Clarence Stream	Wolfden Resources Inc.	Exploration	?	?	?/3
	Stanley Property	Tri Star Resources Inc.	Exploration	?	?	?/?
	Beaver Brook	Great Atlantic Resources Corp.	?	?	?	?/?
Guatemala	San Ildelfonso Ixtahuaca	Minas de Guatemala	?	?	?	?/63
Italy	Poggio Petriecci/Faggio Scritto	Adroit Resources Inc.	?	?	?	?/45
Mexico	Loz Juarez	U.S. Antimony Corp	Extension	1.6	2013	?/18
Russia	Sarylakh Surma/ Sentachan/Kim Kinyaaski	GeoProMining Group	Extension	8.3	2013	?/127
Slovakia	Strieborna	Global Minerals Inc.	Exploration	?	2014	?/22
Turkey	Odemis/Izmir	Armetall Ltd.	Construction	1.8	2013	?
	Göynük	Tri Star Resources Inc.	Exploration	?	?	?/?
USA	Nolan Creek	Silverado Gold Mines	Prefeasibility	?	?	12/6
	Golden Meadows	Midas Gold Corp.	Prefeasibility	?	?	?/86

Future criticality

Comparing estimated reserves, reserve base, and ultimately extractable global resources with the current demand for primary metal can be used to give an idea of the risk of future mismatches between supply and demand, i.e. the future criticality. This is referred to as “static availability” figures, which are often used to estimate how many years identified reserves will last according to current consumption patterns (Behrendt and colleagues 2007). In the case of antimony (Table 18) static availability figures suggest that the identified reserves will be depleted within 11 to 21 years depending which estimate is used, that the reserve base will be exhausted in 27 years, and that the ultimately extractable resources can last another 50 years.

Table 18: Static availability based on current production levels (Tg Sb)

Production 2014 (USGS 2015)	Reserves (USGS 2015, Schwarz-Schampera 2014)	Reserve base (USGS 2009)	Extractable Global Resource (UNEP 2011b)	Years reserves can last	Years reserve base can last	Years resources can last
0.2	1.8-3.4	4.3	8	11-21	27	50

Those figures are based on current consumption levels. If Sb consumption was to increase of decrease, resources and reserves could last shorter or longer, respectively. Using the projected demand for primary Sb according to the different scenarios generated with the dynamic MFA model, static availability figures vary (Figure 34).

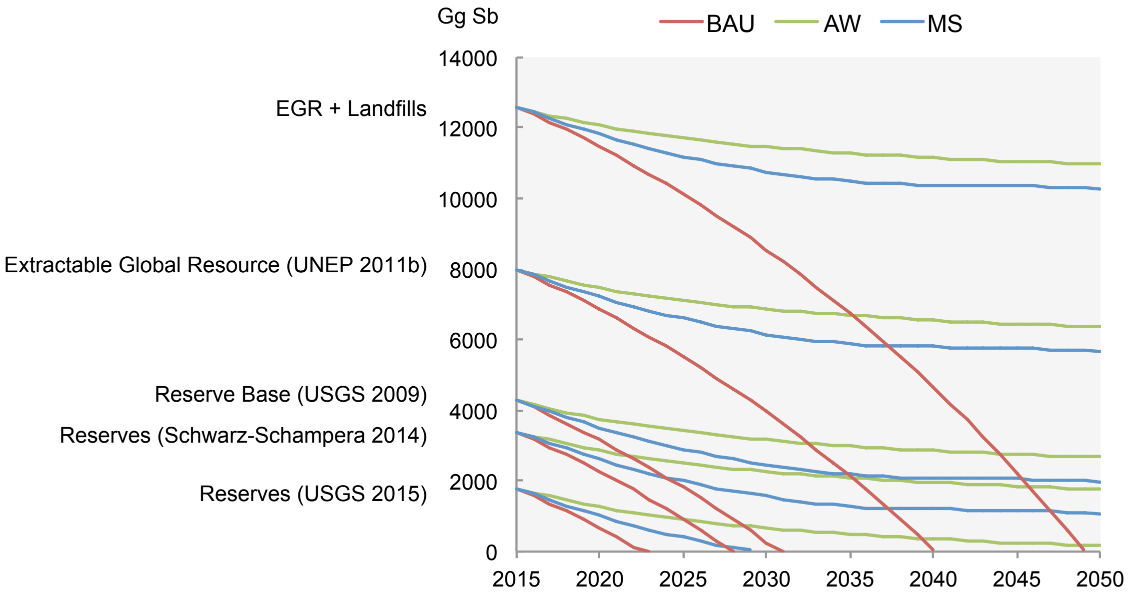


Figure 34: Static availability according to different scenarios

It appears that currently identified reserves as estimated by the U.S. Geological Survey (2015) will be depleted in 2023 in the BAU scenario, in 2029 in the MS scenario, whereas in the AW scenario they will not yet be used up in 2050. Using the figure estimated by Schwarz-Schampera (2014) results in exhaustion by 2029 in a BAU situation, and in no depletion in the other two scenarios. As far as the reserve base and the ultimately extractable global resource are concerned, depletion also only occurs in the BAU scenario, respectively by 2031 and 2041. Antimony resources, approximated with the EGR metric, are depleted by 2040 in the BAU projection and remain high in AW and MS cases.

In reality, resource-related metrics are dynamic and exhaustion of reserves in those relatively short timespans is rather unlikely. Reserves expand as metal prices rise and extraction of lower-grade ores becomes economical, and contract as prices fall. Similarly, increased exploration and new methods for metal extraction and processing can increase the size of reserves. Crowson (2011) has showed that, despite increasing production levels, reserves of many industrial metals have grown since 1930. Nevertheless, the prospect of depletion of reserves as estimated by the U.S. Geological Survey in less than 15 years, both in the BAU and MS scenarios although in the latter Sb consumption decreases after 2011, is worrisome. The entry into operation of a new mine is a long process, and it usually takes more than ten years between the exploration phase and the start of the production due to economic, regulatory and socio-environmental reasons (Graedel and colleagues 2014). As potential new mining projects identified in Table 17 would only marginally increase the annual capacity, the risk of supply disruption within the next decade appears high.

However, geological constraints are only one factor contributing to future supply risks among many others, such as import dependence, country and company concentration of production, state control of domestic resources, availability of secondary resources and substitutes, price volatility, as well as social and environmental impacts of production. In the case of antimony, a crucial factor is the extent to which governments of antimony-producing countries will turn towards resource nationalism to secure their domestic demand. In the last decade, such interventionist policies from the Chinese government have rendered insecure the supply of primary antimony, leading to important price fluctuations. Price volatility makes the planning and development of new mines difficult and, consequently, the assessment of future supply uncertain.

Furthermore, if the primary supply were to be significantly restricted in the future, an alternative of supply may be found at the other end of the chain. Landfills, considered as “tertiary stock” (MacLean and colleagues 2009), represent a huge untapped resource. It is estimated that about 4600 Gg Sb has been landfilled between 1900 and 2011, which means that a stock whose size is slightly above the estimated reserve base could be mined in the future. When landfills are added to the ultimately extractable resources, the demand for antimony as modeled in the BAU scenario can be sustained until 2049.

5.4 SENSITIVITY ANALYSIS

A sensitivity analysis assesses the influence of individual model parameters on the model results. It can be used to identify the most important variables of a system in regards to key indicators, for which research and action should be targeted in priority. In this study, sensitivity analysis is used to indicate which parameters have the greatest influence on key model outputs such as demand for primary Sb, secondary production, in-use stocks, emissions into the environment, and landfilling. The change in seven key model outputs brought up by single a variation of 21 input variables is assessed. The results of the sensitivity analysis are shown in Table 19.

The amount of ore that needs to be extracted to meet the demand for antimony is most sensitive to the efficiency of production, fabrication and manufacture processes, and to the demand for flame retardants, lead-acid batteries and other alloys. Efforts to decrease antimony mining and preserve resources should therefore focus on increasing production and F&M efficiencies, and reduce the demand in flame retardants, lead-acid batteries, and other alloys (e.g. by fostering substitution). Interestingly, increasing by 10% the share of recycling for end-of-life lead-acid batteries (from 0.70 to 0.77), other alloys (from 0.60 to 0.66), and plastic and glass products (from 0.10 to 0.11) would result in a total diminution of only 2% in ore extraction. This is due to the relatively low overall end-of-life recycling rate of the global anthropogenic antimony cycle.

Secondary antimony production is mostly impacted by secondary production efficiency and recycling rates for metallic products. Increasing the efficiency of F&M processes for those applications would decrease the amount of new scrap generated and therefore result in a diminution in total secondary production. However, this increase would also considerably reduce total emissions to air and water, and cause a slight decrease in ore extraction, which is desirable from a sustainability point of view.

System-wide emissions into the environment are mostly sensitive to primary production efficiencies and Sb demand for flame retardants and metallic applications. Emissions to soil are abated by almost 85% with an increase of 5% in ore concentration and extraction efficiencies, which highlights the great contribution of those processes to system-wide soil emissions. Such an increase in efficiency would also decrease by almost 10% the amount of ore needed to be extracted to provide the same primary output from Production. Therefore, increasing primary production efficiencies should be a priority in order to reduce resource depletion and antimony emissions. Emissions to soil are also sensitive to the use of Sb in flame retardants and metallic applications, as those parameters contribute largely to the overall demand for primary antimony. According to the model, emissions to air can be significantly reduced through an increase in F&M efficiencies for metallic product. On the other hand, a growing demand for Sb in the end-use categories “other non-metallic products”, “lead-acid batteries”, and “other alloys” would result in increased atmospheric emissions. This can be explained by the increased emissions during dissipative uses such as brake linings, pigments and lubricants, and increased emissions during F&M of lead-acid batteries and other alloys. Emissions to water are also highly sensitive to efficiency of metallic products F&M processes.

Furthermore, the use of antimony in ammunition and flame retardants contribute importantly to water emissions due to the consumptive losses generated during use of those products.

The sensitivity of Sb flows to landfills to variation in input parameters is relatively low. This is due to the fact that those flows are mainly generated once Sb flows out of use, i.e. at the end of the service lifetime of products. In the sensitivity analysis, only the consequences of variations in inflows to use are assessed. An increased inflow into use will only result in increased landfilling in the future. In the sensitivity analysis, landfilling is therefore mostly affected by the generation of wastes during F&M processes (which depend on demand for the same year), and by the recycling/landfilling ratio of those wastes.

It should be noted that products' lifetime distributions have a major impact on the size of in-use stock and, in turn, on the magnitude of many flows throughout the cycle, such as flows out of use (both EoL flows and emissions) and into waste management processes, and resulting magnitudes of landfilling and secondary production. This sensitivity is difficult to assess as non-normal lifetime distributions were used in the model, for which a 10% variation does not make sense. This constitutes a limitation of the model regarding sensitivity analysis.

Table 19: Sensitivity of the MFA model results for 2011 to a variation in selected input parameters. Red values indicate increase in key model output, while blue values highlight a decrease.

Input to sensitivity analysis			Change in key model output (%)						
					Emissions				
Life cycle stage	Input parameter (current value)	Variation (%)	Ore extraction	Secondary production	To soil	To air	To water	Total	Landfilling
Production	Concentration efficiency (0.94)	+5%	-4.8%	0.0%	-46.5%	0.0%	0.0%	-38.7%	0.0%
	Extraction efficiency (0.95)	+5%	-4.0%	0.0%	-39.0%	0.0%	0.0%	-32.5%	0.0%
	Refining efficiency (Sb2O3: 0.97)	-> 100%	0.0%	0.0%	-0.1%	-0.3%	0.0%	-0.1%	0.0%
	Secondary production efficiency (0.83)	+5%	-1.3%	4.7%	-1.2%	-0.2%	0.0%	-1.0%	-1.8%
Fabrication & Manufacture	F&M efficiency for non-metallic applications (0.98-0.99)	-> 100%	-1.1%	0.0%	-1.8%	-0.2%	-0.3%	-1.5%	-1.3%
	F&M efficiency for metallic applications (0.88-0.91)	+5%	-2.6%	-3.3%	-3.5%	-21.7%	-19.0%	-6.5%	-2.6%
Use	Use in flame retardants (108 Gg)	+10%	6.5%	0.0%	6.0%	0.0%	0.0%	5.0%	0.1%
	Use in PET (15 Gg)	+10%	0.9%	0.0%	0.8%	0.0%	0.0%	0.7%	0.0%
	Use in glass & ceramics (4 Gg)	+10%	0.2%	0.0%	0.2%	0.0%	0.0%	0.2%	0.0%
	Use in other non-metallic products (2 Gg)	+10%	0.1%	0.0%	0.1%	4.6%	0.0%	0.8%	0.0%
	Use in lead-acid batteries (54 Gg)	+10%	3.4%	0.4%	3.1%	2.8%	2.5%	3.1%	0.2%
	Use in other alloys (24 Gg)	+10%	1.5%	0.3%	2.1%	1.9%	3.7%	2.1%	0.1%
	Dissipation from ammunition (0.5)	+10%	0.0%	-0.1%	1.5%	0.5%	4.8%	1.4%	0.0%
	Dissipation from brake linings, pigments lubricants, other (0.7, 0.5, 0.5, 1)	+10%	0.0%	0.0%	0.0%	4.6%	0.0%	0.7%	0.0%
	Leaching from flame retardants (1.0E-04)	+10%	0.0%	0.0%	0.0%	0.0%	2.3%	0.0%	0.0%
	Leaching from rolled & extruded lead products (8.0E-05)	+10%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Waste Management	Share of recycling for plastics and glass (0.1)	+10%	-0.2%	0.5%	-0.1%	0.0%	0.0%	-0.1%	-0.2%
	Share of recycling for lead-acid batteries (0.7)	+10%	-1.6%	5.8%	-1.4%	0.0%	0.0%	-1.2%	-2.2%
	Share of recycling for other alloys (0.6)	+10%	-0.5%	1.8%	-0.4%	0.0%	0.0%	-0.4%	-0.7%
	Share of incineration of non-recycled EoL products	+10%	0.0%	0.0%	0.0%	-1.2%	-2.8%	-0.2%	0.0%
	Share of landfilling of non-recycled EoL products	+10%	0.0%	0.0%	0.0%	-0.6%	-1.4%	-0.1%	3.3%

6 ENVIRONMENTAL AND HEALTH ASPECTS

In this section, a semi-quantitative analysis is performed in order to assess the current and possible future environmental impacts associated with the anthropogenic antimony cycle. Due to time constraints, a thorough life cycle analysis and/or environmental risk assessment cannot be completed. However, by combining existing information with some of the newly generated insights from the material flow analysis, it is possible to identify potential environmental hotspots, providing a basis for further research. Environmental impacts of antimony are investigated with a double focus on the cradle-to-gate energy use of primary and secondary antimony production, and on the human- and eco-toxicity potential of antimony releases to the environment. Those aspects are regarded as particularly important in the case of metals (UNEP 2013b).

6.1 CRADLE-TO-GATE LIFE CYCLE ASSESSMENT

6.1.1 PRIMARY PRODUCTION

The ecoinvent database contains two life cycle inventory (LCI) datasets related to the primary production of antimony (Althaus 2009):

- "Stibnite ore, 70% stibnite, at mine" represents the mining and beneficiation of stibnite, the main antimony ore, in China. Due to a lack of quantitative information, this process is approximated with values from molybdenum mining and beneficiation coupled with copper mining. A comparison of the two datasets is given in Appendix D. Inputs and outputs are the same, except for stibnite and molybdenum flows as well as for electricity source, and values are in the same order of magnitude, although they may differ by a factor of two.
- "Antimony, at refinery" represents extraction of antimony from concentrates and refining in China. As quantitative data is also lacking for these processes, the production of antimony is approximated with the lead smelting process. The LCI is identical to that of "lead, primary, at plant", except that 1.8 kg "lead concentrate, at beneficiation" is replaced by 1.8 kg "stibnite ore, 70% stibnite, at mine" in the inputs, and that 1 kg "lead, primary, at plant" is substituted by 1 kg "antimony, at refinery" as output.

Inflows and outflows for both datasets are given in Appendix D.

Using those datasets and the openLCA software (Ciroth 2007), the relative contribution to cradle-to-gate LCA scores of mining/beneficiation and extraction/refining life cycle stages is assessed (Figure 35). Selected impact categories are: "cumulative energy demand" (CED) and "global warming potential" (GWP) (Frischknecht and colleagues 2007); USETox categories "ecotoxicity" (ET) and "human toxicity" (HT) (Rosenbaum and colleagues 2008); ReCiPe Endpoints (H) "ecosystem quality" (EQ) and "human health" (HH) (Goedkoop and colleagues 2009); and "total eco-factor" (EF) according to the Ecological Scarcity 99 method (Frischknecht and colleagues 2009). Contribution analysis shows that the mining/beneficiation contribute much more to overall scores than the extraction/refining stage, which contrasts with what is observed for most other metals (UNEP 2013b).

High impacts during antimony mining/beneficiation are primarily due to consumption of electricity, mostly produced with coal in China (main contribution to cradle-to-gate GWP, CED, EQ and EF scores), and disposal of sulfidic tailings (main contribution for ET, HT and HH, and second highest contribution for EQ). The relatively high contribution of extraction/refining to the cradle-to-gate EF is mainly due to the emission of particulates and lead into the air.

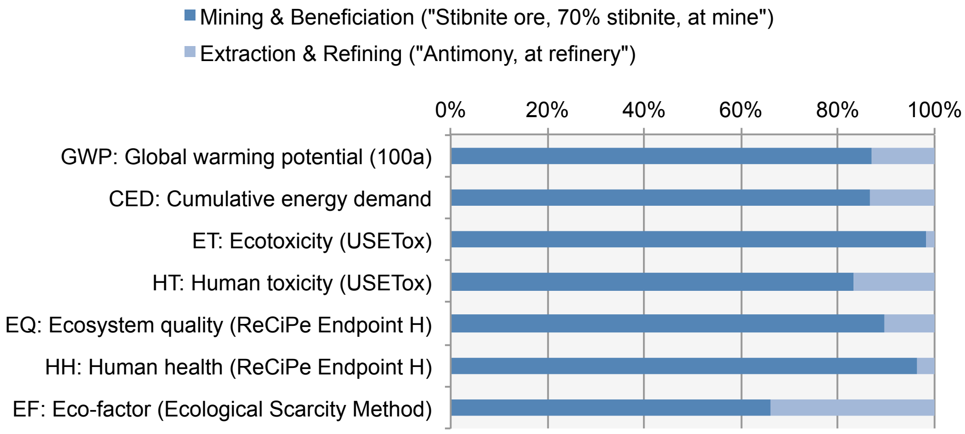


Figure 35: Life cycle stage contribution for selected impact categories using the dataset "antimony, at refinery"

Previously, Nuss and Eckelman (2014) calculated and compared (on a per kilogram basis) the cradle-to-gate environmental burdens associated with the primary production of 63 metals including antimony (using the ecoinvent dataset "antimony, at refinery"), according to several impact categories: CED, GWP, ReCiPe Midpoints "terrestrial acidification" (TA) and "freshwater eutrophication" (FE) for eco-toxicity potential, and USETox category "human toxicity" (HT) for human toxicity potential. In comparison with the other 62 metals assessed, antimony scores in the mid-range for the GWP, CED and TA categories (respectively 26, 24 and 26 metals have a lower score). As far as FE and HT categories are concerned, antimony production has relatively high impacts (respectively 47 and 44 metals have a lower score).

In order to assess the relevance of approximations used in ecoinvent, an extensive knowledge of antimony mining, beneficiation, extraction and refining processes is needed, including information on the relative share of each processing route and on material and energy inflows and outflows of each process. About three quarters of the global primary production originates in China, and relevant literature related to antimony primary production and associated environmental impacts is therefore often in Chinese, which limits its accessibility for the author. Furthermore, the mining and beneficiation of molybdenum coupled with copper and the smelting of lead must also be well understood. This represents a considerable amount of work that is beyond the time scope of this thesis. Hereafter, limited information related to primary antimony production gathered during the thesis research is compared to ecoinvent datasets, and the consequence of potential inconsistencies on cradle-to-gate cumulate energy demand, global warming potential, and toxicity impacts of antimony production is investigated.

Energy demand and global warming potential

Both open pit mining and underground mining are applied to extract antimony ores (Butterman and Carlin 2004). Chinese deposits in Xikuangshan are mined in open pit, whereas underground mining is used in the Consolidated Murchinson mine in South Africa (BRGM 2012; Schwarz-Schampera 2014). Overall, the relative importance of each method in the global supply is not well understood. It is likely that the share of underground mines will increase in the future as high-grade and low depth Chinese deposits are running low (BRGM 2012). Underground mining is much more energy-intensive that open pit mining (UNEP 2013b).

After the ore has been mined, ore grade is increased (beneficiation) via concentration methods such as crushing, gravity separation and flotation. According to Althaus (2009), author of the ecoinvent datasets for antimony, the approximation with molybdenum mining and beneficiation coupled with copper mining ‘seems reasonable since molybdenum occurs in about the same concentration as antimony together with copper and since the beneficiation processes are basically the same’. However, antimony is mined as the main product in the world’s largest sources, including top-producing mines in China, South Africa, Russia and Bolivia (Butterman and Carlin 2004), suggesting that mining and beneficiation processes could differ significantly in terms of energy use. Unfortunately, no information was found on the energy consumption of antimony mining and beneficiation processes.

Once crude antimony ores have been mined and concentrated, smelting processes are used to extract antimony from its ores. As mentioned in Section 4.3.2, several pyrometallurgical and hydrometallurgical methods can be used to extract antimony from its ores, and their relative importance in the global supply is largely unknown. It is however reported that a method combining the roasting of concentrates and the reduction of resulting antimony trioxide to metallic Sb is used in Xikuangshan (Yang and colleagues 2011) and in Consolidated Murchinson (Grund and colleagues 2011), where a large share of the global production originates (respectively 60% and 2% (U.S. Geological Survey 2012)). Both processes require temperatures of 1100-1300°C, typically provided by the combustion of coal in antimony-producing countries. It is reported that more than three tons of coal are required to extract one ton of antimony from its ores in Xikuangshan (Yang and colleagues 2011). Antimony refining processes require temperatures between 400°C and 950°C (Grund and colleagues 2011), suggesting significant energy consumption as well. Usually, metal extraction and refining processes consume much more energy than the mining and concentration stages (Norgate and Haque 2010), although this seems not to be the case for antimony according to the ecoinvent datasets.

In ecoinvent, the data for antimony extraction and refining is approximated with that of lead smelting. This is justified by the fact that ‘metallurgical processes in the antimony production are comparable to those in lead and zinc production’ (Althaus 2009). According to the resulting “antimony, at refinery” dataset, extraction/refining processes needed to produce 1 kg refined antimony require 6.7 MJ of energy in the form of “hard coal, burned in industrial furnace 1-10 MW”. To provide 6.7 MJ of energy in this form, 0.23 kg “hard coal mix” is used, according the “hard coal, burned in industrial furnace 1-10 MW” ecoinvent dataset. Therefore, following the “antimony, at refinery” dataset, 230 kg of coal are needed to extract 1 ton of antimony from its ores, which differs greatly with the 3 tons of coal per ton Sb needed through the roasting method reported by Yang and colleagues (2011). The validity of approximations used in ecoinvent for the extraction/refining of antimony can therefore be doubted.

The value for “hard coal, burned in industrial furnace 1-10 MW” in the “antimony, at refinery” dataset was changed to 86.7 MJ, which is the energy produced with 3 kg of “hard coal mix” according to above-mentioned relations. The resulting dataset is called “antimony, at refinery (3t)”. Significant differences can be observed between the two datasets in cradle-to-gate GWP, CED, and EQ (Figure 36). The variation in the latter category is mainly due to the emission of carbon dioxide during the combustion of coal.

Logically, using the new dataset gives a quite different picture of the relative contribution of mining/beneficiation and extraction/refining stages to cradle-to-gate GWP, CED, and EQ (Figure 37), compared to results using the original dataset (Figure 35). With these new figures, antimony moves up respectively five and three places in the ranking proposed by Nuss and Eckelman (2014) for the categories GWP and CED (i.e., 31 and 27 metals now have a lower score, respectively).

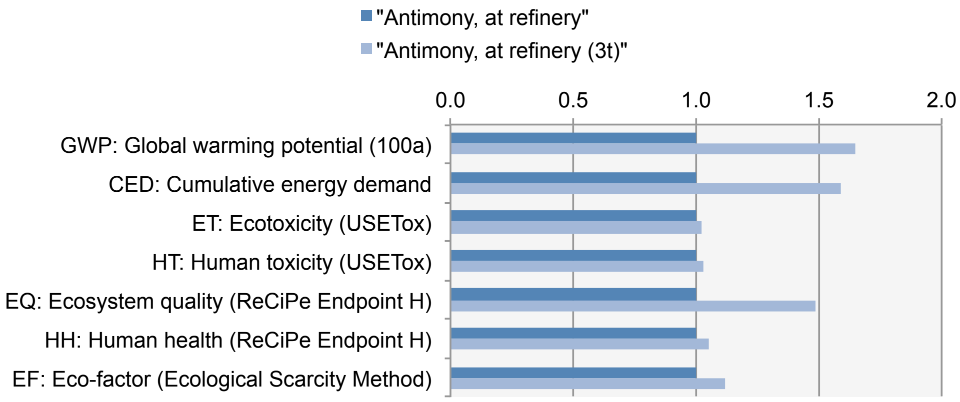


Figure 36: Variation in cradle-to-gate LCA scores between “antimony, at refinery” and “antimony, at refinery (3t)” datasets

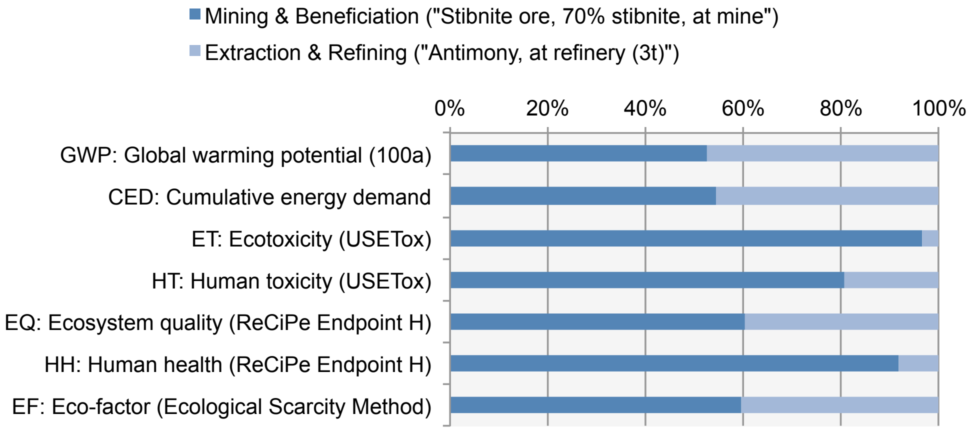


Figure 37: Life cycle stage contribution for selected impact categories using the dataset “antimony, at refinery (3t)”

Toxicity for humans and ecosystems

As previously mentioned, the cradle-to-gate ET, HT and HH scores of primary antimony production as modeled in ecoinvent are mainly affected by the disposal of sulfidic tailings during mining/beneficiation processes (respective contributions of 90%, 65% and 78% in the original dataset, slightly less in the “antimony, at refinery (3t)” dataset).

In reality, antimony is mostly mined from sulfide ores and, although little quantified information was found on this subject, it is likely that large quantities of sulfidic tailings are generated during the mining and beneficiation of antimony ores. This suggests that approximation with molybdenum is relevant, at least qualitatively. Furthermore, serious environmental pollution has been reported in Xikuangshan due to the extraction and refining of antimony. The high temperatures required by the roasting process cause the volatilization and emission of considerable quantities of antimony sulfide and other low-boiling heavy metals found in antimony ores such as lead, arsenic, mercury and cadmium, as well as the emission of sulfur dioxide (Yang and colleagues 2011). As a result, the concentrations of Sb, Pb, As, Hg and Cd in the soil, water, plants and human hair measured around the Xikuangshan mine are much higher than those observed in non-mining areas (Wang and colleagues 2010; Guo and colleagues 2014).

The ecoinvent dataset "antimony, at refinery” effectively contains outflows of Sb, Pb, As, Cd, Hg and SO_2 into the environment (Table 20), suggesting that approximation is with lead smelting is qualitatively relevant. With the lack of quantified information on emissions during Sb production processes, assessing the validity of approximated emission factors is difficult. It is however likely that emissions of Pb are lower and of Sb higher. Tian and colleagues (2014) estimate that 75 grams Sb are emitted into the air per ton of primary Sb produced, which is 34 times more than assumed in the ecoinvent dataset. As regards other substances, data unavailability prevents from assessing the relevance of approximations.

To assess the consequences of higher Sb emissions and lower Pb emissions, the dataset "antimony, at refinery (75g)" is created, identical to the original ecoinvent dataset except for antimony and lead emissions. Modified values are indicated in Table 20, and consequences on toxicity relevant LCA scores are given in Figure 38. HT and EF are reduced by about 15%, as a result of a 99% reduction in lead emissions.

Table 20: Selected emissions factors (in gram per ton refined Sb) contained in the "antimony, at refinery" dataset

Fate	Substance	"Antimony, at refinery"	"Antimony, at refinery (75g)"
Air, low population density	Antimony	2.2	75.0
	Arsenic	3.9	3.9
	Cadmium	3.2	3.2
	Lead	301.6	3.0
	Mercury	0.08	0.08
	Sulfur dioxide	31932	31932
Water, river	Arsenic, ion	1	1
	Cadmium, ion	2.5	2.5
	Lead	17.4	1.7
	Mercury	0.04	0.04

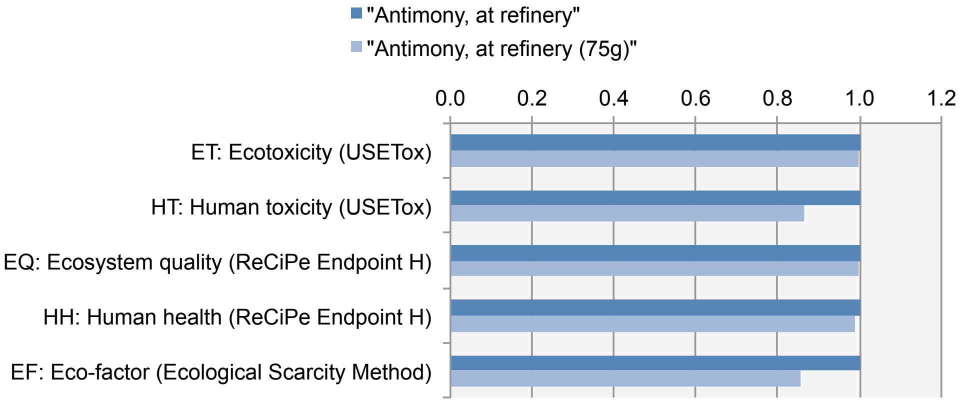


Figure 38: Variation in cradle-to-gate LCA scores between "antimony, at refinery" and "antimony, at refinery (75g)" datasets

Contribution to global emissions

In order to assess the contribution of primary antimony production to global environment problems, impact category indicators are calculated for a global primary production of 170 Gg as estimated for the year 2011, and the results are then compared with reference values for the global situation (i.e., normalization). To do this are used the LCI dataset "antimony, at refinery (3t)", the CML 2001 characterization method (Guinée and colleagues 2001) and its integrated "World 2000" normalization data (Wegener Sleeswijk and colleagues 2008). Results, shown in Figure 39, indicate that the contribution of global antimony production to global environmental problems is very small. Comparison between impact categories suggest that primary antimony production contributes more to damages to ecosystems and human health than to climate change. The high contribution for marine aquatic ecotoxicity is mainly caused by the emission of hydrogen fluoride into the air (87% contribution for this impact category). It has however previously been noted that the contribution of hydrogen fluoride for normalized marine aquatic ecotoxicity is severely overestimated (Heijungs and colleagues 2007).

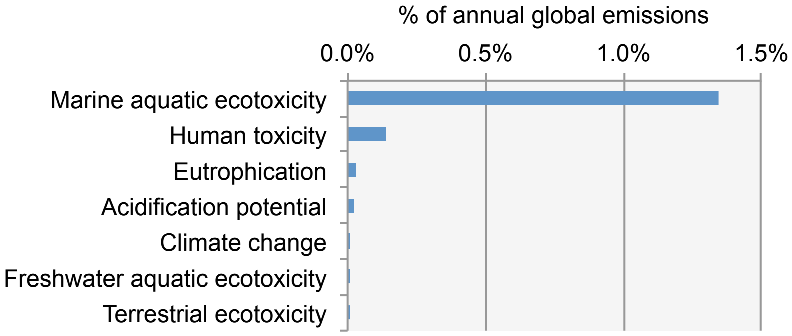


Figure 39: Cradle-to-gate environmental impacts for the primary production of 170 Gg Sb normalized to the total annual worldwide emissions.

Conclusions

Based on these limited information, it can be inferred that primary antimony production generates significant impacts on the environment, both in terms of contribution to global warming and damaging effects on human health and ecosystems. The environmental hotspots identified are the high electricity consumption and disposal of sulfidic tailings during mining and beneficiation processes, and the high coal consumption at the extraction and refining stages. The normalization of total impacts to the global situation however suggest that environmental impacts of antimony production play a negligible role in the grand scheme of global environmental problems.

In view of the information gathered during the research, it appears that existing ecoinvent datasets on antimony mining/beneficiation and extraction/refining, based on approximations, may be inconsistent with values for actual processes. In particular, the approximated energy demand of extraction and refining processes is much lower (more than one order magnitude) than reported empirical data, which has considerable impacts over the cradle-to-gate cumulative energy demand, global warming potential, and damages to ecosystem quality. Furthermore, emissions of antimony during extraction and refining processes are likely higher than approximated, whereas those of lead are probably smaller. Very little quantified information is available regarding other emissions.

Overall, the assessment of cradle-to-gate environmental impacts related to primary antimony production is accompanied by large uncertainties, caused by the use of approximations for the life cycle inventories of antimony mining and processing, as well as by inherent uncertainties encountered in LCA. Further research is needed to improve the accuracy of life cycle inventories related to primary antimony production.

6.1.2 SECONDARY PRODUCTION

Information on the recycling of antimony in terms of quantities involved and technologies used is scarce, even in industrialized countries. Most secondary antimony comes from the recycling of lead products, and particularly of lead-acid batteries. Some quantities may also be recovered through the recycling of antimony-containing plastics and glass products. In the absence of quantified information, only rough estimates can be generated regarding the energy use of secondary antimony production.

Previous studies have estimated that, on a life cycle basis, lead recycling consumes about 65% less energy than needed for primary production (Norgate 2004). Using ecoinvent dataset "lead, primary, at plant" (Classen and colleagues 2009), the cradle-to-gate CED of primary lead production is 25 MJ-eq per kilogram of primary lead produced. Therefore, the CED of secondary lead production can be estimated at 9 MJ-eq/kg secondary lead. As antimony is mostly recycled from together with lead, it is considered that the CED of secondary lead production is a valid proxy for CED of secondary antimony production. Taking 9 MJ-eq/kg secondary antimony as a basis, antimony recycling would consume about 94% less energy than needed for primary production based on the "antimony, at refinery" dataset (CED: 141 MJ-eq/kg), and about 96% less when "antimony, at refinery (3t)" (CED: 225 MJ-eq/kg) is considered. Similar energy savings are obtained through the recycling of aluminum, gold, magnesium, platinum-group metals, and silver (UNEP 2013b). Although the reduction in terms of GWP also depends on the energy sources used for recycling processes, it is probably very high as well given that energy requirements are much lower.

Considerable quantities of antimony-containing products end up in the feed for waste incineration. According to the MFA results, this flow amounted to 41 Gg in 2011, representing about 24% of the demand for primary Sb and 33% of the Sb being landfilled for the same year. Therefore, recovery of Sb from waste incineration residues could potentially help "closing the loop" by alleviating the demand for primary antimony by a fourth as well as decrease the amount of Sb being landfilled by a third. As far as the author is aware, such recovery has not yet been implemented. Based on experimental data from laboratory tests (Li and colleagues 1991; Anderson and colleagues 1994; Anderson and Twidwell 2008), Werner (2014) calculated the "grave-to-gate" CED, GWP and EF of an hypothetical recovery of antimony from MSWI (Municipal Solid Waste Incinerator) fly ash. The resulting values, published in a study by the Swiss Geotechnical Commission (SGTK 2014), indicate that the recovery of antimony from incineration residues would require considerably more energy (354MJ-eq/kg) than needed for primary production, mainly because of the production of chemicals required for the recovery process. Depending on the dataset used for primary antimony production, the global warming potential of recovery from MSWI (assuming a Swiss electricity mix) may be higher or lower than that of primary production. Furthermore, the overall environmental burden of such recovery process, approximated with the EF impact category, is less than half than that of primary production as energy consumed is less carbon-intensive (Swiss electricity mix) and emission of toxic substances during primary production is avoided.

Cradle-to-gate GWP, CED and EF scores of primary production obtained with the "antimony, at refinery" and "antimony, at refinery (3t)" datasets are compared with those assumed for secondary production ("grave-to-gate") from lead products and from waste incineration residues (Figure 40).

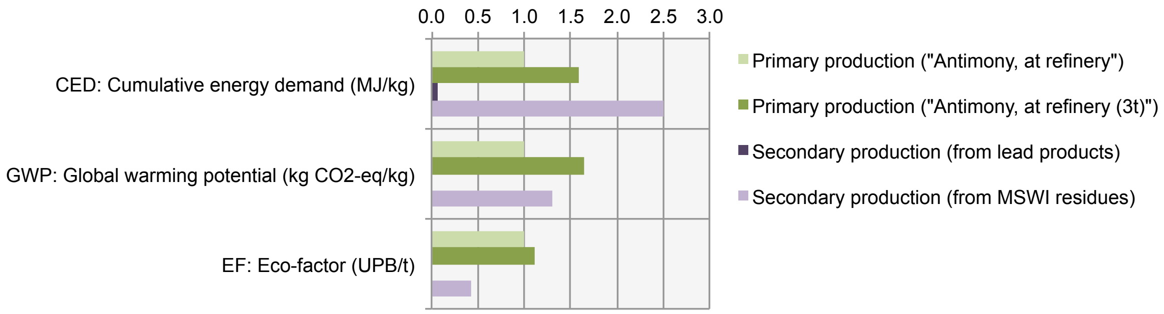


Figure 40: Comparison of LCIA scores between different datasets for primary and secondary production. Data sources and assumption relative to each dataset are given in the text.

It appears that recovery of antimony through the recycling of lead alloys can deliver major energy savings. According to the MFA model, 46 Gg Sb was recycled from old and new metal (mostly lead) scrap in 2011. Assuming an energy saving of 95% compared to primary production, this represents about 8 PJ of avoided energy consumption. To give an idea of scale, this is roughly equivalent to the daily energy use of the Dutch economy (CBS 2012). The diminution of related greenhouse gases emissions is likely considerable as well, although its extent depends on the energy mix used for recycling processes. Furthermore, recycling avoids environmentally damaging processes during primary production, such as the high consumption of coal-based electricity and disposal of sulfidic tailings during mining and beneficiation, and the high consumption of coal during extraction and refining. Therefore, the eco-factor of antimony recycling from lead products is likely lower also.

If implemented, the recycling of antimony from waste incineration residues could considerably reduce the demand for primary antimony as well as the volumes being landfilled each year. However, the energy required to produce chemicals needed for the recovery could offset the energy savings from avoided primary production. If the energy used for recovery processes is based on less carbon-intensive energy, the overall contribution to global warming could be reduced. For the same reasons as in the case of recycling from lead products, recovery from waste incinerations would likely result in a decreased eco-factor. It must however be stressed that there are high uncertainties concerning figures on recovery from waste incineration, as they are based on extrapolations from laboratory scale data.

Even more than in the case of primary production, assessing the environmental impacts of secondary antimony production is limited by the lack of qualitative and quantitative information. The conclusions reached above must therefore be considered as indicative rather than accurate, and additional research is needed to provide a clearer picture.

6.2 Environmental Risk of Emissions

In order to assess the risk for human health and ecosystems related to the release of antimony into the environment, it is important to identify the sources of such releases, assess their fate in the environment and their bioavailability, and characterize the type of adverse health effects that can be caused by exposure to antimony for humans and other living species (i.e., hazard identification). Due to time constraints and data unavailability, a thorough risk assessment cannot be completed. Rather, the semi-quantitative analysis offered below serves as a preliminary study on the human and ecosystem health risk related to global anthropogenic emissions of antimony.

6.2.1 SOURCES

Antimony is widely dispersed in the environment, as a result of both natural and anthropogenic processes. Volcanic eruptions, weathering of antimony-bearing rocks and minerals, soil runoff, forest fires and sea salt spray were identified as major natural sources of antimony emissions (Nriagu 1989). Anthropogenic emissions are generated through the mining, smelting and refining of antimony ores as well as during manufacture, use and disposal of antimony-containing products. Furthermore, antimony may be released into the environment as a result of the production, consumption and waste management of resources in which antimony occurs as a contaminant, such as fossil fuels (mainly coal, containing between 0.05 and 10 ppm Sb (U.S. Geological Survey 2014e)), other metal ores, and municipal/solid waste (containing 10-60 ppm Sb (van Velzen and colleagues 1998)). Using the distinction proposed by van der Voet (1996), these two types of anthropogenic emissions are referred to as emissions from intentional applications, i.e., purposely using antimony for its intrinsic properties, and emissions from non-intentional applications, i.e., arising from the natural occurrence of antimony in other anthropogenic flows.

In this section, the sources of antimony emissions are identified and their magnitude is assessed. To this end, emissions estimated with the MFA model for the year 2011 are compared with previous estimates of global antimony emissions. Based on this comparison, conclusions are drawn on the absolutes quantities of antimony being released into the environment, as well as on the relative magnitude of natural and anthropogenic emissions, on the one hand, and on the relative magnitude of emissions from intentional and those from non-intentional emissions, on the other.

MFA results

The MFA model focuses on the anthropogenic flows of antimony resulting from intentional applications. Natural emissions and anthropogenic emissions from non-intentional applications of antimony are therefore not assessed by the model.

According to the MFA model, about 23 Gg Sb was emitted into the environment during production of antimony, and manufacture, consumption and disposal of antimony-containing products in 2011 (Figure 41). About 84% of those emissions are into soils (19.2 Gg), 15% into the atmosphere (3.5 Gg), and about 1% in surface waters (0.3 Gg).

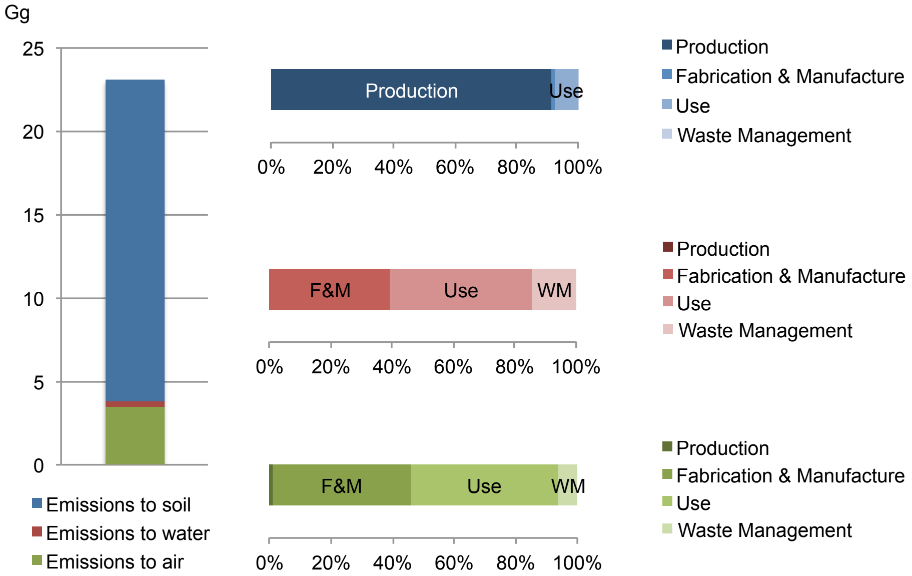


Figure 41: Global anthropogenic antimony emissions from intentional applications in 2011 according to the dynamic MFA model. The contribution of each life cycle stage to soil, water and air emissions is indicated

Emissions to soil are mainly generated by primary production processes (91% of total), where a significant fraction of antimony contained in ores cannot be recovered and is disposed on soils as mine tailings and smelter slag. Tailings and slag account for respectively 60% and 40% of emissions of antimony to soils at the Production stage. The Use phase is the second largest contributor to emissions to soil (7% of total), resulting mainly from the use of antimony in ammunition (1.5 Gg/y)

Emissions to air are dominated by the Fabrication & Manufacture (45%) and Use (48%) phases. In particular, F&M of metallic products generate significant atmospheric emissions according to the model. Temperatures involved in the production of metal alloy products are usually much higher than those needed for manufacture of plastic, glass and ceramic products, thereby causing the volatilization of more antimony. At the Use phase, most emissions to air result from dissipation in brake pads, pigments, and lubricants. About 6% of total air emissions are generated by Waste Management processes (mainly incineration), whereas air emissions from Production are very small according to the model (30 tons in 2011). Due to lack of information, atmospheric emissions from extraction (smelting) processes were not included in the MFA, although they are likely significant. This would suggest that atmospheric emissions from primary production processes are in reality higher than estimated. However, (Tian and colleagues 2014) estimated global atmospheric emissions from antimony production at 10 tons in 2010. It can therefore be concluded that emissions to air from antimony production are very uncertain.

Emissions to water are relatively small according to the model, with about 300 tons worldwide in 2011. F&M processes contribute to about 39% of the total (mainly from F&M of metallic products), and Use to some 46% (mostly from leaching of flame retardants). Wastewater treatment also generates significant emissions to water (15% of total).

Comparison with previous estimates

Previously, global emissions of antimony have been estimated in a three studies, focusing mostly on anthropogenic emissions from non-intentional applications.

Nriagu and Pacyna (1988) estimated the worldwide anthropogenic emissions of antimony into air, water and soils for the year 1983 along with that of 15 other trace metals. In total, they estimated that about 79 Gg Sb were released into the environment as a result of anthropogenic activities in 1983 (Figure 42). This is about 50% more than the primary antimony production for the same year (British Geological Survey 2015), indicating a high contribution of non-intentional uses of antimony. About 73% of those emissions were into soil, resulting mainly from tailings of Pb, Cu, Ni and Zn mines (34%), coal fly and bottom ash (21%), and Pb, Cu, Ni, and Zn smelter slag (21%). Emissions into water represent 23% of the total and arise mainly from manufacture of metal products (49%), nonferrous metal (Pb, Cu, Ni, Zn) production (21%), and wastewater effluents (13%). Air emissions represent 4% of the total, and are generated primarily by nonferrous metal (Pb, Cu, Ni, Zn) production (43%), fossil fuel combustion (37%), and waste incineration (19%). It must be noted that emissions due to the primary and secondary production of antimony, as well as to the use of antimony-containing products, were not taken into account by Nriagu and Pacyna. Global anthropogenic emissions of antimony into soils and water have since not been inventoried.

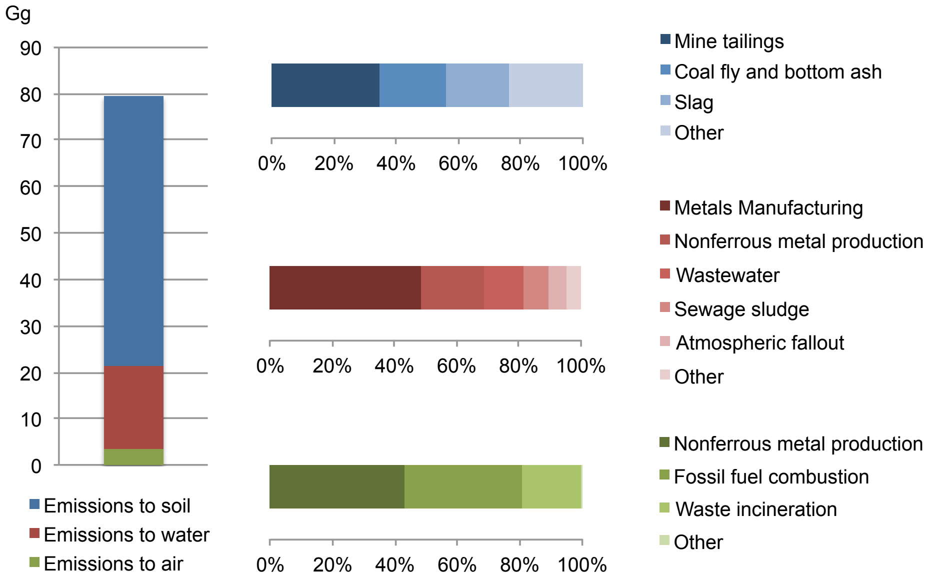


Figure 42: Estimation of 1983 global anthropogenic antimony emissions from non-intentional applications (Nriagu and Pacyna 1988)

As far as global atmospheric emissions are concerned, Pacyna and Pacyna (2001) provided an update for the mid-1990s. Sb emissions into air were estimated at 1.6 Gg per year, less than half of the estimate for 1983. Combustion of fossil fuels was estimated to be the largest source (47%), followed by nonferrous metal (Pb, Cu, Ni, Zn) production (35%) and waste incineration (17%). More recently, Tian and colleagues (2014) estimated the global emissions of antimony into the atmosphere at 1.9 Gg in 2010, resulting mainly from fossil fuel combustion (42%), waste incineration (24%), nonferrous metal production (17%, with Cu: 173t; Zn: 69t; Pb: 68t; and Sb: 10t), and brake wear (17%). Brake linings wear was not included in the other studies, although it was identified as a major source of Sb emissions (von Uexküll and colleagues 2005; Hjortenkrans and colleagues 2007; Quiroz and colleagues 2009). A comparison of previous estimates of annual atmospheric antimony emissions from anthropogenic activities is given in Figure 43.

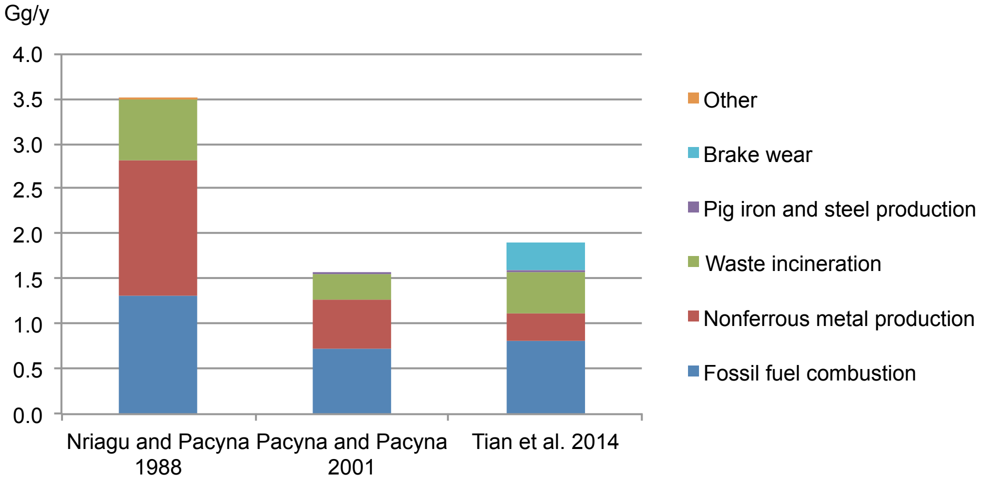


Figure 43: Previous estimates of annual global anthropogenic emissions of Sb into the atmosphere

As seen in Figure 44, the magnitude of global anthropogenic emissions resulting from the MFA model is almost equal to that estimated by Nriagu and Pacyna (1988), and about twice as high as estimated by Pacyna and Pacyna (2001) and Tian and colleagues (2014). However, the sources of emissions are different, as the MFA model generated in this study only accounts for atmospheric emissions resulting from intentional uses of antimony, whereas previous estimates focused on emissions related to non-intentional applications of antimony, with the exception of brake pad wear which is included in Tian and colleagues' study. Regarding the latter, there is a remarkable similitude between the value estimated through the MFA model and that estimated by Tian and colleagues (330 tons per year and 318 tons per year, respectively), although the estimation method is entirely different. Tian and colleagues used a bottom-up approach by assuming a share of about 60% of vehicles in use worldwide being equipped with Sb-containing brake pads, and an emission factor of 0.59/car/year. In the current study, emissions from brake pads are estimated using a top-down approach based on the estimated global Sb consumption in this application (475 tons in 2011) and an assumed dissipation factor of 0.7, as used by Månsson and colleagues (2009) in their antimony SFA for Stockholm.

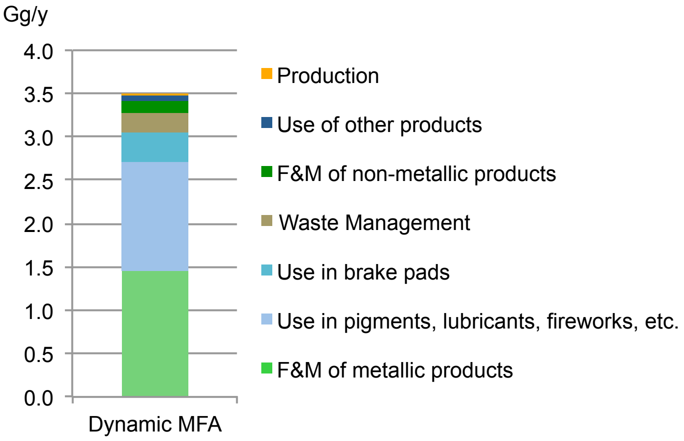


Figure 44: Global anthropogenic emissions of Sb into the atmosphere in 2011 according to the MFA model

Because the system boundaries of previous estimations of global antimony emissions differ to those used for this study, comparison cannot be used to assess the quality of figures estimated with the MFA model. The only figure for which comparison is possible is the emissions of antimony to air resulting from the dissipation in brake pads. In this regard, results from this study and from that of Tian and colleagues (2014) are remarkably similar.

Nevertheless, this difference in system boundaries can be harnessed to provide information on the relative magnitude of anthropogenic emissions arising from intentional and non-intentional uses of antimony (Figure 45).

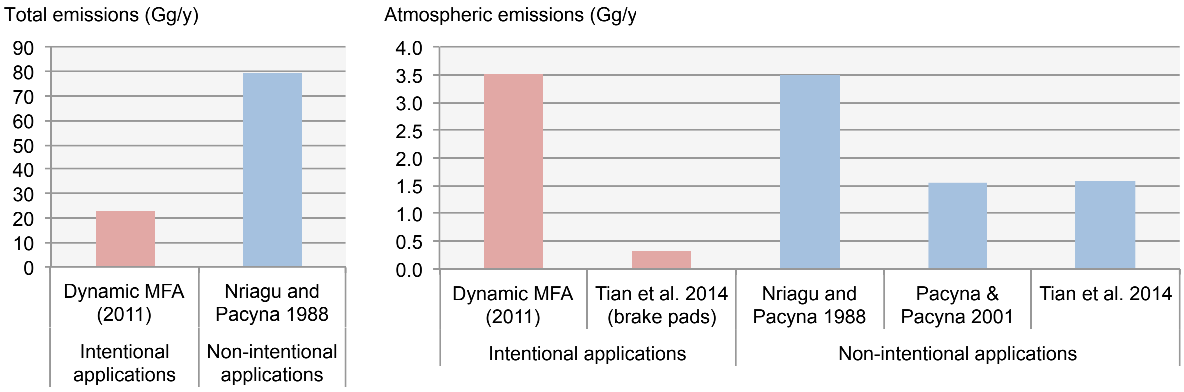


Figure 45: Comparison of emissions from intentional and non-intentional applications according to different estimates

Intentional versus non-intentional anthropogenic emissions

Assuming that both the results of the MFA and the figures estimated by Nriagu and Pacyna (1988) are correct and valid for the current situation, it can be estimated that about 100 Gg Sb is emitted each year into the environment as a result of human activities, and that almost 80% of the total can be attributed to non-intentional applications. Those are mainly the mining and smelting of nonferrous metals such as Pb, Cu, Ni and Zn, coal combustion, and manufacture of metal products. In all those processes, antimony occurs as a contaminant. About three quarters of all emissions are into soils, followed by emissions to water (about 20%) and emissions (about 5%). The share of non-intentional applications in emissions to soil is of about 75%, and in those to water of about 98%. Emissions to water account for about 23% of emissions from non-intentional uses of antimony according to Nriagu and Pacyna (1988), whereas they represent less than 2% of emissions from intentional applications according to the MFA model. This could either indicate that emissions to water are more common for non-intentional applications than intentional ones, that they are underestimated in the MFA model, or that they are overestimated in the study by Nriagu and Pacyna (1988). As emissions to soils and waters resulting from non-intentional uses have since not been estimated, cross-checking with other studies is not possible.

Atmospheric emissions are more documented than emissions to other environmental compartments. Previously, emissions of antimony into the atmosphere resulting from non-intentional applications (mainly fossil fuel combustion, nonferrous metal production, and waste incineration) have been estimated at between 1.5 Gg and 3.5 Gg per year. Atmospheric emissions arising from intentional uses of antimony (mainly manufacture of antimony alloys and use of antimony in brake pads, lubricants and pigments) are estimated at 3.5 Gg per year in the MFA model. Based on these information, it can be inferred that 5-7 Gg Sb are emitted each year into the environment, with a share of 50-70% of emissions resulting from intentional applications of antimony.

Such a large contribution of non-intentional application in emissions has previously been observed for copper, cadmium, and lead in the Netherlands. Van der Voet (1996) estimated that non-intentional applications contributed to 90% of emissions of copper from the Dutch economy to the atmosphere, surface water, and soils (excluding landfills) in 1990. When landfill and emissions are considered together, the contribution of non-intentional applications falls to 24%. In the case of cadmium, those contributions were calculated at 94% and 75%, respectively. In another study, Elshkaki and colleagues (2009) estimated that intentional and non-intentional applications have equivalent shares in the emissions of lead into the atmosphere resulting from the Dutch economy, and that non-intentional uses of lead contribute to about 80% of the landfilled stream of lead.

Natural versus anthropogenic atmospheric emissions

In order to assess the extent of human influence in the natural antimony biogeochemical cycle, natural and anthropogenic emissions can be compared. In the case of antimony, no estimation of natural emissions to soil and water could be found in the literature, and the comparison is therefore limited to atmospheric emissions (Figure 46).

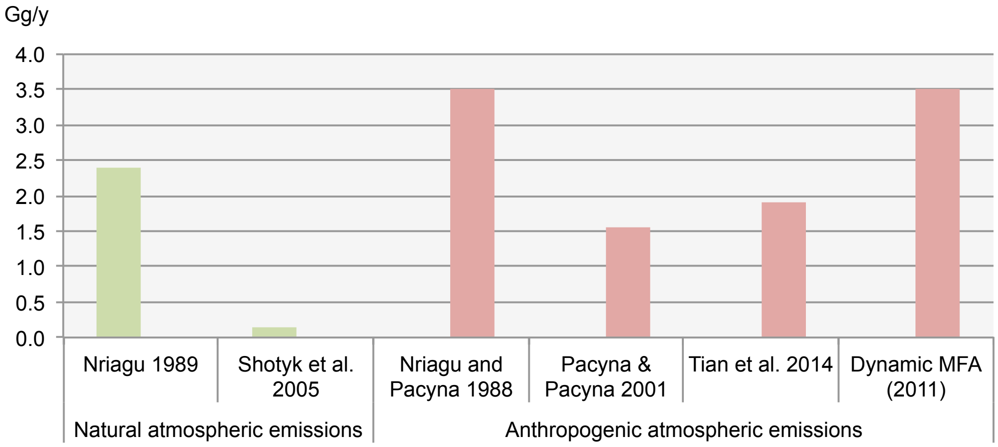


Figure 46: Comparison of natural and anthropogenic atmospheric emissions of antimony according to different estimates

Nriagu (1989) estimated global natural emissions of antimony to the atmosphere at 2.4 Gg per year for the year 1983, resulting mainly from wind-borne soil particles (33%), volcanoes (30%), and sea salt spray (23%). This lead Pacyna and Pacyna (2001) to conclude that anthropogenic and natural atmospheric emissions of Sb were comparable in size, with an anthropogenic/natural emissions ratio of 0.7. However, based on measurements of antimony concentrations in peat bog cores, Shotyk and colleagues (2005) argue that Nriagu severely overestimated natural atmospheric emissions, and those only amount to 0.15 Gg per year. The authors therefore assert that 'natural Sb inputs during the past two centuries are dwarfed by industrial inputs', assuming that the estimate of 1.6 Gg/y for anthropogenic emissions provided by Pacyna and Pacyna (2001) is correct. The resulting anthropogenic/natural emissions ratio is 10.7, higher than for any other metals included in the comparison performed by Pacyna and Pacyna (2001). Lead comes second, with a ratio of 9.9. Combining the emissions from non-intentional and intentional applications, the total anthropogenic atmospheric emissions of antimony amount to 5-7 Gg per year, and the anthropogenic/natural ratio rises to 33-47. This suggest that human activities have a considerable influence on the global atmospheric antimony cycle, much higher than for any other trace metals, and that the natural cycle is negligible in comparison in terms of size.

Conclusions

Overall, there are considerable uncertainties regarding sources and magnitude of both anthropogenic and natural emissions of antimony. Previous estimates have mostly focused on atmospheric emissions from non-intentional applications, such as from the mining and smelting of other metal ores and the combustion of fossil fuels, both being resources in which antimony naturally occurs. Very little research has previously been conducted on global emissions to water and air, either from intentional or non-intentional applications.

Bearing in mind these uncertainties, several observations can nevertheless be made by comparing the results of the MFA model with information from the literature:

- In total, it is estimated that about 100 Gg Sb is emitted into the environment each year as a result of human activities. Approximately 75% of those emissions are into soils, while some 20% are to waters, and 5% to the atmosphere;
- It appears that emissions resulting from non-intentional applications of antimony are about four times greater than those arising from its intentional uses. For atmospheric emissions specifically, the intentional/non-intentional ratio falls to 50-70%. This has important implications for

environmental policy, as an effective antimony emission reduction policy should not be limited to intentional uses of the metal, but also target the emissions from non-intentional applications.

- Measurements from peat bog cores suggest than natural atmospheric emissions of antimony are much smaller than anthropogenic releases, differing by a factor of about 40. This indicates that the natural Sb cycle is negligible in size compared to the anthropogenic cycle, and that human activities have a huge influence on the natural Sb biogeochemical cycle.

6.2.2 FATE

To assess the potential risk to human and ecosystem health posed by emissions of antimony in the environment, it is important to know the ultimate fate of those emissions, i.e. in which environmental compartment they end up and under which form (species), as well as their bioavailability, i.e. the proportion of total antimony in the environment that is available for incorporation into living organisms.

Information on transformation and transport of antimony in the different environmental compartments is scarce and often contradictory (Filella and colleagues 2009). In oxic environmental conditions, antimony is rapidly (in a few days) oxidized from Sb (0) to Sb (III) and then to Sb (V) (Filella and colleagues 2002). Antimony is therefore predominantly found in its pentavalent form in the atmosphere, waters, soils and sediments.

Concentrations of antimony in airborne particulate matter vary from a few pg/m^3 in remote areas such as the South Pole or oceanic locations to a few ng/m^3 in urban areas and even hundreds of ng/m^3 or close to major sources of pollution such as waste incinerators, mining and smelting sites and high-traffic areas (Belzile and colleagues 2011). Antimony compounds have an average residence time of one to two weeks in the atmosphere (Tian and colleagues 2014), after which they deposit on surface waters, soils and sediments.

Concentrations of antimony in unpolluted waters are usually well below 1 µg/l (Filella and colleagues 2002), but they can be much higher in the proximity of anthropogenic sources. In Xikuangshan, concentrations of 163 µg/l have been measured in surface water, and of 5-30 mg/l in water streams flowing through tailing piles (He and colleagues 2012). Most antimony compounds exhibit low water solubility and eventually end up either in soil or sediment (Tylenda and Fowler 2007). Thus, most antimony released into air and water ultimately makes its way into soils.

In soils, the mobility of antimony is mainly controlled by pH and by the presence of hydrous oxides of iron, manganese and aluminum, to which the antimony is adsorbed (Schwarz-Schampera 2014). It is generally accepted that antimony is essentially immobile in soils (Filella and colleagues 2009). Concentration of antimony in soil usually ranges from 0.1–10 mg/kg (dry weight), but can be much higher close to anthropogenic sources, especially related to mining, shooting and traffic activities. For instance, concentration ranging from 5 to 12 g/kg have been measured in soils of Xikuangshan (Okkenhaug and colleagues 2011), up to 15 g/kg in those of a former mining and smelting area in Tuscany (Tschan and colleagues 2009), up to 14 g/kg in topsoils of Swiss shooting ranges (Tschan and colleagues 2009), and up to 10 g/kg in soils along roads (Turer 2005). The risk of leaching to groundwater from soils appears low due to the immobility of antimony in soils (Hou and colleagues 2013).

The bioavailability of Sb in soils is not well understood and results of studies conducted so far are not consistent. For instance, Flynn and colleagues (2003) have measured low water solubility levels in soils of British mining and smelting sites (only 2.5% of Sb found in samples was water soluble) suggesting low reactivity and mobility in the upper soil horizon, as well as low bioavailability for biological organisms. The authors therefore argue that soil contamination by Sb due to human activities does not constitute a severe risk to the environment or to human health. In contrast, Okkenhaug and colleagues (2011) observed higher levels of soluble Sb in soils of Xikuangshan and significant uptake by plants proved by concentrations between 100 and 4,000 mg/kg in plants (average 650 mg/kg, N=10), much greater that background Sb levels in terrestrial plants (0.2-50 µg/kg). This suggests that antimony can enter the food chain.

6.2.3 EFFECTS

Antimony is a non-essential element in plants and animals. It belongs to the same group of the periodic table as arsenic and their toxicological behavior is considered similar (Grund and colleagues 2011). Evidence however suggests that, on a weight basis, arsenic is much more toxic to living organisms (Tylenda and Fowler 2007). Exposure to high concentrations of antimony can induce cellular and tissue injury, but the mechanisms of these toxicities are not well understood (Cavallo and colleagues 2002). Overall, information on ecotoxicology of antimony is very limited and of variable reliability (Filella and colleagues 2009). There is evidence of carcinogenicity of antimony trioxide for animals, as female rats exposed to long-term, high concentration inhalation developed lung tumors (EU 2008a). There is insufficient evidence for carcinogenicity of antimony trioxide in humans, and the substance is classified as "possibly carcinogenic to humans" by the International Agency for Research on Cancer (IARC 1989), and as "suspected of causing cancer via inhalation" by the European Union (EU 2008b). It is often considered that trivalent species are more toxic than pentavalent species, although data supporting such claim is lacking (Filella and colleagues 2009). Below, toxic effects on humans and on other species are distinguished.

Human Health

Exposure to high concentrations of antimony can cause adverse effects to humans. The main routes of exposure are inhalation of contaminated air, ingestion of contaminated food or water, and dermal contact with antimony. Beside the exposure route, several factors influence the toxicity of antimony, such as the form under which it is intaken (e.g. trioxide, trisulfide, etc.), the exposure dose and duration, other chemical exposures, age and sex of exposed person, etc. So far, toxicological studies have mostly focused on antimony trioxide, as it is the most used compound by far. Previous risk assessments (EU 2008a; Environment Canada 2010; U.S. EPA 2014) concluded that significant health hazards exist for workers in the antimony industry, while exposition to antimony through use of antimony-containing products and from environmental sources (water, food, air) pose a low health risk.

Some workers in the antimony processing industry suffer from inflammation of the skin (dermatitis), lung diseases (pneumoconiosis), stomach pain, diarrhea, vomiting and stomach ulcers (Cooper and Harrison 2009; Sundar and Chakravarty 2010). Effects on the heart, sometimes fatal, have been associated to long-term industrial exposure to antimony trioxide (Tylenda and Fowler 2007). Significant correlations between occupational exposure to antimony and rates of lung cancers were observed in some studies, but not in others (Sundar and Chakravarty 2010). In many industrial setting, coexposure to antimony and arsenic occurs as arsenic often occurs as a contaminant in antimony compounds, so that health problems observed in workers could be caused by arsenic more than antimony (Tylenda and Fowler 2007). Additional experimental and epidemiologic data is needed to better assess the risks of occupational exposure to antimony. The international occupational standard limit for antimony concentration in air is 0.5 mg/m^3 (Cooper and Harrison 2009), about ten times below the concentrations to which female rats who developed lung tumors were subjected (IAA 2014).

Exposure from environmental sources occurs mainly as a result of ingestion of contaminated food and water. The World Health Organization (WHO 2003) recommends a maximum total daily intake of 0.6 µg/kg body weight, representing 36 mg (36,000 µg) per day for a person with a body weight of 60 kg.

Estimated values for total daily intake of antimony for a typical diet are generally lower than 10 µg per day (Belzile and colleagues 2011). Using data on levels of antimony in food and water for the USA, Health Canada (1997) estimated a daily intake for adults of 7.5 µg of antimony per day, with about 62% coming from food and 38% from water (rounded values, air inhalation contributes to 0.5% of the total intake). In normal conditions, the total daily antimony intake from food and water is therefore about four orders of magnitudes below the WHO value. However, the total daily intake of a person living in the vicinity of antimony mining and smelting sites could be much higher. If the average antimony concentrations of 650 mg/kg measured in plants in Xikuangshan (Okkenhaug and colleagues 2011) is representative of the content in edible plants in the area, the total daily intake of humans consuming locally grown vegetables would likely exceed 36 mg. Those populations are also exposed to high concentrations of antimony in water and air. Based on these information, risks to human health due to environmental exposure are considered low in most situations, but could be considerable for populations living close to antimony mining and smelting sites.

The health risks related to the use of antimony-containing products are considered as negligible for most applications due to the low concentrations involved in most consumptive losses. There is evidence of water and food contamination due to storage in PET containers. Sb content in (PET) bottled water can be ten times higher than in tap water (Shotyk and colleagues 2006), and the heating of food contained in PET oven-proof trays with microwave and conventional oven provokes the doubling of antimony concentration in food (Cooper and Harrison 2009). Nevertheless, the total daily intake of a person consuming most of its water and food from PET containers would probably still be well below the value recommended by the WHO. Another possible source of intake could be through polyester textiles, from which antimony can leach into sweat or saliva, however studies have showed that resulting exposure is well below the acceptable daily intake (Belzile and colleagues 2011).

The risks posed by the use of other antimony-containing products are considered insignificant by the European Union (EU 2008a). However, emissions of antimony from brake linings are increasingly considered as a considerable health hazard. Brake pad wear has been identified as the main source of antimony emissions from intentional applications in several studies (Mathys and colleagues 2007; Tsunemi and Wada 2008; Månsson and colleagues 2009). Although it is antimony trisulfide that is used in brake linings, the high temperatures reached when brakes are used provoke the oxidization of antimony trisulfide to antimony trioxide (von Uexküll and colleagues 2005). An estimated 70% of antimony used in brake pads will eventually be released into the air (Månsson and colleagues 2009), and about 90% of this antimony is inhalable by humans (von Uexküll and colleagues 2005). This poses a threat to humans living or working in the proximity of high traffic areas as antimony trioxide is suspected of causing cancer by inhalation. One study measured that the average antimony concentration in the blood of port workers exposed to heavy-weight vehicle traffic was five to ten times higher than the blood content of a control group (Quiroz and colleagues 2009). The health effects of exposure to antimony emissions from brake pad wear are however not well understood, and coexposure to other particulate matter renders the health risk assessment difficult.

Ecosystem health

Antimony has no known biological function and is not known to be used by any organism (Schwarz-Schampera 2014). It can however be absorbed by plants and animals, and higher than background concentrations are found in terrestrial and aquatic biota (e.g. plants, fishes, invertebrates, rabbits, birds) in the vicinity of antimony processing sites (EU 2008a).

Reliable ecotoxicological data of antimony is very scarce (Filella and colleagues 2009). Out of 16 studies on antimony ecotoxicity reviewed by Vangheluwe and Hyfte (2001), 13 have been rated as “not reliable”. In the three studies considered as reliable, the LC_{50}[2] for five different aquatic species ranged between 16 and 60 mg Sb/l, which is well above values commonly found in the environment (usually well below 1 µg/l). Concentrations of 5-30 mg/l have however been measured in water streams flowing through tailing piles in Xikuangshan (He and colleagues 2012), suggesting that antimony mining and smelting may significantly harm aquatic life locally.

Ecotoxicological data for terrestrial organisms is limited. EC_{50}[3] values for 11 soil organisms and terrestrial plants reviewed by Tschan and colleagues (2009) range between 70 and 7500 mg/kg, with lower values measured for soil organisms. As noted above, concentrations of antimony in soil usually range from 0.1–10 mg/kg dry weight, but can exceed 10000 mg/kg in mining and smelting sites, shooting ranges, and along traffic roads, which suggests that those activities may harm terrestrial organisms.

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[2] LC_{50} is the median lethal concentration, i.e. dose required to kill half the members of a tested population within 96 hours

[3] EC_{50} is the half maximal effective concentration, i.e. concentration that causes adverse effects in 50% of the test organisms

6.2.4 RISK CHARACTERIZATION

Based on the estimated anthropogenic releases of antimony into the environment, and the limited information on the fate of those emissions in the environment and their effects on human and ecosystem health, the following conclusions can be drawn:

Sources and fate:

- Considerable uncertainties exist regarding antimony emissions;
- It is estimated that about 100 Gg Sb is emitted each year into the environment as a result of human activities. About 75% of the total emissions are into soil, 20% into water, and 5% into air;
- Most antimony released into the environment is rapidly oxidized to the pentavalent form;
- Most antimony released in water and air compartment will eventually end up in soils, where antimony is essentially immobile;
- Bioavailability of antimony is not well understood, but evidence suggests that it can be taken up by plants and therefore enter the food chain.

Risks for human health:

- Significant risks for workers in antimony mining, smelting, refining and manufacture sites;
- Risks related to environmental exposure are generally low, but could be considerable in the vicinity of antimony mining and smelting sites and close to busy vehicle traffic arteries;
- Risks to users of antimony-containing products are considered low for most applications. Although antimony intake can be significantly increased if ingested water and food is stored PET containers, the resulting total daily intake is still well below the values recommended by the WHO.

Risks for aquatic and terrestrial organisms:

- Relevant and reliable ecotoxicological data is lacking;
- Existing information suggests that risks for aquatic and terrestrial organisms are generally low, but that harmful effects may occur in mining sites, shooting ranges, and along vehicle traffic roads.

Previously, environmental agencies of the European Union, Canada and the USA have conducted risk assessments on antimony (EU 2008a; Environment Canada 2010; U.S. EPA 2014). The three studies focused on antimony trioxide and reached similar conclusions. Overall, human health risks associated with exposure of the general population to antimony in products and in the environment were considered too low to adopt additional risk reduction measures. The only area of concern identified was for workers in the antimony supply chain, for which additional risk reduction measures are needed. It is noteworthy that those risk assessment studies did not quantify the risk related to emissions of antimony from brake pad wear, although it is a concerning issue. In all studies, harm to aquatic and terrestrial organisms exposed to antimony was considered as unlikely, although considerable uncertainties in this area were acknowledged.

Overall, the risks to human health and ecosystems posed by the release of antimony in the environment are not well understood. Much research is needed to provide a better picture of the fate, speciation, and bioavailability of antimony in environmental compartments on the one hand, and on the toxicology of antimony compounds for humans and other living organisms on the other.

7 DISCUSSION

In this chapter, answers offered by the research results to the research questions initially formulated are presented and discussed. Following the discussion, some of the limitations of the research are outlined, and a reflection is offered on the theories and methodologies used, as well as on the research project in general.

7.1 ANSWERS TO RESEARCH QUESTIONS

The aim of this study was to provide a first systemic picture of the global anthropogenic antimony cycle, explore its possible future development (at the 2050 horizon), and investigate its associated environmental impacts. In order to reach this threefold aim, the main research question (MQ) was formulated as follows:

MQ: What characterizes the current and possible future global anthropogenic antimony cycle, in terms of supply, demand and environmental impacts?

This broad research question was subsequently divided into a set of sub-questions, the answers to which are given below.

7.1.1 CURRENT ANTHROPOGENIC ANTIMONY CYCLE

Due to the better availability of data for this year, 2011 was chosen as the base year for the characterization of the "current" anthropogenic antimony cycle. In order to understand the current pathways of antimony in the anthroposphere (i.e., the part of the environment that is made or modified by humans), a material flow analysis (MFA) was conducted to identify and quantify the flows of antimony entering, circulating within, and leaving the global economy, from cradle-to-grave, i.e., from the extraction of the ore, its transformation into refined metal and compounds, the incorporation of these substances into products, the use of those products, and the waste management processes related to those products. The magnitude of flows of antimony being lost to the environment along these lifecycle stages was also assessed.

The results of the MFA model can be visualized in Figure 47 and Figure 48, both representing the 2011 cycle with high and medium levels of aggregation, respectively.

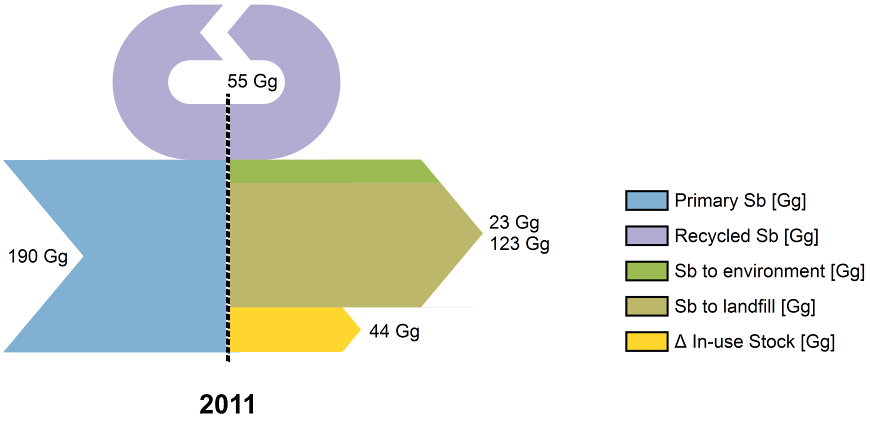
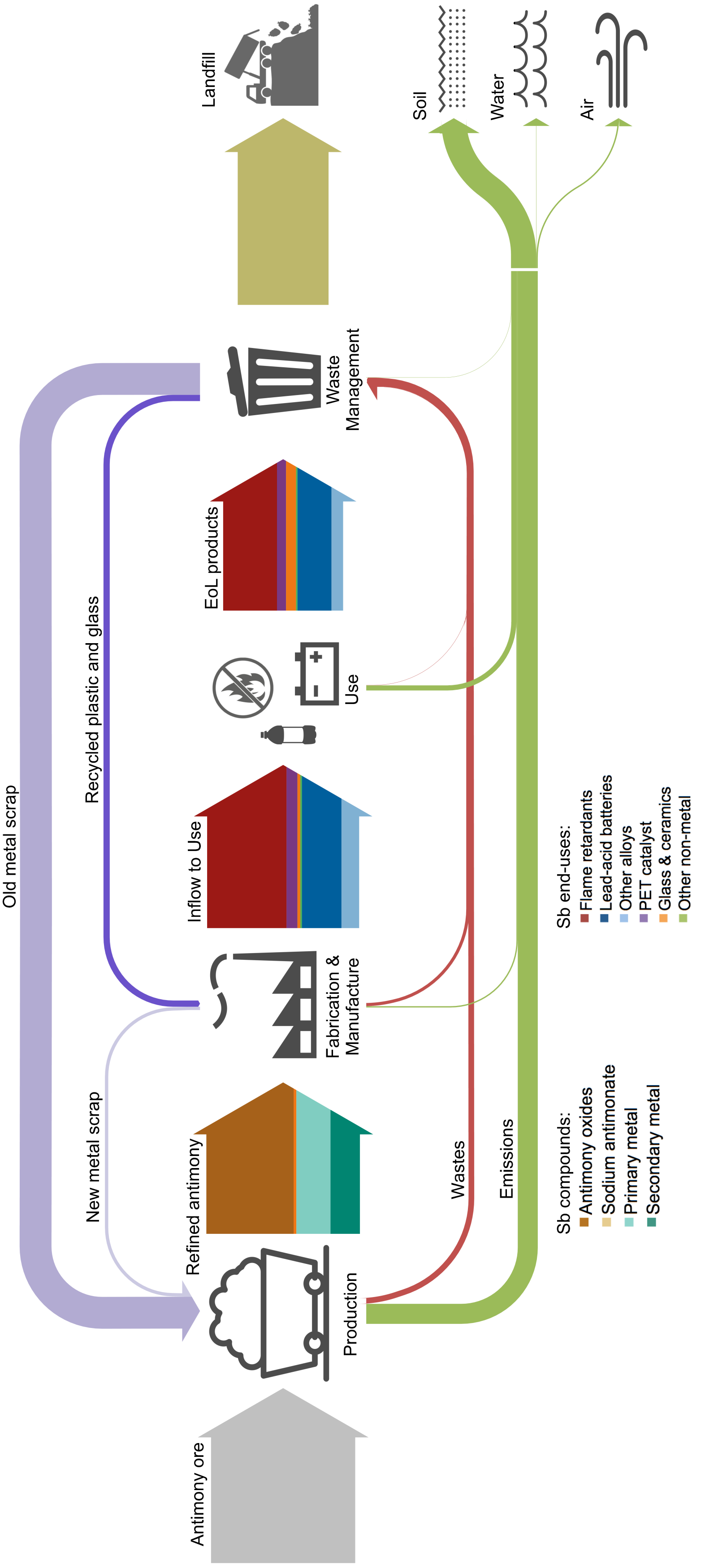


Figure 47: Global anthropogenic antimony cycle, 2011 (high aggregation)

Figure 48: Global anthropogenic antimony cycle, 2011 (medium aggregation)



SQ1: *What is the system-wide material efficiency of the cycle? (i.e., how circular is it?)*

Different metrics can be used to assess the material efficiency of a system. In the case of anthropogenic metal cycles, most used indicators are the end-of-life recycling rate (EoL-RR), i.e. the percentage of metal in end-of-life products that returns to the production and manufacture of new products, and the recycled content (RC), i.e. the share of recycled metal in the total input to production and manufacture stages. Those indicators are calculated using Eqs. 13 and 14:

$$\mathrm{EoL-RR} = \frac{OS + R}{\sum_i^A EoL(i)} \quad (13) \qquad RC = \frac{OS + NS + R}{O + OS + NS + R} \quad (14)$$

where OS is Sb in old metal scrap (in Gg), R is Sb in recycled plastic and glass (in Gg), and $EoL(i)$ is Sb in end-of-life product i (in Gg), A is the number of different antimony-containing product categories, and O is Sb extracted from its ores (in Gg).

In a fully circular anthropogenic antimony cycle, the value for both of those indicators would reach 100% (and 0% for a fully linear system). This is a hypothetical case, as it would require the complete recycling of all Sb leaving the Use phase, which is technically unfeasible due to unavoidable losses throughout the system, as well as a steady-state situation where demand and in-use stocks do not grow, which is not the case at global level.

Using the values calculated in the MFA (Section 5.2.2) gives an end-of-life recycling rate of 32% for 2011, meaning that about a third of antimony contained in end-of-life products is recycled (the rest being incinerated and/or landfilled), and a recycled content of 23%, which means that secondary sources represents almost a fourth of the total input to production and manufacture stages (the rest being supplied by primary sources). An uncertainty range of ±15% (i.e., EoL-RR=0.32±0.05, RC=0.23±0.03) is calculated for those indicators, by propagating the assumed uncertainties of input variables using the least square method (i.e., Gaussian error propagation).

The calculated EoL-RR places antimony at the 20th position among the 60 metals reviewed by the International Resource Panel (UNEP 2011a), with similar rates estimated for magnesium, molybdenum, and iridium. In this same report, the global average end-of-life recycling rate for antimony is estimated at <5%, based on 'expert opinion of the group', without any further information on the assumptions behind such a low estimate. Previous, MFA-based, estimates of national EoL-RRs are closer to the figure generated in this study (Section 5.2.3). Carlin (2006) estimated that the EoL-RR of antimony in the United States reached about 24% in 2000, accounting only for recycling of metallic antimony. Excluding non-metallic applications from Eq. 13 results in an EoL-RR of 26% in 2011. Tsunemi and Wada (2008) estimated the EoL-RR at 29% for Japan in 2008, including both metallic and non-metallic recycling. As far as the recycled content is concerned, antimony ranks in the medium range of the 60 metals reviewed by the IRP (UNEP 2011a), with a similar value estimated for beryllium, chromium, copper, zinc, tin, tantalum, rhenium and iridium. IRP experts estimate the global average RC at <10% for antimony, with no information on data sources and assumptions used, whereas it has been estimated at 18% for 2010 by Roskill (2011). Carlin (2006) calculated a value of 20% for the USA in 2000, excluding non-metallic recycling. When only metallic recycling is taken into account in Eq. 14, the recycled content falls to 20%.

The end-of-life recycling rate depends on the amount of antimony in end-of-life products as well as on the recycling rate for each end-use category. Data sources and assumptions used to estimate those variables are detailed in Sections 5.2.2 and 4.3.3, respectively. In the model, the recycling of antimony in lead-acid batteries represents 63% of the total stream of recyclates leaving the Waste Management stage, followed by antimony in recycled other alloys (19%). Non-metallic applications represent 18% of the total recyclates. Based on several sources, recycling rates of 70%, 60% and 10% were assumed for lead-acid batteries, other alloys (mainly lead sheets and pipes), and plastic and glass products, respectively. Recycling rates are further discussed in the answer to sub-question 6. The magnitude of end-of-life flows is estimated using delay and leaching models based on past inflows to Use, lifetime distributions, and dissipation/leaching factors. All those parameters entail considerable uncertainties. The recycled content mainly depends on the same variables, as well as on the amount of antimony returning to the Production stages from Fabrication & Manufacture (F&M) processes as new metal scrap, and on the extraction of Sb from its ores. Very little information exists regarding the F&M efficiencies for antimony products, and new scrap coefficient for metallic products were approximated with those used in a study on the global anthropogenic lead cycle (Mao and colleagues 2008b), as most metallic antimony is used in lead alloys. The resulting new-to-old scrap ratio is 10%, whereas it was estimated at 25% by Carlin (2006) for the USA, which could either indicate that the new scrap flow is underestimated in the MFA model or that the old scrap flow is overestimated, that Carlin's figures are inaccurate, or that US and global old scrap ratios differ. The inflow of antimony from ores into Production is estimated using information of primary production and primary production efficiencies from several sources, and is considered rather accurate.

In sum, it can be concluded that the system-wide material efficiency of the global anthropogenic cycle is rather low, and that the cycle resembles, in fact, more a linear system than a cyclic one. It is characterized by a mostly linear functioning, with relatively low recycling rates, and high levels of resource extraction, emissions, and landfilling. The end-of-life recycling rate is estimated at 32% and the recycled content at 23%. These values are slightly higher than estimated in most previous studies, and considerably higher than assumed by experts from the International Resource Panel. Considering that end-of-life recycling rates and recycled content are generally higher in countries such as Japan and the USA than globally, and deeming that IRP experts' opinion are overly pessimistic, it is likely that the global average end-of-life recycling rate is rather in the 15-25% range and not as high as estimated in the MFA. Such an overestimation is most likely due to lower actual global recycling rates for antimony-containing products. Using respective recycling rates of 60%, 50% and 0% for end-of-life lead-acid batteries, other alloys, and plastic and glass products, the EoL-RR falls to 22%, and the RC to 16%.

SQ2: *What is the size of current in-use stocks?*

Using a top-down approach, the total in-use Sb stock was estimated at 1800 Gg in 2011 (Section 5.2.2). This represents approximately a fourth of the cumulative primary production since the beginning of the 20th century (i.e., 7700 Gg). The rest has been lost into the environment (including landfills) over time. Furthermore, the size of the in-use stock is roughly equal to that of geological reserves as estimated by the U.S. Geological Survey (Section 5.3.5), meaning that as much antimony remains in "above-ground reserves" as in currently identified geological reserves. Figure 49 shows the breakdown of the 2011 in-use Sb stock by end-use category.

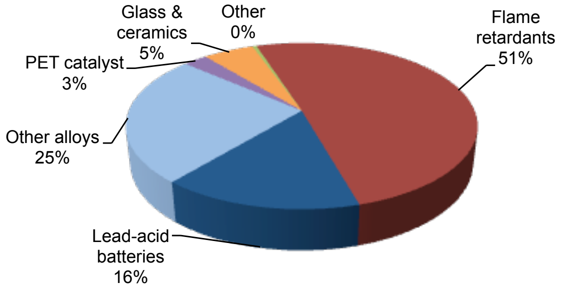


Figure 49: In-use Sb stock, 2011

Most of the in-use Sb stock consists of flame retardants (mainly in plastics used in electrical and electronic equipment), followed by other alloys (mainly lead sheets and pipes), and lead-acid batteries. Most of the antimony in those societal stocks will eventually reach the end of their useful lifetime, become discards, and be either recycled or landfilled. The size and composition of in-use stocks therefore indicate future waste streams and recycling potential. Applying the top-down approach, in-use stocks were estimated using information on past inflows to Use and on lifetime distribution of antimony-containing products (delay model), as well as on leaching from the in-use stock into the environment (leaching model). The uncertainty of these variables is difficult to assess, and so is therefore the accuracy of the estimated in-use stocks. A comparison with in-use stocks estimated using a bottom-up approach (combining information on the amount of antimony-containing products in use with their average antimony content) would provide a way to crosscheck the estimates, and therefore assess their accuracy. However, this estimation method is very data intensive and hardly feasible for global estimates, and was not employed in this study.

Normalized to the global population and Gross World Product (global GDP), the in-use stock amounts to 0.3 kilograms Sb per capita, and to 32 kilograms Sb per million US 1990$. The comparison of normalized values with previous estimates suggests that the estimation of global Sb in-use stock is accurate (Section 5.2.3). Indeed, the global per capita in-use Sb stock is two to five times lower than previously estimated for highly developed countries and cities, which is commonly observed in metal in-use stocks (Gerst and Graedel 2008). Furthermore, a strong correlation (R^2=0.99) was observed between Sb in-use stock and GDP (Section 5.2.3), which is has previously been observed for other metals (Rauch 2009). The validity of a statistical analysis is however limited by the small sample size (five in-use Sb stock estimates).

Globally, in-use Sb stocks are growing, as indicated by the larger size of inflows to Use than end-of-life flows. In 2011, about 207 Gg Sb entered the Use phase, while some 163 Gg Sb outflowed as end-of-life products. Therefore, net additions to the in-use stock amounted to 44 Gg Sb (about 21% of the inflow). Flame retardants and PET are the fastest growing in-use stocks.

SQ3: *How much antimony is lost to the environmental throughout the cycle, and in which environmental compartments? (i.e., how permeable is it?)*
According to the MFA results (Section 6.2.1), about 23 Gg Sb left the global anthropogenic antimony cycle as emissions (excluding landfills) in 2011, with an uncertainty range of ±30% (calculated using Gaussian error propagation). Considering that 207 Gg Sb entered use that year, this means that for each ton of antimony being used in products, about 100 kilograms are emitted into the environment.

About 84% of all emissions were into soils (19.2 Gg), 15% into the atmosphere (3.5 Gg), and about 1% into waters (0.3 Gg). Emissions to soil consist mainly of mine tailings (10 Gg) and smelter slag (7 Gg) that contain the fraction of antimony in ores that is not recovered and that is disposed of around mining and smelting sites. Emissions to soil resulting from the use of antimony in ammunition are also significant (1.5 Gg). Emissions to air originate mainly in the fabrication and manufacture of metallic products (1.6 Gg), during which large amounts of antimony are volatilized, as well as in dissipative uses of antimony as brake linings, pigments, and lubricants (1.6 Gg). Emissions to water arise mainly from F&M processes (0.13 Gg, i.e., 130 tons), and as a result of leaching from in-use flame retardants (0.08 Gg).

The MFA model focuses on the anthropogenic flows of antimony resulting from intentional applications. Natural emissions and anthropogenic emissions from non-intentional applications of antimony (resulting from the natural occurrence of antimony in other resources) are therefore not assessed by the model. Those emissions have however been previously estimated in a few studies. In contrast, no inventory of global emissions from intentional applications of antimony has been published so far as far as the author is aware, which limits the ability to assess the validity of estimated emissions. Comparing the results of previous studies with those of this study suggests that emissions arising from non-intentional uses of antimony – mainly through the mining and smelting of lead, copper, nickel and zinc ores where antimony occurs as a contaminant, through the combustion of coal, which contains on average between 0.05 and 10 ppm Sb (U.S. Geological Survey 2014e), and through the incineration of municipal/industrial waste, containing 10-60 ppm Sb (van Velzen and colleagues 1998) – are as much as four times greater than those caused by intentional applications (p.102). This has important implications for environmental policy, as an effective antimony emission reduction policy should not be limited to intentional uses of the metal, but also and more importantly target the emissions from non-intentional applications. Combining releases from both intentional and non-intentional applications, the total anthropogenic emissions are estimated to reach about 100 Gg Sb per year, mostly to soils (75%) and waters (20%). Furthermore, evidence suggests that the natural antimony cycle is much smaller than the anthropogenic one, with a difference of about 40 times as far as atmospheric emissions are concerned (p.102). Human activities therefore have a considerable influence on the global "anthrobiogeochemical" antimony cycle.

Overall, considerable uncertainties exist regarding emissions of antimony into the environment, both from natural and anthropogenic (intentional and non-intentional) sources. It is however considered that the orders of magnitude of estimated emissions, as well as the relative share of each environmental compartment, are close to the reality.

7.1.2 FUTURE ANTHROPOGENIC ANTIMONY CYCLE

Using dynamic MFA, the evolution of the global anthropogenic antimony cycle over time was investigated. Firstly, a retrospective analysis for the period 1900-2011 was conducted in order to assess demand trends and in-use stock dynamics. Secondly, a prospective analysis was performed for the period 2012-2050, with the aim of modeling the future anthropogenic antimony cycle according to different demand scenarios. The resulting cycles were analyzed from the perspectives of circularity, permeability, and supply outlook. Three demand scenarios were developed (Section 5.3.2):

- "Business-as-Usual" (BAU): Extrapolation based on the historical relationship between GDP and Sb consumption;
- "American World" (AW): Assumption that global demand trends will follow those that have been observed in developed countries (taking the USA as a proxy) since the 1990s;
- "Maximum Substitution" (MS): Substitution of antimony where and when it is considered possible.

It must be noted that those scenarios were intended to represent 'what if?' analyses rather than realistic projections. The goal was not so much to predict the future (which is deemed impossible), but to consider the consequences of important changes in demand on several indicators, related to resource use, recycling, and emissions, and to identify tipping points in the system. It is probable that the actual future development of the global anthropogenic cycle will take place between those extremes growth scenarios.

Figure 50 shows the (aggregated) global anthropogenic antimony cycles in 2050 as modeled in each scenario (Section 5.3.4).

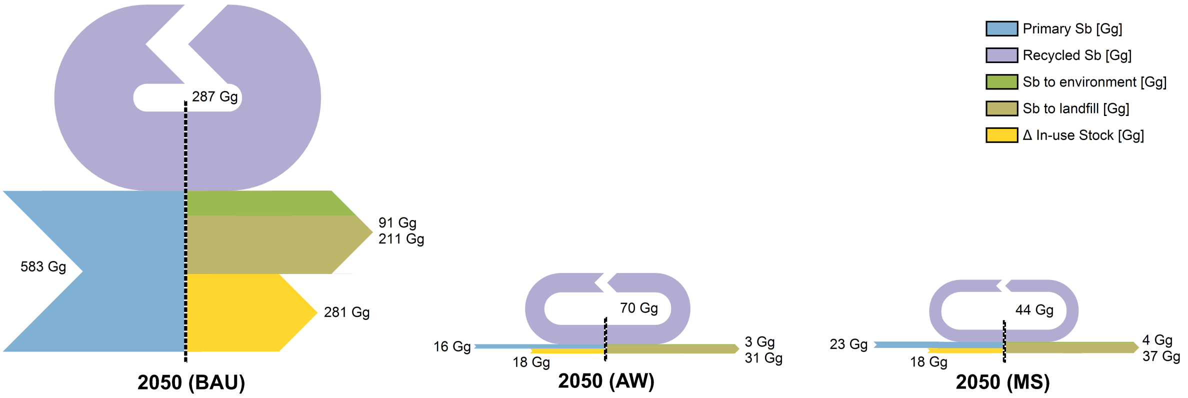


Figure 50: Global anthropogenic antimony cycle in 2050 according to three scenarios.
"Δ In-use Stock" refers to additions/subtractions from the in-use Sb stock. If the yellow arrow is on the right side of the system, antimony is added to the in-use stock, and vice versa. As they are comparatively very low, emissions (green outflow) are hardly visible in the flowcharts for AW and MS scenarios

SQ5: *What are the trends in demand?*

Throughout most of the 20th century, antimony was almost entirely used as an alloying element in lead-acid batteries and in other alloys, such as those used in lead pipes and sheets and in lead ammunition. The 1970s marked a change in global antimony consumption. On the one hand, use in lead-acid batteries and other alloys started to decrease due to technological developments (in the former case) and environmental concerns (in the latter). On the other hand, demand for antimony in polymers started to increase rapidly, mainly related to its use as a synergist in flame retardants (mostly in thermoplastics), and, to a lesser degree, as a catalyst in the production of PET. Since then, demand in those latter two end-uses have grown steadily, whereas the demand in metallic products has recovered due to the increasing demand from industrializing countries, where developments in lead-acid battery technology and environmental regulations are less pronounced. Other applications include the use of antimony in high-quality glass (as fining agent), in porcelain enamels (as opacifier), as well as for various functions in brake linings, paints, pigments, lubricants, pesticides, and pharmaceuticals. Over the last decade, global demand has grown for all end-uses with the exception of glass and ceramics, for which an average annual growth rate of -7% over the period 2000-2011 was measured (Section 5.3.1). The highest growth rates over this period were observed in demand for non-battery alloys (+10%/y) and PET (+8%/y), followed by demand in flame retardants (+5%/y), other non-metallic applications (+5%/y), and lead-acid batteries (+3%/y).

Without the emergence of antimony-consuming disruptive technologies, the global demand for antimony will remain very dependent on trends in flame retardants, lead-acid batteries, and other alloys in the future, as those three end-use categories together account for about 85% of the total consumption, and that the share of other current end-uses will most likely remain small. The following trends were observed:

- The outlook on demand for flame retardants is very uncertain as contrasting trends are observed. On going substitution of halogenated flame retardants (with which antimony acts as a synergist) in several applications, pushed by both environmental concerns and raising Sb prices, suggests that the relative share of antimony in the total flame retardants consumption will decrease in the future. However, the strong growth of the world demand for flame retardant could result in an increasing demand for antimony in absolute terms. The future demand for antimony in flame retardants depends mainly on the evolution of the flame retardants market, environmental regulations regarding halogenated flame retardants, and antimony prices.

- Regarding the use of antimony as an alloying element in lead-acid batteries, contrasting trends can also be observed. On the one hand, the increased need for maintenance due to the presence of antimony in the plate grids fostered its substitution with calcium since the 1970s, and the average Sb content in lead alloys used for lead-acid batteries has decreased from 8-12% in the 1960s to 0.5-3% nowadays in industrializing countries (Linden and Reddy 2002; Grund and colleagues 2011). On the other, alloys containing about 10% Sb are still used in emerging countries (BRGM 2012), where most of the growth of the global automotive market takes place. The future demand for antimony in this end-use therefore depends on the extent of substitution effects in developing countries, as well as on the evolution of the global demand for lead-acid batteries.
- Other antimony-consuming alloys consist mainly of rolled and extruded lead products (pipes and sheets) used in buildings and, to a lesser extent, of lead ammunition. Due to the build-up of infrastructure in many parts of the world, demand in this end-use has grown rapidly over the last decades, although the use of lead alloys has been reduced in several applications in industrialized countries due to environmental regulations. In the future, demand for antimony in this end-use category will likely increase with GDP, unless more stringent environmental regulations are implemented in industrializing countries.
- The requirement for antimony in emerging technologies was considered as low at the horizon 2030 (Angerer and colleagues 2009), and are hardly assessable beyond that. The emergence of a disruptive technology consuming larges amounts of antimony is considered as unlikely.

Overall, trends in antimony demand over the last decade could be relatively well characterized. No clear patterns could however be observed in the three main end-uses (i.e., flame retardants, lead-acid batteries, and other alloys), as trends contrast between industrialized and industrializing nations.

SQ6: *What is the outlook on primary and secondary supply?*

Regarding primary production (Section 5.3.5):

- Most of the primary production of antimony takes place in China (about 80% of the total), followed by Myanmar, Russia, Bolivia, and Tajikistan (U.S. Geological Survey 2015). Over the last decade, the Chinese government imposed constraints on mining and processing of antimony ores in order to preserve dwindling resources and limit environmental impacts. As a result, antimony prices reached very high levels in 2011, peaking at 18$/kg, whereas prices were below 2$/kg in the early 2000s. Since then, prices have decreased to about 8$/kg at the start of 2015 (Metalprices.com 2015). It is considered unlikely that Chinese antimony supply will increase in the near future. Underpinned by high prices and decreasing Chinese output, several countries increased their primary antimony supply. If antimony prices continue to decrease, it however is probable that several mining operations in those countries will be halted. If realized, announced potential antimony mining projects would only slightly increase annual primary supply in the coming years. In the short-term, it is therefore considered unlikely that primary antimony supply will increase significantly if prices remain at current levels. However, if demand continues to increase, prices could be driven up and the global mining capacity would probably grow as well.
- To assess the outlook on primary supply in the longer-term (>10 years), it is useful to have an idea of the size of geological stocks. Previously, antimony reserves (i.e., identified deposits that are recoverable under current technical and economic constraints) were estimated at between 1800 Gg and 3400 Gg (Schwarz-Schampera 2014; U.S. Geological Survey 2015), the reserve base (including

also marginally economic and subeconomic resources) at 4300 Gg (U.S. Geological Survey 2009), and the quantity of ultimately extractable global Sb resources at 8000 Gg (UNEP 2011b). Most of those resources are located in China. If primary production remained at its current level (about 200 Gg) in the future, identified reserves would last between 11 and 21 years, depending on the estimate used, the estimated reserve base would be depleted in 27 years, and the ultimately extractable resources would suffice for another 50 years. Those figures suggest that primary antimony supply will be substantially restricted in the next decades, even if demand remains stable.

Regarding secondary production:

- Secondary production of antimony is poorly documented, and reliable figures on global recycling rates of antimony-containing products are generally not available. Recycling rates for lead-acid batteries are somewhat better characterized than those for other antimony-containing products, as the disposal of this product is strictly regulated in most countries, and a large recycling infrastructure is in place. Global recycling rates of antimony-containing alloy, plastic, and glass products are very uncertain. In the case of flame-retarded plastics, uncertainties are further increased by the fact that the use and disposal of plastics containing brominated flame retardants (in conjunction to which most antimony is used in this end-use sector) are regulated in several countries, such as by the Restriction of Hazardous Substances Directive (ROHS) in the European Union. The consequences of such regulations on the recovery of antimony from end-of-life flame-retarded products are unknown, but could mean that recycling rates for antimony-containing plastics are lower than the average recycling rate of plastics.
- It is assumed that when antimony-containing products are recycled, antimony is recovered and reused in the same matrix, although information on that matter is very limited. The recycling of those products is mainly driven by the value of the material itself, and not by that of antimony. The recycling of antimony is therefore mostly non-intentional, and, consequently, often not acknowledged. This adds to the uncertainty regarding secondary antimony production.
- Based on the best available information, recycling rates for lead-acid batteries, other alloys, and plastic and glass products were estimated at 70%, 60%, and 10% in 2011, respectively (Section 4.3.5). Recycling from other products was considered negligible. Combined with estimated end-of-life flows, this results in a share of 63% to lead-acid batteries in the total recyclate stream in 2011, followed by other alloys (19%), and plastics and glass products (18%). As discussed in the answer to the first sub-question, using those assumptions results in presumably slightly overestimated end-of-life recycling rate and recycled content. It is therefore likely that actual recycling rates are lower, especially for other alloys, and glass and plastic products. Although the exact magnitudes and shares of recycling flows could not be estimated with a high confidence level in this study, the dominance of lead-acid batteries in secondary sources is regarded as certain, and confirms findings of previous studies.
- The future secondary supply depends strongly on the extent of recovery of antimony contained in flame-retarded plastics, lead-acid batteries, and other alloys, as most antimony is used in those products. In the scenarios used for the prospective MFA, a significant increase in recycling rates for lead-acid batteries, other alloys, and plastic and glass products, is assumed. These reach respectively 90%, 90%, and 50% in 2050 (Section 5.3.3). Such an increase over this time period is considered possible, but its likelihood was not assessed in detail. Further research is needed to identify the challenges and opportunities for increasing global recycling rates of antimony in each of its end-uses.

- The prospective MFA showed that the end-of-life recycling rate and recycled content are inversely proportional to the share of non-metallic applications in the total demand. The evolution of the recycled content also depends on the growth in the total demand, as it increases more rapidly if the demand stabilizes or decreases. At the horizon 2050, the overall end-of-life recycling rate ranges between 56% and 77% between the three scenarios, and the recycled content between 33% and 82% (Section 5.3.4). On this basis, it can be concluded that the extent to which secondary production can meet the total demand for antimony, and therefore reduce the dependence on primary sources, is maximized by a high share of metallic end-uses in the total demand, and a stable or declining total demand.

As discussed in the answer to the first research sub-question, secondary antimony production may have been overestimated in the MFA model. The share of secondary sources in the total supply was estimated at 23%, but could be as low as 16% assuming lower recycling rates for metallic applications and no recycling for non-metallic products. Considering a rather grim outlook on primary production, this share would have to increase significantly in the future if demand were to grow. Such an increase in recycling rates raises technical, economic, and environmental challenges, which could not be thoroughly appreciated during the research, therefore limiting the extent to which this research question can be answered. Further research is needed in this domain.

SQ7: *How critical is the future Sb cycle according to different supply-demand scenarios?*

The criticality of metals is a hotly debated concept that lacks a widely accepted definition and assessment methodology (Section 2.2). It is commonly used to denote metals that combine high economic importance and high risk of supply disruptions. Several indicators can be considered to assess the criticality of a specific metal, mostly related to supply factors (e.g. geological availability, supply concentration, recycling potential, etc.) and demand factors (e.g. added value of main consuming sectors, past demand growth, future demand projections, substitutability). Some methodologies also include environmental aspects, generally restricted to the primary production of the metals.

Antimony was previously identified as one of the most critical metal, primarily because of the high concentration of primary supply and reserves in China, as well as the low reserves-to-production ratio. Other supply factors considered as critical include relatively low recycling rates and high price volatility. Demand-side factors were generally less decisive in the identification of antimony as a highly critical element, while environmental aspects were only included in one study (Graedel and colleagues 2015) and not considered as particularly critical in the case of antimony, based on cradle-to-gate impacts of primary production (using ecoinvent datasets). In all of these studies, the criticality of antimony was assessed along with that of many other metals using commonly available or readily derivable indicators, which limits the depth of the analysis of the complex antimony production and consumption system. Furthermore, most previous criticality studies used static indicators and failed to account for the dynamics of antimony supply and demand.

In this study, several factors contributing to the current and future criticality of antimony were considered, going further than previous criticality assessments. In particular:

- Geological availability and projected demand for primary antimony were compared in order to assess the risk of future demand-supply mismatches (Section 5.3.5). It was showed that, if demand were to grow in a Business-as-Usual scenario (based on regression analysis between world GDP and Sb demand over the period 1980-2011), the risk of mismatches between supply and demand in the near future (next 15 years) is high, with a depletion of identified reserves (as estimated by the U.S. Geological Survey (2015)) within 10 years and an exhaustion of the estimated reserve base before 2030. On the other hand, if Sb demand were to decrease significantly and rapidly (as a result of prices hikes and/or environmental concerns, for instance), resources would remain abundant at the horizon 2050;

- Current and potential future recycling rates for each end-use were estimated, and the resulting current and possible future overall end-of-life recycling rate and recycled ratio were quantified. Those aspects are discussed in answers to sub-questions 1 and 6. Overall, recycling of antimony is limited as this element is mostly used in non-metallic products, for which an adequate recycling infrastructure is lacking. However, recycling rates for those products will likely increase in the future, and those for metallic applications will also further grow, so that the overall end-of-life recycling rate could reach 60-80% in 2050, as compared to about 20% nowadays;
- Demand trends since 1900 were reconstructed, and scenarios on the evolution of the demand until 2050 were generated, including an analysis of the substitutability of antimony in each end-use. Past demand trends are discussed in the answer to sub-question 5, and demand scenarios are detailed in Section 5.3.1. Regarding substitutability, it was concluded that antimony could be fully substituted in flame retardants, lead-acid batteries, and other alloys, whereas no satisfying substitute exists for its use as a PET catalyst. Demand for glass and ceramics will most likely drop to negligible levels in the future, and demand for other non-metallic applications will probably remain small;
- Environmental aspects were analyzed with a double focus on cradle-to-gate impacts of primary and secondary production (Section 6.1), and on the human and eco-toxicity potential of antimony emissions generated throughout its anthropogenic life cycle (Section 6.2). Results related to these aspects are discussed in answers to sub-questions 4 and 8.

Despite the multitude of criticality-related factors included in the analysis, it is difficult to answer this research question in a satisfactory manner. Criticality is a relative concept, as a metal is not critical in itself, but for a specific actor (e.g. company, country, region, world), at one point in time, and in comparison to other metals. This fact, coupled with the general fuzziness surrounding the notion of criticality and the lack of standardized assessment methodologies, prevents from providing a synthetic answer to this question.

7.1.3 ASSOCIATED ENVIRONMENTAL IMPACTS

In this study, environmental impacts were assessed with a double focus on cradle-to-gate impacts of primary and secondary production, and on the human and eco-toxicity potential of antimony releases into the environment throughout its anthropogenic cycle. Those two aspects were considered of highest concern in the case of antimony. Life Cycle Analysis and Environmental Risk Assessment are the most relevant methodologies to assess such environmental risks and impacts. They are however time and data intensive and, as both resources were lacking for this research, thorough assessments could not be conducted. Nevertheless, semi-quantitative analyses based on existing information and MFA results were performed in order to provide an understanding of key environmental issues related to the production and consumption of antimony. The results should therefore be considered as indicative rather than complete and accurate, and additional research is needed to provide a clearer picture of environmental impacts associated with the global anthropogenic antimony cycle.

SQ4: *What are the environmental impacts associated with the cycle?*

As far as primary antimony production is concerned, an LCA-based analysis (Section 6.1) showed that environmental hotspots were the high electricity consumption (mainly coal-based in antimony-producing countries) and the disposal of sulfidic tailings during the mining and beneficiation of antimony ores, as well as the high coal consumption at the extraction and refining stages. The normalization to global emissions however suggests that environmental impacts of antimony production play a negligible role in the grand scheme of global environmental problems. These conclusions are accompanied by large uncertainties, as they were reached using existing ecoinvent LCI datasets on primary antimony production, which are based on approximations with primary production of other metals. In view of the information gathered during the research, it appears that these approximations may be inconsistent with values for actual processes.

Secondary production of antimony from metallic products can deliver major energy savings and avoid the above-discussed environmentally damaging processes of primary production (Section 6.1.2). Simple calculations suggest that recovery of antimony through the recycling of lead alloys consumes 95% less energy than primary production processes. In 2011, the consumption of about 8 PJ was thus avoided globally, equivalent to the daily energy use of the Dutch economy (CBS 2012). Recycling of antimony from end-of-life plastic and glass products (representing less than a fifth of the current recyclate stream) was not considered due to a lack of time and information, but it is likely that it also more environmentally benign than primary production. The hypothetical recovery of antimony from waste incineration residues, where about a third of non-recycled antimony ends up, could alleviate the annual demand for primary antimony by a fourth and decrease the amount of antimony being landfilled each year by a third. However, extrapolations from laboratory measurements (Werner 2014) suggest that the energy required to produce chemicals needed for such a recovery could offset the energy savings resulting from avoided primary production. This last observation should however be viewed with caution as such extrapolations are accompanied by large uncertainties and further research is needed in this area.

In order to characterize the risk for human health and ecosystems posed by anthropogenic releases of antimony into the environment, sources, fate, and effects of such emissions were investigated. Sources of emissions were discussed in answers to sub-question 3. It was estimated that about 100 Gg Sb is emitted each year into the environment as a result of human activities. Those emissions result mainly of non-intentional uses of antimony, and are mostly to soil. Most antimony released into the environment ends up in soils, where it is essentially immobile (Section 6.2.2). Bioavailability of antimony is not well understood, but evidence suggest that it can be taken up by plants and therefore enter the food chain. The toxicological behavior of antimony is considered as similar to that of arsenic although, on a weight basis, arsenic is much more toxic (Section 6.2.3). Exposure to high concentrations of antimony can induce cellular and tissue injury, and antimony trioxide is classified as “possibly carcinogenic to humans” by the International Agency for Research on Cancer (IARC 1989). Diseases of the skin, lung, and gastrointestinal tract have been observed in workers of the antimony processing industry, and occupational health risks are thus considered as significant. In most cases, exposure from environmental sources (air, food, water) and use of antimony-containing products pose a low health risk (Section 6.2.4). Areas of concern were however identified for populations working and/or living in the vicinity of antimony mining and smelting sites (due to the release of antimony into soils and waters) and high traffic areas (due to the release of antimony from brake pads into air). As regards risks for aquatic and terrestrial organisms, relevant and reliable ecotoxicological data is lacking. Existing information suggests that risks are generally low, but that harmful effects may occur in mining sites, shooting ranges, and along vehicle traffic roads.

Overall, the risks to human health and ecosystems posed by the release of antimony in the environment are not well understood. Much research is needed to provide a better picture of the fate, speciation, and bioavailability of antimony in environmental compartments on the one hand, and on the toxicology of antimony compounds for humans and other living organisms on the other.

SQ8: *How can associated environmental impacts be reduced in the future?*

Based on the answer to the previous sub-question, the following strategies can be followed to reduce the environmental impacts associated with the global anthropogenic antimony cycle:

- In order to decrease cradle-to-gate environmental impacts of antimony production:
    - Base as much as possible primary production on low-carbon energy sources to reduce overall contribution to global warming;
    - Increase mining/beneficiation efficiencies to reduce tailings;
    - Increase recycling rates for all end-uses;
    - Research and implement methods for environmentally friendly recovery of antimony from waste incineration residues.
- In order to reduce human and eco-toxicological risks of antimony emissions:
    - Increase beneficiation and extraction efficiencies to reduce emissions from intentional applications (total reduction of about 70% with an increase of 5% in efficiencies for both processes, cf. sensitivity analysis p. 89);
    - Impose stricter regulations on emissions and disposal of antimony during mining and smelting processes;
    - Ban the use of antimony in lead ammunition and in brake linings, applications for which substitutes exist;
    - Adopt further exposure reduction measures for workers in antimony processing facilities and in high vehicle traffic areas.

7.1.4 ANSWER TO MAIN RESEARCH QUESTION

Based on answers for research sub-questions, the main research question can be addressed.

What characterizes the current and possible future global anthropogenic antimony cycle, in terms of supply, demand and environmental impacts?

The current global anthropogenic antimony cycle is characterized by a mostly linear material functioning, with relatively low recycling rates, and high levels of resource extraction, emissions, and landfilling. Primary supply is concentrated in China, and secondary supply results mainly from the recycling of alloys contained in lead-acid batteries and, to a lesser degree, of other alloys, plastics and glass products. The share of secondary sources in the total supply is estimated at around 20%, meaning that the supply is strongly dependent on primary sources. Antimony demand results mostly from its use in flame retardants (about 50% of total demand, mainly in EEE plastics), lead-acid batteries (25%), and other alloys (10%, mainly in rolled and extruded lead products, and in lead ammunition). Primary antimony production entails significant environmental impacts, both in terms of energy use, contribution to global warming, and damages to ecosystems. Furthermore, considerable amounts of antimony are released into the environment throughout its anthropogenic cycle, which involves risks for the health of humans and other living organisms, as antimony can be toxic, and possibly carcinogenic, at high doses.

In the future, primary supply of antimony could be further constrained, as the size of identified reserves is low compared to annual primary production. It is estimated that about as much antimony remains in "above-ground reserves" (i.e., in-use stock) as in geological reserves, which indicates that secondary supply could potentially alleviate the demand for primary antimony. For this to happen, recycling rates for end-of-life antimony-containing products must be considerably increased, which raises technical, economic, and environmental challenges. Those could not be thoroughly appreciated during the research. The existence of substitutes for most applications suggests that if prices were to rise as a result of constraints on supply, global demand could be reduced in the future. This, in turn, would decrease resource depletion, emissions, landfilling, as well as probably increase the circularity of the global anthropogenic cycle (due to the fact that in-use stocks are not growing). On the other hand, if demand were to increase in correlation with GDP as it did in the last 30 years (i.e., Business-as-Usual scenario), the share of secondary sources in the total supply would have to grow considerably. Such an increase would be accompanied by rising levels of resource depletion, emissions, and landfilling, even if a more circular material functioning were achieved.

7.2 LIMITATIONS OF THE RESEARCH

Overall, all research questions formulated at the beginning of the research could be answered to an at least acceptable extent. However, the large gaps on information, coupled with the limited amount of time available for this study, made it difficult to address all questions in an equally comprehensive manner. Furthermore, significant uncertainties are associated with the results, due to uncertainties of model input data, as well as to modeling limitations.

7.2.1 DATA UNCERTAINTIES

In order to quantify the global anthropogenic flows and stocks of antimony and assess their environmental impacts, an extensive data collection was performed, involving various sources such as geological surveys, scientific literature, corporate reports, and various online databases. All these sources differ in terms of temporal and spatial scope, completeness, reliability, etc., and very rarely include information on uncertainties. The results are therefore inherently limited in accuracy, and their uncertainty is difficult to assess.

Based on the availability and (perceived) quality of information gathered throughout the research, it is considered that particularly high levels of uncertainty are associated with the following aspects:

- Global consumption of antimony in specific products. Most available information is aggregated and it is difficult to quantify the use of antimony in particular applications, especially for minor ones. This has a limited impact on the quality of total flows and stock estimates, but considerably limits the accuracy of estimated emissions, as those often result from minor uses (e.g. brake linings, pigments, pesticides, etc.);
- Waste management pathways of antimony-containing products. Global recycling rates of antimony-containing products are poorly known and must often be assumed. Similarly, the incineration/landfilling ratio of non-recycled antimony-containing wastes differs among countries and global averages must be assumed. This has a significant influence on estimated amounts of antimony being recycled, incinerated, or landfilled;
- Magnitude of anthropogenic antimony emissions, both from natural and anthropogenic sources. The latter include emissions from non-intentional uses of antimony (i.e., resulting from its occurrence in coal, other metal ores, etc.) and those arising from intentional applications (characterized in this study). Studies on global natural emissions and anthropogenic emissions from non-intentional applications are scarce, and inexistent when it comes to emissions from intentional uses. This study provides the first characterization of those emissions, which prevents crosschecking the results with previous findings;
- Cradle-to-gate life cycle inventories on antimony primary and secondary production. Data only exists on primary production, and is approximated with production of other metals. Very little information exists on the inputs and outputs related to mining and processing of antimony ores and recycling of antimony-containing wastes.

- Fate, speciation, bioavailability and health effects of antimony emissions. Information is scarce and often contradicting on those aspects, which renders a risk assessment difficult.

7.2.2 MODEL SHORTCOMINGS

This study also suffers from a number of limitations caused by the use of models itself. Models, such as used in MFA and LCA, are a simplified representation of highly complex real world phenomena, used to understand, quantify, and visualize those phenomena. Due to this simplification, models are never completely accurate and, as a famous quote goes, 'essentially, all models are wrong, but some are useful' (Box 1987). The key is, paraphrasing another quote attributed to Albert Einstein, to build models that are 'as simple as possible, but not simpler'.

Due to the large scope of the system investigated in this study (i.e., the world), the scarcity of information on many parts of this system, and the time constraints, the generated model of the anthropogenic antimony cycle is a very simplified representation of the actual cycle. Major simplification steps include the focus on intentional anthropogenic flows, the division of the cycle in four basic stages (i.e., Production, Fabrication & Manufacture, Use, and Waste Management), the aggregation of antimony flows and stocks within and between those stages, and the assumption of average values for many system variables.

These simplifications may limit the validity of the model results, to an extent that is difficult to assess. In particular, it is considered that misrepresentations may occur as a result of the following limitations:

- In the MFA model, average values were assumed for production, manufacture, and waste disposal process efficiencies, emission and waste factors, product lifetime distributions, and ratios between recycling, incineration, and landfilling for each end-use. Except for waste management ratios, those variables were also constant in the dynamic analyses. In reality, these parameters vary between units (i.e., plants, products, wastes) and evolve over time, which may considerably influence the MFA results.
- Furthermore, antimony compounds and antimony-containing products were aggregated in a limited number of flows and stocks. This aggregation was driven by both data availability and simplification purposes. For most processes, it was considered that inter-variability is sufficiently higher than intra-variability to justify such aggregations. However, the aggregation is problematic when it comes to assessing products lifetime distribution and emission factors, as those variables can be very different for flows belonging to the same category. For instance, ammunition and lead sheets used in building have very different average service lifetimes and emission factors, but they belong to the same end-use category in the MFA model. This limitation has therefore significant consequences on the estimation of in-use stocks and emissions.
- It is assumed that all antimony entering Use will eventually flow out as end-of-life products to Waste Management, or as emissions to the environment. In fact, a fraction of the inflow will end up in "hibernating stocks" – representing products that are no longer used but not yet discarded (e.g. underground cables, stored electronic products, etc.) – where they can stay for a much longer time than their average useful lifetime. Including those stocks would therefore influence the estimated yearly emission and end-of-life flows.
- Although inefficiencies in secondary production processes were taken into account, it was assumed that antimony could be recycled an unlimited amount of times without losing its properties. In reality, it is probable that downcycling takes place, thus reducing the amount of end-of-life antimony that can be recovered.

- The MFA focused on the anthropogenic and intentional part of the antimony cycle. Natural flows of antimony as well those resulting from non-intentional uses of the metalloid (resulting from its natural occurrence in fossil fuels, other metal ores, etc.) were not included in the MFA modeling. Based on the limited available information, it appears that emissions arising from non-intentional applications are considerably greater than those generated through intentional uses. This suggests that non-intentional flows represent a substantial share of the global anthropogenic antimony cycle, and that they should have been included in the MFA model to provide a more complete picture.

7.2.3 VALIDITY OF THE RESULTS

In view of the above-mentioned uncertainties and model limitations, it follows that the results of this thesis should be regarded as estimates rather than accurate quantifications. The aim of this research was to provide a first picture, even imprecise, of the global anthropogenic antimony cycle and of its environmental impacts. It was achieved by providing an understanding of the relative magnitude of antimony flows and stocks from the extraction of ores to the manufacture, use, recycling, and final disposal of antimony-containing products, and by identifying key environmental issues.

As far as the author is aware, no study has previously been conducted on this topic and with such a scope, which limits the possibility to assess the validity of the research findings. However, studies have been published on specific parts of the cycle, generally at smaller geographical scope and, in general, this study's results are in line with previous findings in comparable terms.

Overall, it is considered that data sources and modeling assumptions used in this study represent the best currently available options to fill the knowledge gaps regarding current and future global antimony stocks, flows, and associated environmental impacts. Further, the models developed in this study provide a basis upon which more accurate information can be added if it becomes available.

7.3 REFLECTIONS

Looking back at this thesis research project, a number of reflections can be made on the concepts and theories used, on the methodology employed, and on the research in general.

On criticality

The identification of antimony as a highly critical raw material in several studies provided one of the motivation to investigate its anthropogenic cycle. In this context, an implicit aim was to use dynamic MFA in order to provide a more complete picture of the criticality of antimony, as opposed to the "simple" assessments based on static indicators that are usually done in criticality studies. Factors related to the criticality of metals are numerous, multi-dimensional, evolving, and often interrelated. Dynamic MFA offers a systemic, holistic, and dynamic approach to integrate those factors, and it was thought that it would allow addressing the complexity of the criticality concept.

As admitted in the discussion, it has proven difficult to provide a synthetic answer to the research question addressing the future criticality of antimony, despite the multitude of criticality-related factors included in the analysis. The main reasons for that is that criticality is a fuzzy notion, as well as a relative concept. There are not widely accepted criticality definitions and assessment methodologies, and it is usually assessed in relation to other metals. Therefore, the same methodology has to be applied to different metals, with well-defined criteria and scoring methods. Reducing the complexity of the criticality to a single score cannot be done without considerable simplification and loss of information. It should however be noted that the criticality assessment method used by researchers at the Yale Center for Industrial Ecology (Graedel and colleagues 2012, 2015) is remarkably comprehensive, although it is still mostly based on static indicators for which a comparable database exist for all metals.

Based on the research, it is considered that dynamic MFA can potentially offer rich insights on the criticality of metals, including a systemic picture of how criticality-related factors are interrelated and coevolve over time. In order to allow comparison between different metals, the dynamic MFA methodology used must however be the same. Over the last decade, dynamic MFA has been increasingly used to characterize global anthropogenic metal cycles, and although they differ in terms of scope and purpose, they are generally based on the same modeling principles and assess similar variables (e.g. in-use stocks, recycling indicators, etc.). It would be desirable that, in the future, a database will be created to integrate the findings of dynamic metal MFA studies. The methodologies should therefore be harmonized, although they can remain flexible enough to be adapted to each metal's specificities (e.g. emphasis on emissions for toxic metals).

Furthermore, environmental impacts should be a fundamental dimension of criticality, along with supply risk and economic importance. The inclusion of those should however be extended to the full metal life cycle, and not be restricted to impacts of primary production. In particular, LCIs on secondary production of metals should be developed and included in criticality studies. Furthermore, the dissipation of metals into the environment during their life cycle is considered as important, especially in the case of potentially toxic metals. For other metals, the inclusion of cradle-to-gate impacts alone can be justified.

On the methodology

For this study, a stepwise methodology was designed and followed, based on state of the art methods and refined according to the research purposes. As a first step, a static MFA model was generated using the STAN software, which allows drawing, visualizing and balancing the flow system, and propagating the uncertainties of known flows into calculated flows. Thus, the value and uncertainty of about 80 flows and 150 transfer coefficients was determined for the year 2011. This system was then transformed into a relational data model in Microsoft Excel, in which all flows depend on the value for Sb demand in each end-use, and all transfer coefficient remain constant except those related to waste management pathways. Using estimated past demand and the projected future demand, retrospective and prospective dynamic MFA analyses were performed. Lastly, MFA results were used in combination with LCA and risk assessment methods in order to assess the environmental impacts associated with the global anthropogenic antimony cycle.

STAN and Excel integration

The decision to first conduct a static MFA in STAN and then to export its results into an Excel spreadsheet was motivated more by the tools themselves than by methodological logic. STAN is free, well documented and easy to use. It allows drawing a material system, entering the value of known flows and transfer coefficient and their uncertainties, and to calculate the value and uncertainty of unknown flows and transfer coefficients by applying mass balance and error propagation based on the least square method. STAN results include both numerical outputs, which can be exported into other software applications (e.g. Microsoft Excel), and graphical outputs such as Sankey diagrams of the balanced material system. One thing that STAN was not designed for, however, is dynamic modeling. Although it is possible to use the time period feature to create a material system for each year of the period under investigation, this is impractical when a long period is investigated, such as 150 years in this study. For this reason, STAN results for on year (2011) were exported into Microsoft Excel. The relation between flows and transfer coefficients were manually entered (using formulas to link different cells), and the data was set out in such a way that the whole material flow system for one year fits into one column (with about 80 rows for each flow, transfer coefficients are contained in another sheet). The Excel model is a demand-driven model, meaning that all flows are dependent on the inflows into Use. Except waste management parameters, all transfer coefficients remain were assumed constant over time. Different Excel files were created for the retrospective MFA and for each scenario of the prospective MFA. The strengths of Excel are its user-friendliness and ease-of-use, as well as the possibility to conduct statistical analyses and generate a large variety of charts.

The main disadvantage of this method is that it takes time and several steps to add/remove flows to the material system, of to change the transfer coefficients for processes. This has to firstly be done in STAN in order to balance the new system and propagate the uncertainties accordingly, and the resulting changes must subsequently be entered in the Excel model. Quite some time was lost in this process, as MFA is an inherently iterative methodology where new information must regularly be added to the MFA model.

MFA and LCA

Due to the paucity of information and time constraints, a thorough LCA study could not be completed in this study. However, useful insights could be generated for a potential future LCA on environmental impacts of primary and secondary antimony production:

- The information gathered and generated during the MFA was used to assess the accuracy of existing LCI data on primary antimony production. It was observed that considerable differences exist between empirical data and approximations used, and modified LCI datasets were proposed accordingly;
- LCA scores were scaled up to the global situation using MFA results in order to assess global environmental impacts related to primary antimony production and normalize those to global emissions;
- Potential global energy and primary resource savings of secondary antimony production were discussed on the basis of MFA results and available LCA information on recycling processes.

Those aspects confirm that MFA and LCA are complementary, and that a subsequent application of both methods can bring useful results. Overlaps exist in the data requirements of both methodologies, meaning that some time can be saved through the combination, compared to conducting those assessments separately.

It would have been interesting to combine the results of the prospective MFA with LCA aspects, in order to compare the environmental impacts associated with the primary and secondary production modeled in each scenario. However, the uncertainties associated with LCA scores were considered too high for such an analysis to be meaningful.

MFA and risk assessment

In order to assess the risk for human health and ecosystems related to emissions of antimony throughout the anthropogenic cycle, MFA results on emissions were combined with information on their ultimate fate in environmental compartment, on the bioavailability of antimony in those compartments, and on the adverse health effects observed when humans or other living forms are exposed to antimony. This represents a very simplified risk assessment, which does not include a dose-response assessment and limits the consideration of exposure to the absolute amount of antimony in the environment. As a result, risks were not quantified but only qualitatively discussed.

Besides time constraints and the paucity of (eco-)toxicological data, performing a thorough risk assessment was made impossible by the great difference in scope between a global-level MFA and a risk assessment study. The model generated in this study has a very low spatial resolution; global emissions to air, water and soil are estimated, with no further disaggregation. In contrast, risk assessment is highly context-specific and requires precise information on the concentration of substances in different environmental compartments at the local level (dose), as well as on the frequency, timing and level of contact with these substances (exposure).

Therefore, the risk assessment proposed in this study is at best a preliminary assessment. It can be used as a basis to identify hotspots for a more thorough study. An interesting area of research in this context is the coupling of the MFA model with environmental fate models and/or environmental risk assessment models. In the future, the usefulness of such a combination to assess global health and environmental risks should be investigated.

On the research in general

In view of the above-mentioned limitations of, and reflections on, the research, it becomes clear that the conduction of this study was constrained by the insufficient availability of time and information required to address all research questions in a comprehensive manner. This indicates that the research scope and purpose were perhaps too broad for a master thesis, and that a focus on fewer aspects would have been beneficial.

A more in-depth focus on the MFA part, for instance deepening the prospective MFA with additional scenarios on both flows and transfer coefficients, would have brought a better understanding of the challenges and opportunities related to the future anthropogenic antimony cycle. Alternatively, a more pronounced focus on the environmental issues could have enabled to develop more accurate LCI datasets and/or risk assessment models. In fact, each of the research areas investigated would have benefitted from more exclusive dedication.

Nevertheless, this study offers rich, albeit limited, insights on several crucial aspects of the global anthropogenic antimony cycle, such as current global flows and stocks, demand trends and substitution potential, recycling rates and challenges, environmental impacts of production processes, and health and environmental risks of exposure to antimony. All these aspects are interrelated, and their integration into a single study is necessary to offer a holistic picture of the sustainability issues facing the future antimony cycle.

8 CONCLUSIONS

This thesis was set out to uncover the global anthropogenic antimony cycle, explore its possible future development, and identify key associated environmental issues. The results suggest that, currently, this cycle resembles in fact more a linear system than a circular one; it is characterized by high levels of resource extraction (estimated at 190 Gg Sb in 2011) and landfilling (123 Gg Sb), a relatively low overall recycling rate (estimated at 20-30%), and considerable emissions into the environment (23 Gg in 2011), mostly to soils. Economic and environmental risks are associated with this situation, as antimony can be considered as both critical and toxic. Critical, because its primary supply is heavily concentrated in China and subject to political, geological, and economic constraints. Toxic, as exposure to it can induce cellular and tissue injury, possibly leading to cancer, in living organisms. Furthermore, results indicate that primary antimony production results in significant environmental impacts, at both local and global levels.

In order to reduce those risks in the future, several strategies can be envisaged:

- To reduce the criticality of antimony, recycling and substitution are identified as the main mitigating options, because they reduce the demand for primary antimony. Results indicate that a considerable amount of antimony is currently being used in various products; this “in-use stock” is equivalent in size to geological reserves (i.e., 1800 Gg in 2011). This represents a great potential for future recycling. Almost half of in-use stock consists of EEE plastics, the recycling of which poses great challenges. Most of the remaining stock is made up of lead alloys used in lead-acid batteries, and other lead products, for which recycling rates are already relatively high – the current share of lead-acid batteries and other lead products in the total recyclate stream were estimated at 63% and 19%, respectively. As a result of this discrepancy in recycling rates, scenarios show that the future end-of-life recycling rate and recycled content are inversely proportional to the future share of non-metallic applications in the total demand. Projections generated in this study however suggest that an increase in recycling rates could not suffice to avoid a resource crisis in the next decade if the demand for antimony increases as rapidly as it did since the 1980s. Such as situation could lead to high prices and, in turn, to a reduced demand, as substitutes exist in most applications.
- To reduce the environmental risks, the priority should be to make primary production processes more efficient, less polluting, and based as much as possible on low-carbon energy sources. According to MFA and LCA results, primary production processes are the main source of antimony emissions, and they consume large quantities of coal-based energy. Furthermore, results show that secondary production of antimony can enable very high energy savings (up to 95% in the case of recycling of antimony contained in lead products), and therefore reduce the carbon footprint of antimony. Recycling also avoids environmentally damaging processes related to primary production (e.g. disposal of sulfidic tailings) and, for all these reasons, should be encouraged. Although it is not yet implemented, the recovery of antimony from waste incineration residues could potentially reduce the demand for primary demand by a fourth and decrease the amount of antimony ending up in landfills by a third according to calculations realized. It is however not sure whether the direct and indirect energy demand of such a recovery is lower than that of primary production. Lastly, results indicate that, in order to reduce the human and eco-toxicological risks related to antimony emissions, the use of antimony in ammunition and in brake linings should be reduced or eliminated, and that workers exposed to high concentrations of antimony – mostly in antimony processing facilities but also close to high traffic areas – should be adequately protected. Considering that the effects of antimony exposure of human and ecological health are poorly understood, the precaution principle is applicable.

As with all studies on global metal flows and stocks, the uncertainties that accompany the results are significant but hardly quantifiable. They result mainly of uncertainties in data sources, as well as of simplifications caused by the use of models. Comparison with previous findings is limited, as no study has previously been conducted on this topic and with such a scope. However, research has been conducted and published on specific parts of the cycle, generally at smaller geographical scope and, in general, this study's results are in line with previous findings. Overall, it is considered that data sources and modeling assumptions used in this study represent the best currently available options to fill the knowledge gaps regarding current and possible future global antimony stocks, flows, and associated environmental impacts. Lastly, the models developed in this study provide a basis upon which more accurate information can be added if it becomes available.

Based on the results of the research and their implications, several recommendations can be offered to a variety of stakeholders.

Industrial actors

Companies involved in mining and processing of antimony ores probably have the largest influence on environmental impacts associated with the global anthropogenic antimony cycle, due to the large emissions, wastes and energy use that production processes cause. Furthermore, the highest risks for human health concern workers in that part of the cycle, exposed to antimony by inhalation. Therefore, it is recommended that primary producers:

- Improve ore recovery technologies to increase output and decrease losses to the environment;
- Use renewable electricity for mining and beneficiation processes, and low-carbon/recycled fuels and reducing agents (e.g., biochar, polymers, tires, etc.) for smelting processes;
- Minimize occupational risks by monitoring antimony levels in air, improving air-cleaning systems, and providing protective clothing and respirators. Adopt a precautionary approach in the absence of conclusive studies on long-term risks of occupational exposure to antimony.

Manufacturers of antimony-containing products also play a key role, as they are at the same time most at risk of supply disruptions, and largely responsible for the use and dissipation of antimony resources. For those actors, it is suggested to:

- Substitute, if possible, antimony for less problematic materials in terms of supply risks and environmental impacts. This substitution should however not shift the problem onto other critical materials and, ideally, should use one of the plentiful 'elements of hope' (Diederen 2009), which include aluminum and magnesium, the hydroxides of which are widely accepted substitutes for flame retardants, and calcium, which is the main substitute for antimony in lead alloys;
- Limit the dissipation of antimony during use of the products;
- Facilitate the recycling or safe disposal of antimony-containing products (e.g. through Design for the Environment);
- Minimize occupational risks by monitoring antimony levels in air, improving air-cleaning systems, and providing protective clothing and respirators. Adopt a precautionary approach in the absence of conclusive studies on long-term risks of occupational exposure to antimony.

Policymakers

As legislators and environmental stewards, policy makers have a large role to play in making the anthropogenic antimony cycle a more sustainable one. In order to reduce the criticality and environmental impacts of antimony, several policies can be implemented:

- Promote the recycling of antimony-containing products through economic incentives (e.g. recycling fee);
- Support research on antimony recycling technologies. In particular, on recycling of antimony-containing plastic wastes and recovery of antimony from incineration ashes;
- Impose stricter limits on antimony emissions during production, manufacture, and waste disposal processes;
- Restrict or ban the use of antimony in ammunition and in dissipative applications such as brake linings, lubricants, pigments, and pesticides;
- Support research on exposure to and health effects of antimony for humans and other living organisms. Also, commission further risk assessments on antimony including substances other than antimony trioxide, and emissions other than those from intentional applications.

Researchers

As noted throughout this study, several knowledge gaps exist along the global anthropogenic antimony cycle. Some of these gaps were addressed with this research, but due to scope limitations as well as partially answered questions, large uncertainties still remain on several aspects. It is the role of researchers to improve the understanding of challenges and opportunities associated with the global flows and stocks of antimony. The following research priorities were identified:

- Assess the potential of recovery of antimony from end-of-life plastics products, and from waste incineration residues. According to the MFA model, those flows contained, respectively, about 20 Gg (~10% of total demand) and 40 Gg Sb (~20% of total demand) in 2011, very little of which is currently recovered.
- Investigate the role of landfills as "tertiary resources" of antimony. MFA results suggest that about 4600 Gg Sb has been landfilled globally since 1900, which is roughly equivalent to the size of the estimated reserve base (U.S. Geological Survey 2009).
- Create and improve existing life cycle inventories for antimony primary and secondary production, and conduct comparative LCAs to compare various ways to produce antimony (from primary or secondary sources);
- Inventory antimony emissions from natural sources and from non-intentional anthropogenic sources;
- Improve knowledge on fate, speciation, and bioavailability of antimony in the environment on the one hand, and on toxicology of antimony compounds for humans and other living forms on the other.

9 REFERENCES

Achzet, B., A. Reller, and V. Zepf. 2011. *Materials critical to the energy industry: An introduction.*

ALABC. 2013. *Do Hybrid Electric Vehicles Use Lead-Acid Batteries? Yes! Here's why. Advanced Lead Acid Battery Consortium (ALABC)*. Durham, USA.

Alonso, E., A.M. Sherman, T.J. Wallington, M.P. Everson, F.R. Field, R. Roth, and R.E. Kirchain. 2012. Evaluating rare earth element availability: a case with revolutionary demand from clean technologies. *Environmental Science & Technology* 46(6): 3406–14. http://www.ncbi.nlm.nih.gov/pubmed/22304002.

Althaus, H. 2009. *Life Cycle Inventories of Metals. Final report ecoinvent data v2.1, No 10. Part XVI: Antimony*. Dübendorf.

Anderson, C.G. 2012. The metallurgy of antimony. *Chemie Der Erde - Geochemistry* 72: 3–8. http://linkinghub.elsevier.com/retrieve/pii/S0009281912000293. Accessed July 14, 2014.

Anderson, C.G., S.M. Nordwick, and E. Krys. 1994. Antimony Separation Process.

Anderson, C.G. and L.G. Twidwell. 2008. The Alkaline Sulfide Hydrometallurgical Separation, Recovery and Fixation of Tin, Arsenic, Antimony, Mercury and Gold. *The Southern African Institute of Mining and Metallurgy*(3): 121–132.

Angerer, G., L. Erdmann, F. Marscheider-Weidemann, M. Scharp, A. Lüllmann, V. Handke, and M. Marwede. 2009. *Rohstoffe für Zukunftstechnologien*.

Areppim. 2015. Converter of current to real dollars. http://stats.areppim.com/calc/calc_usdlrxdeflator.php.

Avery, D.W. 2009. Regulation of Lead-based Ammunition Around the World. In *Ingestion of Lead from Spent Ammunition: Implications for Wildlife and Humans*, ed. by Hunt WG Watson RT, Fuller M, Pokras M, 161–168. The Peregrine Fund, January. http://www.peregrinefund.org/Lead_conference/PDF/0115 Avery.pdf. Accessed October 15, 2014.

Ayres, R. and L. Ayres. 2002. *A Handbook of Industrial Ecology*. Ed. by Robert Ayres and Leslie Ayres. 1st ed. Cheltenham: Edward Elgar.

Ayres, R.U. 1989. Industrial Metabolism. In *Technology and Environment*, ed. by Jesse H. Ausubel and Hedy E. Sladovic. National Academies Press.

Ayres, R.U. and L.W. Ayres. 1994. Consumptive uses and losses of toxic heavy metals in the United States, 1880-1980. In *Industrial Metabolism*, ed. by Robert U. Ayres and Udo E. Simonis. Tokyo: United Nations University Press. http://archive.unu.edu/unupress/unupbooks/80841e/80841E0m.htm#Emissions coefficient for consumption.

Baccini, P. and P.H. Brunner. 2012. *Metabolism of the Anthroposphere*. 2nd ed. Cambridge, Massachusetts: MIT Press.

Behrendt, S., M. Scharp, and L. Erdmann. 2007. *Rare metals: Measures and concepts for the solution of the problem of conflict-aggravating raw material extraction - the exampke of coltan*. Berlin.

Behrens, A., S. Giljum, J. Kovanda, and S. Niza. 2007. The material basis of the global economy. Worldwide patterns of natural resource extraction and their implications for sustainable resource use policies. *Ecological Economics* 64: 444–453.

Belzile, N., Y.-W. Chen, and M. Filella. 2011. *Human Exposure to Antimony: I. Sources and Intake. Critical Reviews in Environmental Science and Technology*. Vol. 41. July 15. http://www.tandfonline.com/doi/abs/10.1080/10643381003608227. Accessed November 19, 2014.

BGR. 2010. *Frühwarnindikatoren und Rohstoff-Risikobewertung: Methodischer Überblick am Beispiel Antimon. Commodity TopNews*. Hannover.

BGR. 2013. *Rohstoffrisikobewertung – Antimon.*

Bloodworth, A. 2014. Track flows to manage technology-metal supply. *Nature* 505: 9–10.

Bonnin, M., C. Azzaro-Pantel, L. Pibouleau, S. Domenech, and J. Villeneuve. 2013. Development and validation of a dynamic material flow analysis model for French copper cycle. *Chemical Engineering Research and Design* 91(8): 1390–1402. http://linkinghub.elsevier.com/retrieve/pii/S0263876213001068. Accessed September 19, 2014.

Bouman, M., R. Heijungs, E. van der Voet, J.C.J.. van den Bergh, and G. Huppes. 2000. Material flows and economic models: an analytical comparison of SFA, LCA and partial equilibrium models. *Ecological Economics* 32(2): 195–216. http://linkinghub.elsevier.com/retrieve/pii/S0921800999000919.

Box, G.E.P. 1987. *Empirical Model-Building and Response Surfaces*. 1st editio. New York, USA: Wiley.

BRGM. 2012. *Panorama 2011 du marché de l'antimoine*.

British Geological Survey. 2011. *Risk List 2011*. Vol. 1.

British Geological Survey. 2012. *Risk List 2012*.

British Geological Survey. 2015. World mineral statistics data. https://www.bgs.ac.uk/mineralsuk/statistics/wms.cfc?method=searchWMS.

Bromby, R. 2013. First rare earths, now antimony — it's all about China. *InvestorIntel*. http://investorintel.com/technology-metals-intel/first-rare-earths-now-antimony-—-china-wants-control-now-faces-falling-prices/. Accessed February 2, 2015.

Brunner, P.H. and H. Rechberger. 2004. *Practical Handbook of Material Flow Analysis*. Lewis.

Brunner, P.H. and H. Rechtberger. 2004. *Practical Handbook of Material Flow Analysis*. Lewis Publishers.

Buijs, B., L. a. Tercero Espinoza, and H. Sievers. 2012. Limits to the critical raw materials approach. *Proceedings of the ICE - Waste and Resource Management* 165: 201–208.

Buser, A.M., L.S. Morf, R. Taverna, and G.E.O. Partner. 2007. *Dynamic Substance Flow Analysis Model for Selected Brominated Flame Retardants as a Base for Decision Making on Risk Reduction Measures*.

Butterman, W.C. and J.F. Carlin. 2004. Antimony. *U.S. Geological Survey Open-File Report 03-019*.

Carlin, J.F. 1995. *Antimony*.

Carlin, J.F. 2006. *Antimony Recycling in the United States in 2000*.

Cavallo, D., I. Iavicoli, A. Setini, A. Marinaccio, B. Perniconi, G. Carelli, and S. Iavicoli. 2002. Genotoxic risk and oxidative DNA damage in workers exposed to antimony trioxide. *Environmental and Molecular Mutagenesis* 40(April): 184–189.

CBS. 2012. Energy consumption down by 7 percent in 2011. *Statistics Netherlands*. http://www.cbs.nl/en-GB/menu/themas/industrie-energie/publicaties/artikelen/archief/2012/2012-3600-wm.htm. Accessed April 27, 2015.

Cencic, O. and H. Rechberger. 2008. Material Flow Analysis with Software STAN. *Journal of Environmental Management* 18(1): 3–7.

Chen, W., L. Shi, and Y. Qian. 2010. Substance flow analysis of aluminium in mainland China for 2001, 2004 and 2007: Exploring its initial sources, eventual sinks and the pathways linking them. *Resources, Conservation and Recycling* 54(9): 557–570. http://dx.doi.org/10.1016/j.resconrec.2009.10.013.

Chen, W.-Q. and T.E. Graedel. 2012. Anthropogenic cycles of the elements: a critical review. *Environmental Science & Technology* 46(16): 8574–86. http://www.ncbi.nlm.nih.gov/pubmed/22803614.

Ciacci, L., B.K. Reck, N.T. Nassar, and T.E. Graedel. 2015. Lost by design. *Environmental Science & Technology*: 150218050634006. http://pubs.acs.org/doi/abs/10.1021/es505515z.

Ciroth, A. 2007. ICT for environment in life cycle applications openLCA — A new open source software for life cycle assessment. *The International Journal of Life Cycle Assessment* 12(4): 209–210.

Classen, M., H. Althaus, S. Blaser, M. Tuchschmid, N. Jungbluth, and M. Emmenegger. 2009. *Life Cycle Inventories of Metals. Final report ecoinvent data v2.1, No 10*. Dübendorf. www.ecoinvent.ch.

Cooper, R.G. and A.P. Harrison. 2009. The exposure to and health effects of antimony. *Indian Journal of Occupational and Environmental Medicine* 13(1).

Crowson, P.C.F. 2011. Mineral reserves and future minerals availability. *Mineral Economics* 24: 1–6.

Cullen, J.M. and J.M. Allwood. 2013. Mapping the global flow of aluminum: from liquid aluminum to end-use goods. *Environmental Science & Technology* 47(7): 3057–64. http://www.ncbi.nlm.nih.gov/pubmed/23438734.

Diederen, A. 2009. Metal minerals scarcity: A call for managed austerity and the elements of hope. *TNO Defence, Security and Safety*: 1–13. http://platform-materiaalschaarste.nl/archive/documenten/Diederen_Metal-minerals-scarcity-final-version-10.pdf.

Dobbs, B.J.T. 1983. *The Foundations of Newton's Alchemy*. Cambridge University Press.

Du, X. and T.E. Graedel. 2011. Uncovering the global life cycles of the rare earth elements. *Scientific Reports* 1: 145. http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=3216626&tool=pmcentrez&rendertype=abstract. Accessed July 9, 2014.

Dufton, P.W. 2003. *Flame Retardants for Plastics: Market Report*.

EEA. 2013. *EMEP/EEA air pollutant emission inventory guidebook 2013*.

EFRA. 2014. *Input to Öko-Institut "Questionnaire for Substance Prioritisation" under RoHS*. Brussels, Belgium. http://www.cefic-efra.com/content/Default.asp?PageID=130.

Elshkaki, A. 2007. Systems Analysis of Stock Buffering: Development of a Dynamic Substance Flow-Stock Model for the Identification and Estimation of Future Resources, Waste Streams and Emissions. Leiden University.

Elshkaki, A. 2013. An analysis of future platinum resources, emissions and waste streams using a system dynamic model of its intentional and non-intentional flows and stocks. *Resources Policy* 38(3): 241–251. http://linkinghub.elsevier.com/retrieve/pii/S0301420713000342. Accessed July 14, 2014.

Elshkaki, A., E. van der Voet, M. Van Holderbeke, and V. Timmermans. 2009. Long-term consequences of non-intentional flows of substances: modelling non-intentional flows of lead in the Dutch economic system and evaluating their environmental consequences. *Waste Management* 29(6): 1916–28. http://www.ncbi.nlm.nih.gov/pubmed/19246186. Accessed November 25, 2014.

Elshkaki, A., E. van der Voet, V. Timmermans, and M. Van Holderbeke. 2005. Dynamic stock modelling: A method for the identification and estimation of future waste streams and emissions based on past production and product stock characteristics*1. *Energy* 30(8): 1353–1363. http://linkinghub.elsevier.com/retrieve/pii/S0360544204000465. Accessed October 8, 2014.

Environment Canada. 2010. *Screening Assessment for the Challenge: Antimony trioxide*.

Erdmann, L. and S. Behrendt. 2011. *Kritische Rohstoffe für Deutschland*. Berlin.

Erdmann, L. and T.E. Graedel. 2011. Criticality of non-fuel minerals: A review of major approaches and analyses. *Environmental Science and Technology* 45: 7620–7630.

EU. 2008a. *European Union Risk Assessment Report: Diantimony Trioxide*. Luxembourg.

EU. 2008b. *Regulation (EC) No 1272/2008*.

European Commission. 2014a. *Report on Critical Raw Materials for the EU: Critical Raw Materials Profiles*.

European Commission. 2014b. *Report on Critical Raw Materials for the EU*.

Filella, M., N. Belzile, and Y.-W. Chen. 2002. Antimony in the environment: a review focused on natural waters. I. Occurrence. *Earth Science Reviews* 57: 125–176.

Filella, M., P. a. Williams, and N. Belzile. 2009. Antimony in the environment: Knowns and unknowns. *Environmental Chemistry* 6(2): 95–105.

Flynn, H.C., A. a Meharg, P.K. Bowyer, and G.I. Paton. 2003. Antimony bioavailability in mine soils. *Environmental Pollution* 124(1): 93–100. http://www.ncbi.nlm.nih.gov/pubmed/12683986.

Freedonia. 2013. World demand for flame retardants forecast to grow 5.4% per year till 2016. *Polymer Additives*: 10–11.

Frischknecht, R., N.J. Editors, H. Althaus, C. Bauer, G. Doka, R. Dones, R. Hischier, and colleagues. 2007. *Implementation of Life Cycle Impact Assessment Methods*.

Frischknecht, R., N. Jungbluth, H.-J. Althaus, G. Doka, R. Dones, T. Heck, S. Hellweg, and colleagues. 2004. The ecoinvent Database: Overview and Methodological Framework. *International Journal of Life Cycle Assessment* 10(1): 3–9. http://www.springerlink.com/index/10.1065/lca2004.10.181.1.

Frischknecht, R., R. Steiner, and N. Jungbluth. 2009. *The Ecological Scarcity Method – Eco-Factors 2006. A method for impact assessment in LCA. Environmental Studies No. 0906*. Bern. http://www.bafu.admin.ch/publikationen/publikation/01031/index.html?lang=en\nhttp://www.environment-switzerland.ch/uw-0906-d.

Frost & Sullivan. 2015. Frost & Sullivan expects 500,000 EVs to be sold worldwide in 2015. http://www.autoblog.com/2015/02/19/frost-and-sullivan-expects-500-000-evs-to-be-sold-worldwide-in-201/.

Gerst, M.D. and T.E. Graedel. 2008. Critical Review In-Use Stocks of Metals: Status and Implications. *Environmental Science & Technology* 42(19).

Gibbs, P. 2012. An Assessment of The Key Drivers of Global Polyester and Raw Material Markets. PCI Xylenes & Polyesters.

Glöser, S., M. Soulier, and L. a Tercero Espinoza. 2013. Dynamic analysis of global copper flows. Global stocks, postconsumer material flows, recycling indicators, and uncertainty evaluation. *Environmental Science & Technology* 47(12): 6564–6572.

Glöser, S., L. Tercero Espinoza, C. Gandenberger, and M. Faulstich. 2015. Raw material criticality in the context of classical risk assessment. *Resources Policy* 44: 35–46. http://linkinghub.elsevier.com/retrieve/pii/S0301420715000021.

Goedkoop, M., R. Heijungs, M. Huijbergts, A. De Schreyver, J. Struijs, and R. Van Zelm. 2009. ReCiPe 2008 . Report 1 : Characterisation. http://www.leidenuniv.nl/cml/ssp/publications/recipe_characterisation_addenum.pdf.

Goedkoop, M. and R. Spriensma. 2001. The Eco-indicator 99 - A damage oriented method for Life Cycle Impact Assessment. *Assessment*: 144.

Gottschalk, F., R.W. Scholz, and B. Nowack. 2010. Probabilistic material flow modeling for assessing the environmental exposure to compounds: Methodology and an application to engineered nano-TiO2 particles. *Environmental Modelling and Software* 25(3): 320–332. http://dx.doi.org/10.1016/j.envsoft.2009.08.011.

Graedel, T.E., R. Barr, C. Chandler, T. Chase, J. Choi, L. Christoffersen, E. Friedlander, and colleagues. 2012. Methodology of metal criticality determination. *Environmental Science & Technology* 46(2): 1063–70. http://www.ncbi.nlm.nih.gov/pubmed/22191617.

Graedel, T.E., D. Beers, M. Bertram, K. Fuse, R.B. Gordon, A. Gritsinin, E.M. Harper, and colleagues. 2005. The Multilevel Cycle of Anthropogenic Zinc. *Journal of Industrial Ecology* 9(3): 67–90. http://doi.wiley.com/10.1162/1088198054821573.

Graedel, T.E., D. Van Beers, M. Bertram, K. Fuse, R.B. Gordon, A. Gritsinin, A. Kapur, and colleagues. 2004. Multilevel Cycle of Anthropogenic Copper. *Environmental Science & Technology* 38(4): 1242–1252.

Graedel, T.E., G. Gunn, and L.T. Espinoza. 2014. Metal resources, use and criticality. In *Critical Metals Handbook*, ed. by Gus Gunn. 1st ed. John WIley & Sons.

Graedel, T.E., E.M. Harper, N.T. Nassar, P. Nuss, and B.K. Reck. 2015. Criticality of metals and metalloids. *Proceedings of the National Academy of Sciences of the United States of America* 112(14).

Graedel, T.E. and P. Nuss. 2014. Employing Considerations of Criticality in Product Design. *Journal of the Mineral, Metals & Materials Society* 66(11): 2360–2366. http://link.springer.com/10.1007/s11837-014-1188-4. Accessed November 10, 2014.

Groß, R., D. Bunke, C.-O. Gensche, S. Zangl, and A. Manhart. 2008. Study on Hazardous Substances in Electrical and Electronic Equipment, Not Regulated by the RoHS Directive. *Öko-Institut*. http://hse-rohs.oeko.info/fileadmin/user_upload/Documents/RoHS_Hazardous_Substances_Final_Report.pdf.

Grund, S.C., H. Kunibert, H.J. Breunig, and H.U. Wolf. 2011. Antimony and Antimony Compounds. In *Ullmann's Encyclopedia of Industrial Chemistry*. 7th ed. Wiley-VCH.

Guinée, J., M. Gorrée, R. Heijungs, G. Huppes, R. Kleijn, A. De Koning, L. van Oers, and colleagues. 2001. *Life cycle assessment; An operational guide to the ISO standards; Parts 1 and 2.* Vol. 26. Dordrecht: Kluwer Academic Publishers, January.

Guo, X., K. Wang, M. He, Z. Liu, H. Yang, and S. Li. 2014. Antimony smelting process generating the solid wastes and dust: Characterization and leaching behaviors Xuejun. *Journal of Environmental Sciences*.

Hageluken, C. 2006. Recycling of electronic scrap at Umicore's integrated metal's smelter and refinery. *Erzmetall* 59(3): 152–161.

Hammond, A., A. Adriaanse, S. Bringezu, Y. Moriguchi, E. Rodenburg, D. Rogich, and H. Schutz. 1997. *Resource Flows: the Material Basis of Industrial Economies.*

Harper, E.M., G. Kavlak, L. Burmeister, M.J. Eckelman, S. Erbis, V.S. Espinoza, P. Nuss, and T.E. Graedel. 2014. Criticality of the Geological Zinc, Tin, and Lead Family. *Journal of Industrial Ecology* 00(0): 1–17.

Harper, E.M., G. Kavlak, and T.E. Graedel. 2012. Tracking the metal of the goblins: cobalt's cycle of use. *Environmental Science & Technology* 46(2): 1079–86. http://www.ncbi.nlm.nih.gov/pubmed/22142288.

Hatayama, H., I. Daigo, Y. Matsuno, and Y. Adachi. 2010. Outlook of the world steel cycle based on the stock and flow dynamics. *Environmental Science & Technology* 44(16): 6457–63.

He, M., K. Kravchyk, M. Walter, and M. V Kovalenko. 2014. Monodisperse antimony nanocrystals for high-rate Li-ion and Na-ion battery anodes: nano versus bulk. *Nano Letters* 14(3): 1255–62.

He, M., X. Wang, F. Wu, and Z. Fu. 2012. Antimony pollution in China. *The Science of the Total Environment* 421-422(19): 41–50. http://www.ncbi.nlm.nih.gov/pubmed/21741676. Accessed July 13, 2014.

Health Canada. 1997. *Guidelines for Canadian drinking water quality: Supporting documentation. Antimony.*

Hedbrant, J. and L. Sörme. 2001. Data Vagueness and Uncertainties in Urban Heavy-Metal Data Collection. *Water, Air and Soil Pollution: Focus* 1(3-4): 43–53.

Heijungs, R., J.B. Guide, G. Huppes, R.M. Lankreijer, H.A.U. de Haes, A.W. Sleeswijk, A.A.M. Ansems, P.G. Eggels, R. van Duin, and H.P. de Goede. 1992. *Environmental life-cycle assessment of products: guide and background.* Leiden, the Netherlands.

Heijungs, R., J. Guinée, R. Kleijn, and V. Rovers. 2007. LCA Methodology Bias in Normalization: Causes, Consequences, Detection and Remedies. *International Journal of Life Cycle Assessment* 12(4): 211–216.

Herzke, D., M. Harju, and E. Heimstad. 2010. Emerging "new" brominated flame retardants: sources and transport. *Proceedings of the 2010 BFR Conference*: 6–9. http://bfr2010.com/abstract-download/2010/90161.pdf.

Hjortenkrans, D.S.T., B.G. Bergbäck, and A. V. Häggerud. 2007. Metal emissions from brake linings and tires: Case studies of Stockholm, Sweden 1995/1998 and 2005. *Environmental Science and Technology* 41(15): 5224–5230.

Hou, H., N. Yao, J.N. Li, Y. Wei, L. Zhao, J. Zhang, and F.S. Li. 2013. Migration and leaching risk of extraneous antimony in three representative soils of China: Lysimeter and batch experiments. *Chemosphere* 93(9): 1980–1988.

Humphreys, D. 2010. The great metals boom: A retrospective. *Resources Policy* 35(1): 1–13. http://dx.doi.org/10.1016/j.resourpol.2009.07.002.

Huo, H., M. Wang, L. Johnson, and D. He. 2006. *Projection of Chinese Motor Vehicle Growth, Oil Demand, and CO2 Emissions Through 2050. Argonne, U.S. DOE.*

Hurley, P.J. 2013. *The Structure, Redox Corrosion and Protection of Commercial Lead-Antimony Shot.*

IAA. 2014. *Antimony trioxide factsheet. International Antimony Association.*

IARC. 1989. Antimony trioxide and antimony trisulfide. *International Agency for Research on Cancer (IARC) - Summaries & Evaluations.* http://www.inchem.org/documents/iarc/vol47/47-11.html. Accessed January 15, 2015.

IEA. 2015. FAQs: Transport. http://www.iea.org/aboutus/faqs/transport/.

IMF. 2014. World Economic Outlook Database. *Data and Statistics.* http://www.imf.org/external/pubs/ft/weo/2014/02/weodata/weorept.aspx?sy=1980&ey=2014&ssd=1&sort=country&ds=.&br=1&pr1.x=39&pr1.y=8&c=001,998&s=NGDPD,PPPGDP&grp=1&a=1. Accessed May 8, 2015.

International Standardization Organization (ISO). 2006. Environmental Management - Life Cycle Assessment. Geneva, Switzerland.

Izard, C.F. and D.B. Müller. 2010. Tracking the devil's metal: Historical global and contemporary U.S. tin cycles. *Resources, Conservation and Recycling* 54(12): 1436–1441. http://linkinghub.elsevier.com/retrieve/pii/S092134491000145X. Accessed July 22, 2014.

JORC. 2012. *Australasian Code for Reporting of Exploration Results, Mineral Resources and Ore Reserves (The JORC Code).* http://www.maneyonline.com/doi/abs/10.1179/aes.2001.110.3.121.

Kapur, A. 2005. The future of the red metal—scenario analysis. *Futures* 37(10): 1067–1094. http://linkinghub.elsevier.com/retrieve/pii/S0016328705000406. Accessed December 11, 2014.

Karlsson, S., C. Azar, G. Berndes, J. Holmberg, and K. Lindgren. 1997. *Man and Material Flows: Towards sustainable materials management.*

Kavlak, G. and T.E. Graedel. 2013a. Global anthropogenic selenium cycles for 1940–2010. *Resources, Conservation and Recycling* 73: 17–22. http://linkinghub.elsevier.com/retrieve/pii/S0921344913000220. Accessed July 21, 2014.

Kavlak, G. and T.E. Graedel. 2013b. Global anthropogenic tellurium cycles for 1940–2010. *Resources, Conservation and Recycling* 76: 21–26. http://linkinghub.elsevier.com/retrieve/pii/S0921344913000943. Accessed July 21, 2014.

Kean, S. 2010. Antimony: It might have killed Mozart. *Blogging the Periodic Table.* http://www.slate.com/articles/health_and_science/elements/features/2010/blogging_the_periodic_table/antimonyit_might_have_killed_mozart.html. Accessed February 11, 2015.

Kleijn, R. 2012. Materials and energy: a story of linkages. Leiden University, the Netherlands.

Kleijn, R., R. Huele, and E. van der Voet. 2000. Dynamic substance flow analysis: the delaying mechanism of stocks, with the case of PVC in Sweden. *Ecological Economics* 32(2): 241–254. http://linkinghub.elsevier.com/retrieve/pii/S0921800999000907.

Knoeri, C., P. a Wäger, A. Stamp, H.-J. Althaus, and M. Weil. 2013. Towards a dynamic assessment of raw materials criticality: linking agent-based demand with material flow supply modelling approaches. *The Science of the Total Environment* 461-462: 808–12. http://www.ncbi.nlm.nih.gov/pubmed/23453658. Accessed September 16, 2014.

Laner, D., H. Rechberger, and T. Astrup. 2014. Systematic Evaluation of Uncertainty in Material Flow Analysis. *Journal of Industrial Ecology* 00(0). http://doi.wiley.com/10.1111/jiec.12143. Accessed September 6, 2014.

Leontief, W. 1966. *Input–Output Economics*. New York: Oxford University Press.

Li, J. 2013. The Trends of China's Policy of Antimony and its Influence on the World's Supply. *Geological Society of America's 125th Anniversary Annual Meeting and Exposition*. https://gsa.confex.com/gsa/2013AM/webprogram/Paper227386.html.

Li, T., P.C.I. Thomas, and J.P. Hager. 1991. Process for treatment of antimony-containing materials. USA.

Liu, G., C.E. Bangs, and D.B. Müller. 2012. Stock dynamics and emission pathways of the global aluminium cycle. *Nature Climate Change* 3(4): 338–342.

Løvik, A.N., E. Restrepo, and D.B. Müller. 2015. The global anthropogenic gallium system: Determinants of demand, supply and efficiency improvements. *Environmental Science & Technology*: 150417125605003. http://pubs.acs.org/doi/abs/10.1021/acs.est.5b00320.

MacLean, H.L., F. Duchin, C. HagelükenK, O. Halada, S.E. Kesler, Y. Moriguchi, D. Mueller, T.E. Norgate, M.A. Reuter, and E. van der Voet. 2009. Stocks, Flows, and Prospects of Mineral Resources. In *Linkages of Sustainability*, ed. by Thomas E Graedel and Ester van der Voet. The MIT Press.

Månsson, N.S., D.S.T. Hjortenkrans, B.G. Bergbäck, L. Sörme, and A. V. Häggerud. 2009. Sources of antimony in an urban area. *Environmental Chemistry* 6(2).

Mao, J.S., J. Dong, and T.E. Graedel. 2008a. The multilevel cycle of anthropogenic lead II. Results and discussion. *Resources, Conservation and Recycling* 52(8-9): 1050–1057. http://linkinghub.elsevier.com/retrieve/pii/S092134490800058X. Accessed July 14, 2014.

Mao, J.S., J. Dong, and T.E. Graedel. 2008b. The multilevel cycle of anthropogenic lead I. Methodology. *Resources, Conservation and Recycling* 52(8-9): 1058–1064. http://linkinghub.elsevier.com/retrieve/pii/S0921344908000591. Accessed July 22, 2014.

Masters, B.H. 2005. *Antimony*.

Mathys, R., J. Dittmar, and C.A. Johnson. 2007. *Antimony in Switzerland: A susbtance flow analysis*. Bern.

Meadows, D.., D. Meadows, J. Randers, and W. Behrens. 1972. *The Limits to Growth*. New York: Universe Books. http://www.donellameadows.org/wp-content/userfiles/Limits-to-Growth-digital-scan-version.pdf.

Melo, M.T. 1999. Statistical analysis of metal scrap generation: The case of aluminium in Germany. *Resources, Conservation and Recycling* 26: 91–113.

Metalprices.com. 2015. Nonferrous and Minor Metals Prices. http://www.metalprices.com/#. Accessed January 16, 2015.

Morf, L., R. Taverna, H. Daxbeck, and R. Smutny. 2003. *Selected polybrominated flame retardants: PBDEs and TBBPA. Substance flow analysis*. Environmental Series. Berne.

Moss, R.H. and S.H. Schneider. 2000. Uncertainties in the IPCC TAR: Recommendations to lead authors for more consistent assessment and reporting. In *Guidance Papers on the Cross Cutting Issues of the Third Assessment Report of the IPCC*, ed. by R. Pachauri, T. Taniguchi, and K. Tanaka, 33–51. Geneva: World Meteorological Organization.

Müller, E., L.M. Hilty, R. Widmer, M. Schluep, and M. Faulstich. 2014. Modeling metal stocks and flows: a review of dynamic material flow analysis methods. *Environmental Science & Technology* 48(4): 2102–13. http://www.ncbi.nlm.nih.gov/pubmed/24494583.

Murakami, S. 2006. Material flows and stocks of metals surrounding Japan. In *Symposium on Advanced Material Flow Analysis for the Sustainable Society*. Sendai, Japan.

Nassar, N.T., R. Barr, M. Browning, Z. Diao, E. Friedlander, E.M. Harper, C. Henly, and colleagues. 2012. Criticality of the geological copper family. *Environmental Science and Technology* 46: 1071–1078.

Norgate, T. and N. Haque. 2010. Energy and greenhouse gas impacts of mining and mineral processing operations. *Journal of Cleaner Production* 18(3): 266–274. http://linkinghub.elsevier.com/retrieve/pii/S0959652609003199. Accessed September 19, 2014.

Norgate, T.E. 2004. *Metal Recycling: An Assessment Using Life Cycle Energy Consumption as a Sustainability Indicator*. Clayton South, Victoria, Australia. http://www.minerals.csiro.au/sd/pubs/recycling_report.pdf.

Nriagu, J. and J. Pacyna. 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* 333.

Nriagu, J.O. 1989. A global assessment of natural sources of atmospheric trace metals. *Nature* 338: 47–49.

Nuss, P. and M.J. Eckelman. 2014. Life cycle assessment of metals: a scientific synthesis. *PLOS ONE* 9(7). http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=4085040&tool=pmcentrez&rendertype=abstract. Accessed July 21, 2014.

Oakdene Hollins. 2008. *Material Security - Ensuring Resource Availability for the UK Economy*. http://www.oakdenehollins.co.uk/pdf/material_security.pdf.

OECD. 2005. OECD Regions at a Glance 2005. http://www.oecd-ilibrary.org/statistics. Accessed March 13, 2015.

Okkenhaug, G., Y.-G. Zhu, L. Luo, M. Lei, X. Li, and J. Mulder. 2011. Distribution, speciation and availability of antimony (Sb) in soils and terrestrial plants from an active Sb mining area. *Environmental Pollution* 159(10): 2427–34. http://www.ncbi.nlm.nih.gov/pubmed/21767897. Accessed September 5, 2014.

Öko-Institut. 2009. *Critical Metals for Future Sustainable Technologies and their Recycling Potentiel.*

Pacyna, J.M. and E.G. Pacyna. 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environmental Reviews* 9(4): 269–298. http://www.nrc.ca/cgi-bin/cisti/journals/rp/rp2_abst_e?er_a01-012_9_ns_nf_er9-01. Accessed August 25, 2014.

Pizzol, M., P. Christensen, J. Schmidt, and M. Thomsen. 2011a. Eco-toxicological impact of " metals " on the aquatic and terrestrial ecosystem : A comparison between eight different methodologies for Life Cycle Impact Assessment (LCIA). *Journal of Cleaner Production* 19(6-7): 687–698. http://dx.doi.org/10.1016/j.jclepro.2010.12.008.

Pizzol, M., P. Christensen, J. Schmidt, and M. Thomsen. 2011b. Impacts of "metals" on human health: a comparison between nine different methodologies for Life Cycle Impact Assessment (LCIA). *Journal of Cleaner Production* 19(6-7): 646–656. http://linkinghub.elsevier.com/retrieve/pii/S0959652610001800. Accessed July 22, 2014.

PlasticsEurope. 2012. *Plastics – the Facts 2012 An analysis of European plastics production, demand and waste data for 2011*. Brussels, Belgium.

Polinares. 2012a. *Fact Sheet: Platinum Group Metals.*

Polinares. 2012b. *Critical Raw Materials: Developing Long-Term Strategies.*

PwC. 2015. *The World in 2050: Will the shift in global economic power continue?*

Quiroz, W., I. De Gregori, P. Basilio, M. Bravo, M. Pinto, and M.G. Lobos. 2009. Heavy weight vehicle traffic and its relationship with antimony content in human blood. *Journal of Environmental Monitoring : JEM* 11(5): 1051–1055.

Radetzki, M. 2012. The perseverance of the ongoing metal and mineral boom. *Mineral Economics*.

Rauch, J.N. 2009. Global mapping of Al, Cu, Fe, and Zn in-use stocks and in-ground resources. *Proceedings of the National Academy of Sciences of the United States of America* 106(45): 18920–5. http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=2776457&tool=pmcentrez&rendertype=abstract.

Rebitzer, G., T. Ekvall, R. Frischknecht, D. Hunkeler, G. Norris, T. Rydberg, W.-P. Schmidt, S. Suh, B.P. Weidema, and D.W. Pennington. 2004. Life cycle assessment part 1: framework, goal and scope definition, inventory analysis, and applications. *Environment International* 30(5): 701–20. http://www.ncbi.nlm.nih.gov/pubmed/15051246. Accessed November 10, 2013.

Rechberger, H., O. Cencic, and R. Frühwirth. 2014. Uncertainty in Material Flow Analysis. *Journal of Industrial Ecology* 18(2): 159–160. http://doi.wiley.com/10.1111/jiec.12087. Accessed July 29, 2014.

Reck, B.K., D.B. Müller, K. Rostkowski, and T.E. Graedel. 2008. Anthropogenic nickel cycle: insights into use, trade, and recycling. *Environmental Science & Technology* 42(9): 3394–400. http://www.ncbi.nlm.nih.gov/pubmed/18522124.

Rochat, D., C.R. Binder, J. Diaz, and O. Jolliet. 2013. Combining Material Flow Analysis, Life Cycle Assessment, and Multiattribute Utility Theory. *Journal of Industrial Ecology* 17(5): n/a–n/a. http://doi.wiley.com/10.1111/jiec.12025. Accessed May 27, 2014.

Rosenau-Tornow, D., P. Buchholz, A. Riemann, and M. Wagner. 2009. Assessing the long-term supply risks for mineral raw materials—a combined evaluation of past and future trends. *Resources Policy* 34(4): 161–175. http://linkinghub.elsevier.com/retrieve/pii/S030142070900035X. Accessed July 22, 2014.

Rosenbaum, R.K., T.M. Bachmann, L.S. Gold, M. a J. Huijbregts, O. Jolliet, R. Juraske, A. Koehler, and colleagues. 2008. USEtox - The UNEP-SETAC toxicity model: Recommended characterisation factors for human toxicity and freshwater ecotoxicity in life cycle impact assessment. *International Journal of Life Cycle Assessment* 13(7): 532–546.

Roskill. 2011. *Study of the antimony market*.

Roskill. 2012. *Antimony: Changes in the pattern of supply and demand*.

Rüegg, P. 2014. Antimony nanocrystals for batteries. *ETH Zurich*.

Saurat, M. 2006. Material Flow Analysis and Environmental Impact Assessment Related to Current and Future Use of PGM in Europe. Chalmers University of Technology.

Schwarz-Schampera, U. 2014. Antimony. In *Critical Metals Handbook*, ed. by Gus Gunn, 121.: 1st ed. John WIley & Sons.

SGTK. 2014. *Antimony: Substance dossier for the recovery of antimony from selected waste compared to primary production*.

Shotyk, W., B. Chen, and M. Krachler. 2005. Lithogenic, oceanic and anthropogenic sources of atmospheric Sb to a maritime blanket bog, Myrarnar, Faroe Islands. *Journal of Environmental Monitoring : JEM* 7(12): 1148–54. http://www.ncbi.nlm.nih.gov/pubmed/16307065.

Shotyk, W., M. Krachler, and B. Chen. 2006. Contamination of Canadian and European bottled waters with antimony from PET containers. *Journal of Environmental Monitoring : JEM* 8(2): 288–92. http://www.ncbi.nlm.nih.gov/pubmed/16470261. Accessed August 16, 2014.

Smith, C. 2014. China cancels antimony mining restrictions; raises rare earths quota. *MetalBulletin*. http://www.metalbulletin.com/Article/3350361/China-cancels-antimony-mining-restrictions-raises-rare-earths-quota.html#axzz3CQyr1gHO.

Speirs, J. and R. Gross. 2013. Materials Availability : Comparison of material criticality studies - methodologies and results Working Paper III(February).

Sundar, S. and J. Chakravarty. 2010. Antimony toxicity. *International Journal of Environmental Research and Public Health* 7(12): 4267–77. http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=3037053&tool=pmcentrez&rendertype=abstract. Accessed July 10, 2014.

Thaler, S., M. Zessner, M. Mayr, T. Haider, H. Kroiss, K. Wagner, and K. Ruzicka. 2011. Der Einfluss von Ernährungsgewohnheiten auf die Nährstoffbilanz Österreichs. *Österreichische Wasser- Und Abfallwirtschaft* 63(5-6): 117–128. http://link.springer.com/10.1007/s00506-011-0292-8.

Thiele, U.K. 2004. Quo vadis polyester catalyst? *Chemical Fibers International* 54.

Thiele, U.K. 2007. Paradigm Shift in Polyester Recycling: From Second Grade Replacements to Green Labels and Virgin Products Cost Cutting. In *3rd China Int'l Recycled Polyester Fiber Market & Tech Forum*.

Thornton, I., R. Rautio, and S. Brush. 2001. *Lead: the facts*. London, UK.

Tian, H., J. Zhou, C. Zhu, D. Zhao, J. Gao, J. Hao, M. He, K. Liu, K. Wang, and S. Hua. 2014. A Comprehensive Global Inventory of Atmospheric Antimony Emissions from Anthropogenic Activities, 1995-2010. *Environmental Science & Technology*. http://www.ncbi.nlm.nih.gov/pubmed/25110938.

Topf, A. 2013. Antimony: Put It on Your Radar. *Resource Investing News*. http://resourceinvestingnews.com/58886-antimony-put-it-on-your-radar.html. Accessed February 2, 2015.

Townsend Solutions. 2012. Global Consumption of Flame Retardants 2011. http://www.flameretardants-online.com/web/en/106/7ae3d32234954e28e661e506e284da7f.htm.

Tschan, M., B.H. Robinson, and R. Schulin. 2009. Antimony in the soil–plant system – a review. *Environmental Chemistry* 6(2): 106. http://www.publish.csiro.au/?paper=EN08111. Accessed September 5, 2014.

Tsunemi, K. and H. Wada. 2008. Substance Flow Analysis of Antimony for Risk Assessment of Antimony and Antimony Compounds in Japan. *Journal of the Japan Institute of Metals* 72(2): 91–98.

Tukker, A., H. Buijst, I.R. van Oers, and E. van der Voet. 2001. *Risks to Health and the Environment Related to the Use of Lead in Products*. Vol. 39.

Tukker, A., R. Kleijn, L. van Oers, and E. Smeets. 1998. Combining SFA and LCA The Swedish PVC Analysis. *Journal of Industrial Ecology* 1(4).

Turer, D. 2005. Effect of non-vehicular sources on heavy metal concentrations of roadside soils. *Water, Air, and Soil Pollution* 166(1-4): 251–264.

Tylenda, C.A. and B.A. Fowler. 2007. Antimony. In *Handbook on the Toxicology of Metals (Third Edition)*, ed. by GF Nordberg, BA Fowler, M Nordberg, and L Friberg, 353–365. Academic Press.

U.S. DOE. 2011. *Critical Materials Strategy*.

U.S. EPA. 2014. *TSCA Work Plan Chemical Risk Assessment: Antimony Trioxide*. August.

U.S. Geological Survey. 2009. *Mineral Commodity Summaries 2009*.

U.S. Geological Survey. 2011. *Mineral Commodity Summaries 2011*.

U.S. Geological Survey. 2012. *Mineral Commodity Summaries 2012*.

U.S. Geological Survey. 2014a. *Antimony Supply-Demand Statistics*.

U.S. Geological Survey. 2014b. Antimony. *Minerals Information*. http://minerals.usgs.gov/minerals/pubs/commodity/antimony/.

U.S. Geological Survey. 2014c. *Antimony in the Third Quarter 2014*.

U.S. Geological Survey. 2014d. *Mineral Commodity Summaries 2014*.

U.S. Geological Survey. 2014e. US Coal Quality Database. *National Coal Resources Data System*. http://energy.er.usgs.gov/coalqual.htm.

U.S. Geological Survey. 2015. *Mineral Commodity Summaries 2015*.

Uexküll, O. von, S. Skerfving, R. Doyle, and M. Braungart. 2005. Antimony in brake pads-a carcinogenic component? *Journal of Cleaner Production* 13(1): 19–31. http://linkinghub.elsevier.com/retrieve/pii/S0959652603001835. Accessed October 29, 2014.

UN. 2014. City population by sex, city and city type. *United Nations Statistics Division - Demographics Statistics*. http://data.un.org/Data.aspx?d=POP&f=tableCode:240. Accessed May 13, 2015.

UNEP. 2010a. *Metal Stocks in Society, Scientific Synthesis, a report of the Working Group on the Global Metal Flows to the International Resource Panel*. Ed. by G. . Graedel, T., Dubreuil, A., Gerst, M., Hashimoto, S., Moriguchi, Y., Müller, D., Pena, C., Rauch, J., Sinkala, T., Sonnemann. United Nations Environment Programme.

UNEP. 2010b. *Final review of scientific information on lead*.

UNEP. 2011a. *Recycling Rates of Metals – A Status Report, A Report of the Working Group on the Global Metal Flows to the Interna- tional Resource Panel*. Ed. by T.E. Graedel, J. Allwood, J.-P. Birat, B.K. Reck, S.F. Sibley, G. Sonnemann, M. Buchert, and C Hagelüken. United Nations Environment Programme.

UNEP. 2011b. *Estimating Long-Run Geological Stocks of Metals*.

UNEP. 2012. *Guidance on best available techniques and best environmental practices for the recycling and disposal of articles containing polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on Persistent Organic Pollutants*.

UNEP. 2013a. *Metal Recycling: Opportunities, Limits, Infrastructure, A Report of the Working Group on the Global Metal Flows to the Inter-national Resource Panel*. Ed. by M. A. Reuter, C. Hudson, A. van Schaik, K. Heiskanen, C. Meskers, and C. Hagelüken. United Nations Environment Programme.

UNEP. 2013b. *Environmental Risks and Challenges of Anthropogenic Metals Flows and Cycles, A Report of the Working Group on the Global Metal Flows to the International Resource Panel*. Ed. by E. van der Voet, R. Salminen, M. Eckelman, G. Mudd, T. Norgate, and R Hischier. United Nations Environment Programme.

US EPA. 2014. Plastics. *Resource Conservation - Common Wastes & Materials*. http://www.epa.gov/osw/conserve/materials/plastics.htm.

Vangheluwe, M. and A. Van Hyfte. 2001. *Critical review on acute ecotoxicity data for antimony*. Gent, Belgium.

Velzen, D. van, H. Langenkamp, and G. Herb. 1998. Antimony, its sources, applications and flow paths into urban and industrial waste: a review. *Waste Management & Research* 16(1): 32–40. http://wmr.sagepub.com/cgi/doi/10.1177/0734242X9801600105. Accessed September 2, 2014.

Voet, E. van der. 1996. Substances from cradle to grave: Development of a methodology for the analysis of substance flows through the economy and the environment of a region. Leiden University.

Voet, E. van der. 2002. Substance flow analysis methodology. In *A Handbook of Industrial Ecology*, ed. by Robert U Ayres and Leslie W Ayres. 1st ed. Cheltenham: Edward Elgar.

Voet, E. Van der, R. Kleijn, R. Huele, M. Ishikawa, and E. Verkuijlen. 2002. Predicting future emissions based on characteristics of stocks. *Ecological Economics* 41: 223–234.

Wäger, P. a, R. Hischier, and M. Eugster. 2011a. Environmental impacts of the Swiss collection and recovery systems for Waste Electrical and Electronic Equipment (WEEE): a follow-up. *The Science of the*

Total Environment 409(10): 1746–56. http://www.ncbi.nlm.nih.gov/pubmed/21342702. Accessed September 8, 2014.

Wäger, P., D. Lang, D. Wittmer, R. Bleischwitz, and C. Hagelüken. 2012. Towards a More Sustainable Use of Scarce Metals: A Review of Intervention Options along the Metals Life Cycle. *GAIA* 4: 300–309.

Wäger, P., M. Schluep, and E. Müller. 2010a. *RoHS substances in mixed plastics from Waste Electrical and Electronic Equipment*.

Wäger, P., M. Schluep, E. Müller, and R. Gloor. 2010b. RoHS substances in mixed plastics from Waste Electrical and Electronic Equipment. *Materials Science and Technology*.

Wäger, P., R. Widmer, and A. Stamp. 2011b. *Scarce technology metals: applications, criticalities and intervention options*. Bern.

Walter, M. 2014. Personal Communication.

Walter, M., R. Erni, and M. V. Kovalenko. 2015. Inexpensive Antimony Nanocrystals and Their Composites with Red Phosphorus as High-Performance Anode Materials for Na-ion Batteries. *Scientific Reports* 5: 8418. http://www.nature.com/doifinder/10.1038/srep08418.

Wang, T., D.B. Müller, and T.E. Graedel. 2007. Forging the anthropogenic iron cycle. *Environmental Science & Technology* 41(14): 5120–9. http://www.ncbi.nlm.nih.gov/pubmed/17711233.

Wang, X., M. He, J. Xie, J. Xi, and X. Lu. 2010. Heavy metal pollution of the world largest antimony mine-affected agricultural soils in Hunan province (China). *Journal of Soils and Sediments* 10(5): 827–837.

Wegener Sleeswijk, A., L.F.C.M. van Oers, J.B. Guinée, J. Struijs, and M. a J. Huijbregts. 2008. Normalisation in product life cycle assessment: An LCA of the global and European economic systems in the year 2000. *Science of the Total Environment* 390(1): 227–240.

Weissman, D. 2014. Catalysing PET. *Plastics in Packaging*: 22–23.

Werner, F. 2014. Personal Communication.

WHO. 2003. Antimony in Drinking-water. Background document for development of WHO Guidelines for Drinking Water Quality. *World Health Organization*.

Wikipedia. 2015a. Antimony. http://en.wikipedia.org/wiki/Antimony. Accessed May 22, 2015.

Wikipedia. 2015b. Antimony trioxide. http://en.wikipedia.org/wiki/Antimony_trioxide. Accessed May 22, 2015.

Wikipedia. 2015c. Abundance of elements in Earth's crust. http://en.wikipedia.org/wiki/Abundance_of_elements_in_Earth's_crust. Accessed January 16, 2015.

World Bank. 2014. World Bank Open Data. http://data.worldbank.org/. Accessed March 17, 2015.

Yang, J.G., C.B. Tang, Y.M. Chen, J. He, and M.M.T. Tang. 2011. Separation of antimony from a stibnite concentrate through a low-temperature smelting process to eliminate so2 emission. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science* 42(1): 30–36.

Yoshimura, A., I. Daigo, and Y. Matsuno. 2013. Global Substance Flow Analysis of Indium. *Materials Transactions* 54(1): 102–109.

10 APPENDICES

APPENDIX A: ERROR PROPAGATION

In STAN, uncertainties of unknown flows are calculated with the method of error propagation based on the least square method:

Addition and subtraction

If

$$A + B = C$$

then

$$\delta C = \sqrt{(\delta A)^2 + (\delta B)^2}$$

where δC is the absolute uncertainty of flow C (e.g., in tons if C is in tons).

Multiplication and division

If

$$\frac{A}{B} = C$$

then

$$\frac{\delta C}{C} = \sqrt{\left(\frac{\delta A}{A}\right)^2 + \left(\frac{\delta B}{B}\right)^2}$$

where δC/C is the relative uncertainty of flow C (in %).

Appendix B: Static Model

Flows description and value (2011)

	Flow	Flow Name	Uncertainty (±)	Gg
Production	O	Antimony from ore	5%	178.0
		Beneficiation		
	Co	Antimony concentrate to extraction	5%	168.0
	T	Antimony in tailings	33%	9.9
		Extraction		
	Cr(Sb)	Crude antimony metal	9%	36.4
	Cr(SbO)	Crude antimony oxide	5%	124.9
	S	Antimony in slag	74%	6.7
	Ea(e)	Antimony in air emissions from extraction	100%	0.0
		Refining		
	SbOx	Refined antimony oxide entering F&M	5%	121.1
	NaSbO3	Refined sodium antimonate entering F&M	5%	3.8
	pSb	Refined primary antimony entering F&M	9%	36.4
	Ep(r)	Antimony emissions from refining	100%	0.0
	Wp(ref)	Antimony in waste from refining	100%	0.0
		Secondary production		
	sSb	Refined secondary antimony metal and alloys entering F&M	13%	42.4
	Ep(sp)	Antimony in emissions from secondary production	101%	0.0
	Wp(sp)	Antimony in unrecovered scrap	52%	8.7
	E(P)	Antimony in emissions from Production	36%	16.7
	Ea(P)	Antimony in emissions to atmosphere from Production	61%	0.0
Traded flow	Eh(P)	Antimony in emissions to hydrosphere from Production	100%	0.0
Recycling flow	Ep(P)	Antimony in emissions to pedosphere from Production	36%	16.7
Waste flow	WW(P)	Antimony in wastewater from Production		
Emission flow	SW(P)	Antimony in solid waste from Production	52%	8.7
Fabrication & Manufacture	P(fr)	Antimony used in the F&M of flame retardants	6%	117.8
	P(pet)	Antimony used in the F&M of PET	10%	12.2
	P(gc)	Antimony used in the F&M of glass & ceramics	10%	4.3
	P(onm)	Antimony used in the F&M of other non-metallic products	10%	1.9
	P(lab)	Antimony used in the F&M of lead-acid batteries	9%	54.7
	P(oa)	Antimony used in the F&M of other alloys	10%	24.1
		P	4%	215.0
	NS(lab)	Antimony in new metal scrap from lead-acid batteries F&M	111%	2.2
	NS(oa)	Antimony in new metal scrap from other alloys F&M	107%	1.4
		Antimony in new metal scrap	80%	3.6
	Em(fr)	Antimony in emissions from flame retardant F&M	100%	0.1
	Em(pet)	Antimony in emissions from PET F&M	100%	0.0
	Em(gc)	Antimony in emissions from glass & ceramics F&M	100%	0.0
	Em(lab)	Antimony in emissions from lead-acid batteries F&M	92%	1.1
	Em(oa)	Antimony in emissions from other alloys F&M	96%	0.6
	Wm(fr)	Antimony in discards from flame retardants F&M	100%	1.9
	Wm(pet)	Antimony in discards from PET F&M	100%	0.0
	Wm(lab)	Antimony in discards from lead-acid batteries F&M	89%	1.7
	Wm(oa)	Antimony in discards from other alloys F&M	94%	0.9
	E (FM)	Antimony in emissions from F&M		1.8
	Ea(FM)	Antimony in emissions to atmosphere from F&M	68%	1.4
	Eh(FM)	Antimony in emissions to hydrosphere from F&M	87%	0.1
	Ep(FM)	Antimony in emissions to pedosphere from F&M	60%	0.2
	W (FM)	Antimony in waste from F&M		4.5
	SW(FM)	Antimony in solid waste from F&M	56%	4.1
	WW(FM)	Antimony in wastewater from F&M	126%	0.3

Use	U(fr)	Antimony in flame retardants entering Use	7%	115.8
	U(lab)	Antimony in lead-acid batteries entering Use	10%	49.7
	U(oa)	Antimony in other alloys entering Use	10%	21.2
	U(pet)	Antimony in PET entering Use	10%	12.2
	U(gc)	Antimony in glass & ceramics entering Use	11%	4.3
	U(onm)	Antimony in other-non metallic products entering Use	13%	1.9
		U	5%	205.2
	EoL(fr)	Antimony in end-of-life flame retardants	7%	115.8
	EoL(lab)	Antimony in end-of-life lead-acid batteries	10%	49.7
	EoL(oa)	Antimony in end-of-life other alloys	10%	21.2
	EoL(pet)	Antimony in end-of-life PET	10%	12.2
	EoL(g)	Antimony in end-of-life glass & ceramics	11%	4.3
	EoL(onm)	Antimony in end-of-life other non-metallic products	13%	1.9
		EoL	5%	205.2
Waste Management		Collection		
	OS	Antimony in old metal scrap from WM	15%	47.6
	R	Antimony in recycled plastic and glass & ceramics	44%	11.3
	L(c)	Antimony in non-incinerable waste	27%	100.8
	I	Antimony in incinerated waste	45%	58.3
		Incineration		
	Ir	Antimony in incineration residues	45%	58.0
	Ea(I)	Antimony in emissions from incineration	110%	0.3
	WW(I)	Antimony in wastewater from waste incineration	67%	0.1
		WWT		
	SSA	Antimony in sewage sludge to agriculture	144%	0.0
	SSI	Antimony in sewage sludge to incineration	115%	0.1
	SSL	Antimony in sewage sludge to landfill	114%	0.2
	Eh(WWT)	Antimony in purified wastewater	144%	0.0
	L	Antimony to landfills	5%	158.9
	E (WM)	Antimony in emissions from Waste Management	92%	0.4
	Ea(WM)	Antimony in emissions to atmosphere from Waste Management	110%	0.3
	Eh(WM)	Antimony in emissions to hydrosphere from Waste Management	144%	0.1
	Ep(WM)	Antimony in emissions to pedosphere from Waste Management	144%	0.0
	Ep	Antimony in emissions to pedosphere		
	Eh	Antimony in emissions to hydrosphere	36%	16.9
	Ea	Antimony in emissions to atmosphere	76%	0.2
		Total emissions	58%	1.8
	EoL-RR	(OS + R) / EoL	16%	29%
	RC	(OS + NS) / (O + OS + NS)	16%	22%
	RC with non-metal		16%	26%

Transfer Coefficients

Production

Production TCs		
C	O -> Co	9.4E-01
C	O -> Ep(c)	5.6E-02
PHP	Co -> Cr(Sb)	2.1E-01
PHP	Co -> Cr(SbO)	7.5E-01
PHP	Co -> Ea(e)	7.5E-05
PHP	Co -> S	4.0E-02
R	Cr(Sb) -> Ep(r)	0.0E+00
R	Cr(Sb) -> NaSbO3	0.0E+00
R	Cr(Sb) -> pSb	1.0E+00
R	Cr(Sb) -> SbOx	0.0E+00
R	Cr(Sb) -> Wp(ref)	0.0E+00
R	Cr(SbO) -> Ep(r)	1.6E-04
R	Cr(SbO) -> NaSbO3	3.0E-02
R	Cr(SbO) -> pSb	0.0E+00
R	Cr(SbO) -> SbOx	9.7E-01
R	Cr(SbO) -> Wp(ref)	5.0E-08
Sp	∑ -> Ep(sp)	4.3E-04
Sp	∑ -> sSb	8.3E-01
Sp	∑ -> Wp(sp)	1.7E-01

Production emissions			
	Ea(P)	Eh(P)	Ep(P)
Ep(c)	0	0	1
Ep(e)	0	0	1
Ep(r)	4.8E-01	1.8E-03	5.2E-01
Ep(sp)	1	0	0

Production wastes		
	SW(P)	WW(P)
Wp(ref)	1	0
WP(sp)	1	0

Fabrication & Manufacture

F&M TCs		
FM(fr)	∑ -> U(fr)	9.8E-01
FM(pet)	∑ -> U(pet)	1.0E+00
FM(g)	∑ -> U(g)	9.9E-01
FM(onm)	∑ -> U(onm)	1.0E+00
FM(lab)	∑ -> U(lab)	9.1E-01
FM(oa)	∑ -> U(oa)	8.8E-01
FM(fr)	∑ -> Em(fr)	7.9E-04
FM(pet)	∑ -> Em(pet)	5.0E-04
FM(g)	∑ -> Em(g)	5.6E-03
FM(lab)	∑ -> Em(lab)	2.0E-02
FM(oa)	∑ -> Em(oa)	2.5E-02
FM(fr)	∑ -> Wm(fr)	1.6E-02
FM(pet)	∑ -> Wm(pet)	1.8E-04
FM(lab)	∑ -> Wm(lab)	3.0E-02
FM(oa)	∑ -> Wm(oa)	3.9E-02
FM(lab)	∑ -> NS(lab)	4.0E-02
FM(oa)	∑ -> NS(oa)	5.6E-02

F&M emissions			
	Ea(FM)	Eh(FM)	Ep(FM)
Em(fr)	7.4E-03	0.0E+00	9.9E-01
Em(pet)	1.0E-02	4.3E-17	9.9E-01
Em(g)	2.2E-01	4.5E-02	7.4E-01
Em(lab)	8.6E-01	7.1E-02	7.1E-02
Em(oa)	8.6E-01	7.1E-02	7.1E-02

F&M wastes		
	SW(FM)	WW(FM)
Wm(fr)	8.3E-01	1.7E-01
Wm(pet)	0.0E+00	1.0E+00
Wm(lab)	1.0E+00	0.0E+00
Wm(oa)	1.0E+00	0.0E+00

Use

Use TCs		
U(fr)	∑ -> Eu(fr)	0.0E+00
U(onm)	∑ -> Eu(onm)	0.0E+00
U(oa)	∑ -> Eu(oa)	0.0E+00
U(fr)	∑ -> Wu(fr)	0.0E+00
U(pet)	∑ -> Wu(pet)	0.0E+00

Use emissions			
	Ea(U)	Eh(U)	Ep(U)
Eu(fr)	0	0.85	0.15
Eu(onm)	1	0	0
Eu(oa)	0.05	0.05	0.9

Use wastes		
	SW(U)	WW(U)
Wu(fr)	0	1
Wu(pet)	0	1

Waste Management

Collection (2011)				
	I	L(c)	OS	RP
EoL(fr)	0.4	0.5	0.0	0.1
EoL(pet)	0.9	0.0	0.0	0.1
EoL(g)	0.0	0.9	0.0	0.1
EoL(onm)	0.5	0.5	0.0	0.0
EoL(lab)	0.0	0.3	0.7	0.0
EoL(oa)	0.0	0.4	0.6	0.0
SW(P)	0.0	1.0	0.0	0.0
SW(FM)	0.0	1.0	0.0	0.0

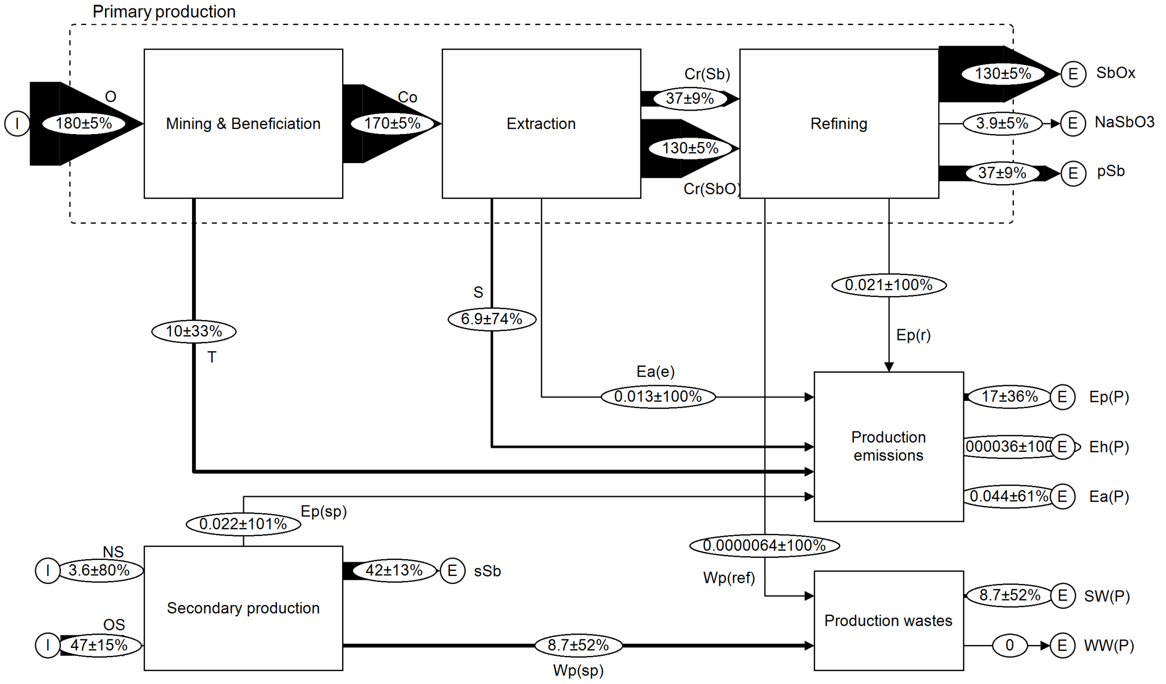
WM emissions			
	Ea(FM)	Eh(FM)	Ep(FM)
Ea(I)	1	0	0
WW(I)	0	1	0
SSA	0	0	1

Incineration			
	Ea(I)	Ir	WW(I)
I	5.5E-03	9.9E-01	1.2E-03

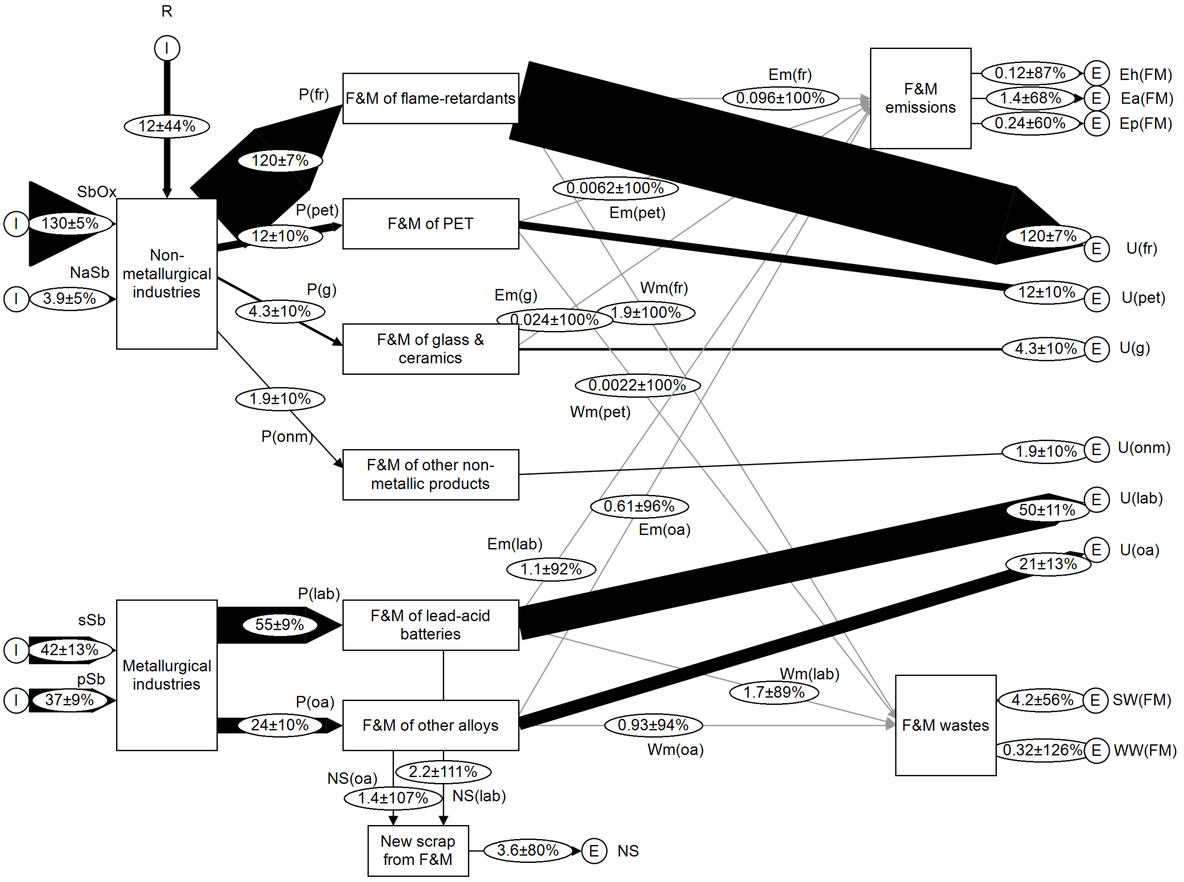
Wastewater treatment				
	Eh(WWT)	SSA	SSI	SSL
∑ WW	0.13	0.13	0.26	0.48

Subsystems Visualization

Production



Fabrication & Manufacture



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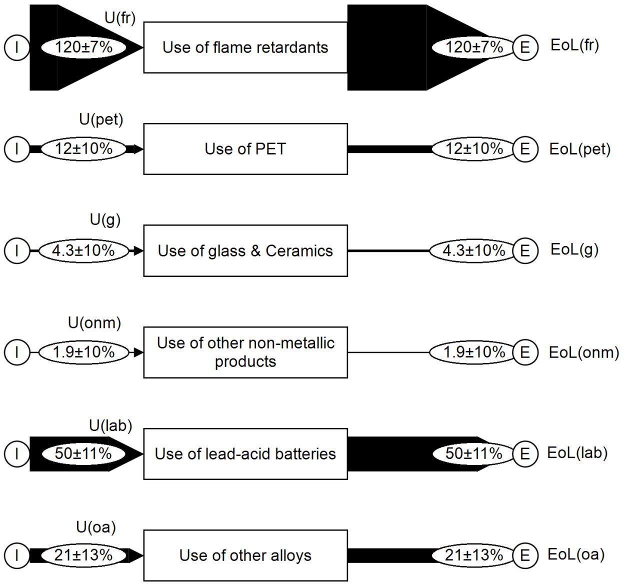
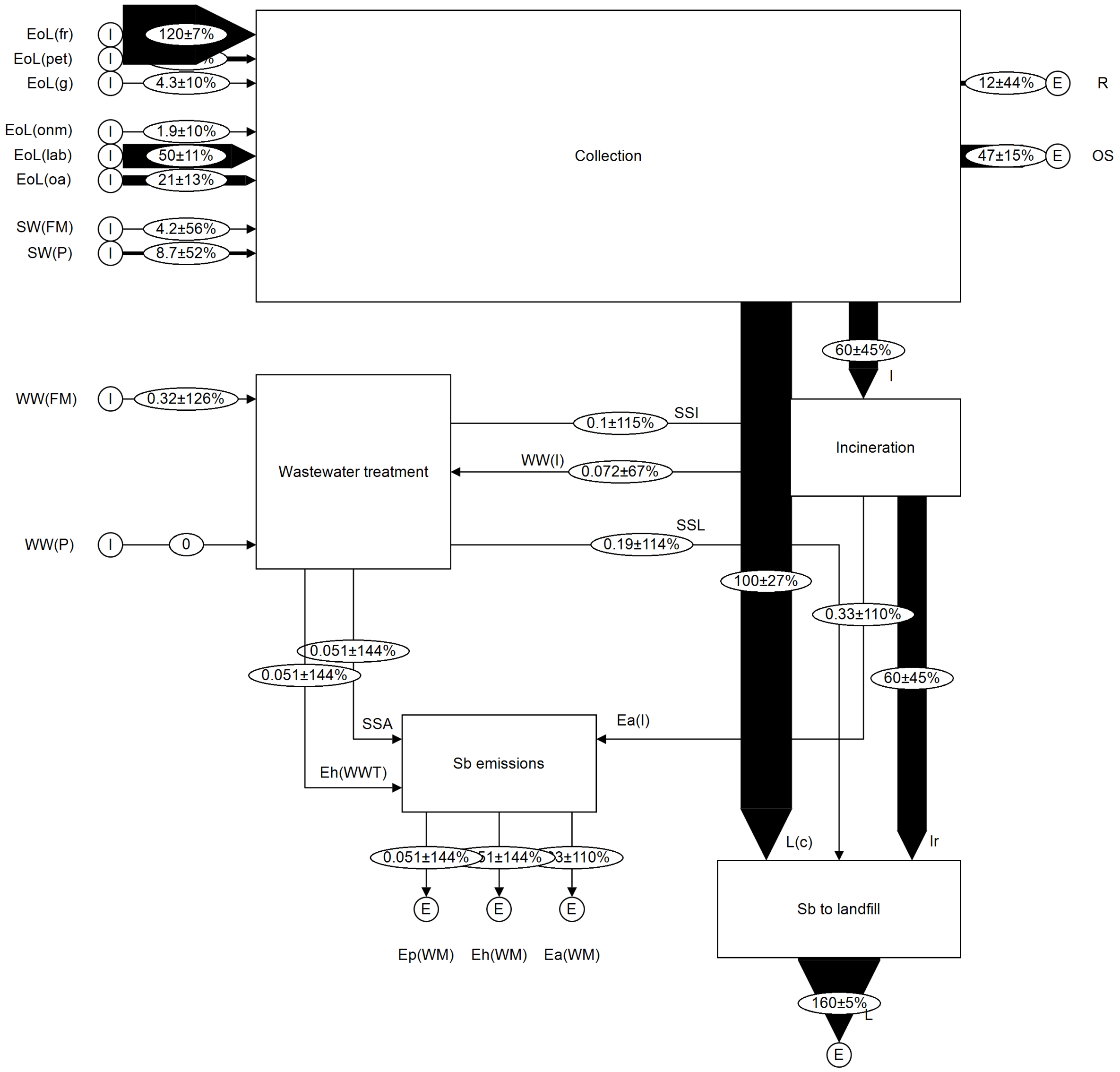


Waste Management

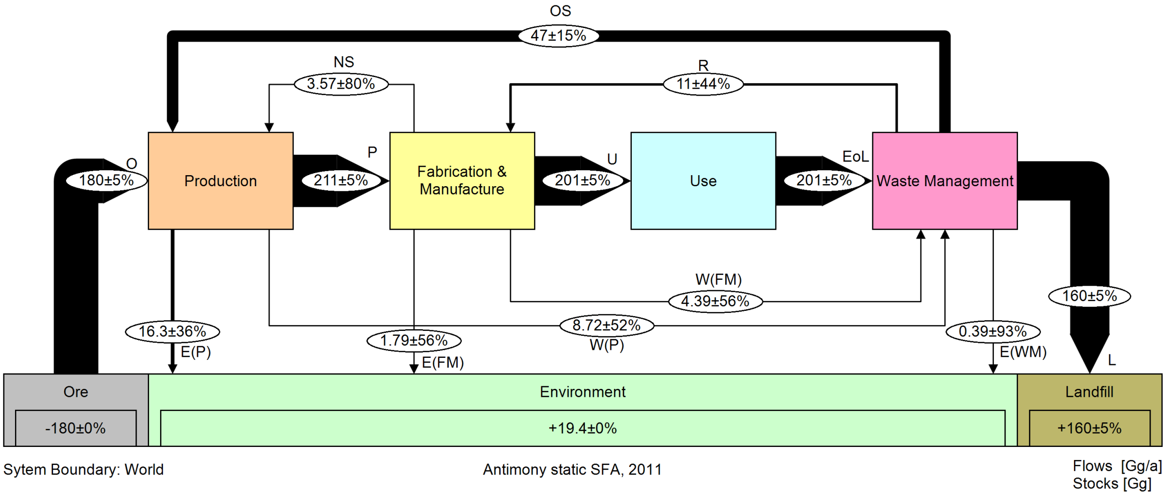


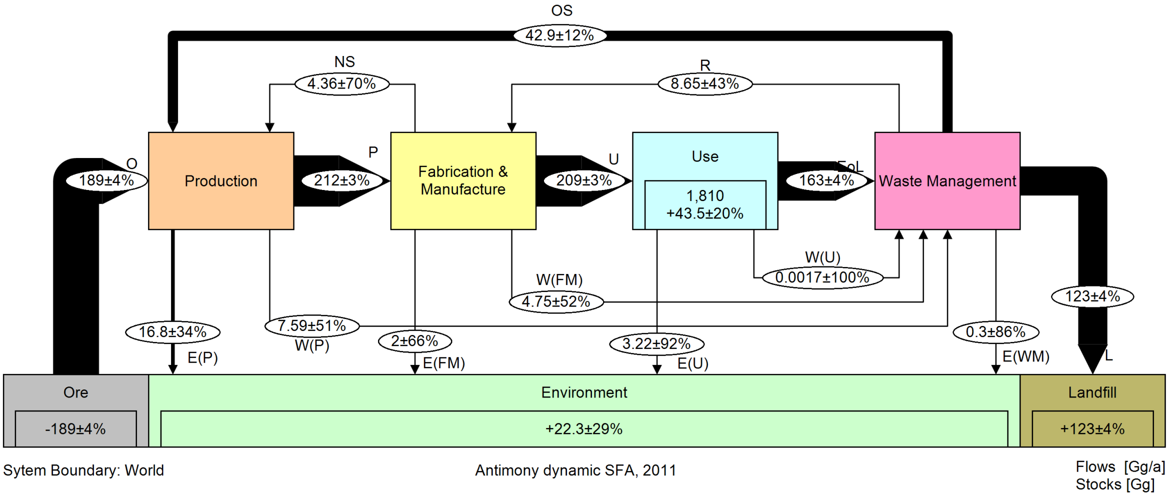
APPENDIX C: DYNAMIC MODEL

Relational data model (Excel)

Retrospective MFA

Comparison results static MFA (steady-state Use phase) and dynamic MFA (delay, leaching, and dissipation at the Use phase) for 2011





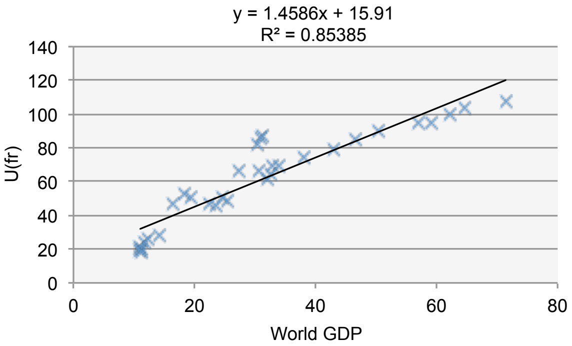
Main differences:

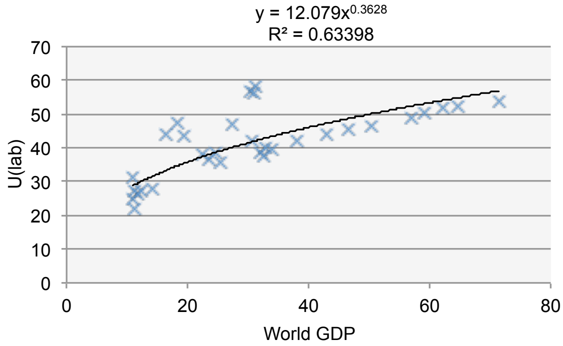
- End-of-life flows are smaller in the second system (delay model), resulting in smaller recycling and landfilling flows;
- Total emissions are higher in the second system, due to emissions from Use (dissipation and leaching);
- Ore extraction is higher in second system (lower secondary production due to lower end-of-life flows).

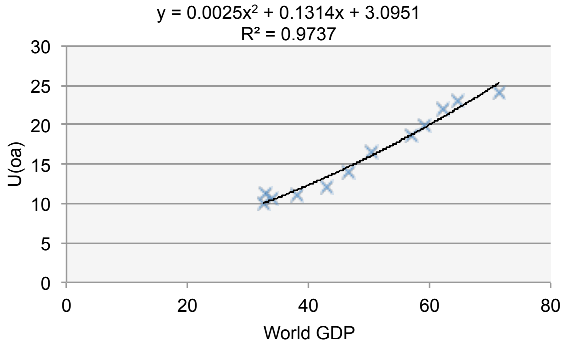
Prospective MFA

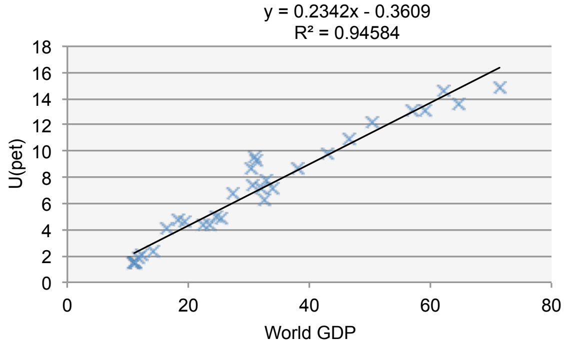
Regression analysis used for the "Business-as-Usual" scenario

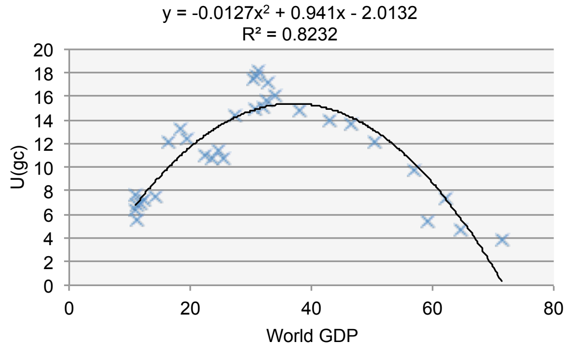
Annual Gross World Product (in 2014 US dollars) was plotted against estimated yearly Sb demand (in Gg) for the period 1980-2011. Parameters of best fitting curves were then used to extrapolate future inflows based on GWP projections.

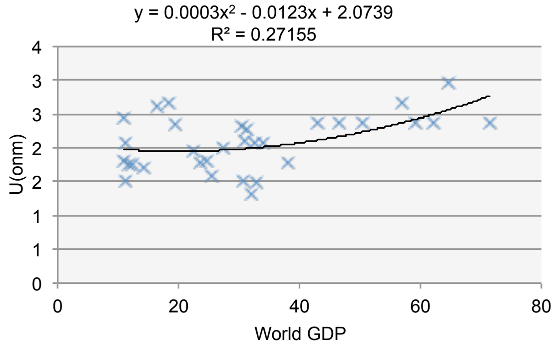












Observations:

- Very strong (linear) correlation with GDP for Sb demand in flame retardants (R^2=0.85) and in PET (R^2=0.95);
- Very strong (polynomial) correlation with GDP for Sb demand in other alloys (R^2=0.97);
- Very strong (polynomial) correlation with GDP for Sb demand in glass & ceramics (R^2=0.82);
- Strong (logistic) correlation with GDP for Sb demand in lead-acid batteries (R^2=0.63);
- Weak (polynomial) correlation with GDP for Sb demand in other non-metallic products.

Appendix D: Life Cycle Inventories

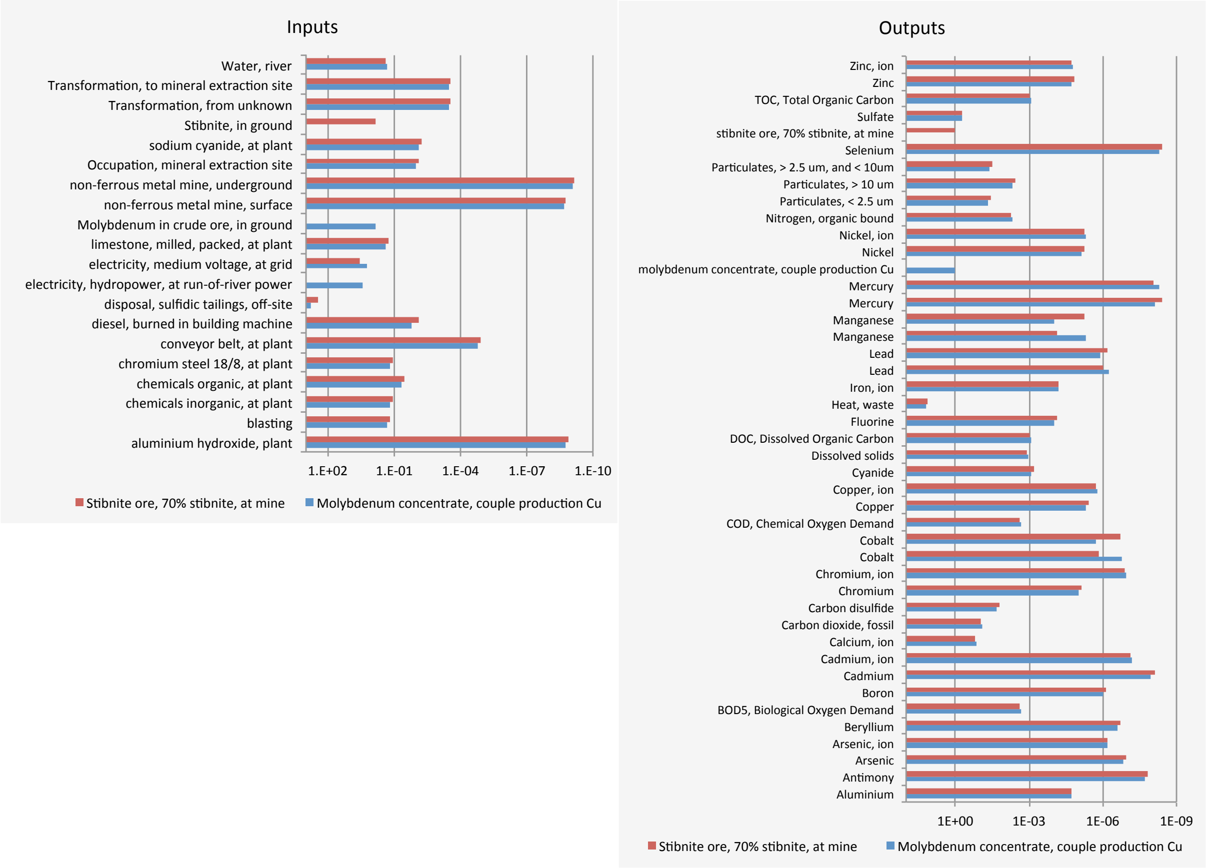
Mining and concentration

Database: ecoinvent v2.1 (Classen and colleagues 2009)

Process name: stibnite ore, 70% stibnite, at mine

Explanations	Name	Location	Infrastructure-Process	Unit	stibnite ore, 70% stibnite, at mine
	Location				CN
	InfrastructureProcess				0
	Unit				kg
Technosphere	electricity, medium voltage, at grid	CN	0	kWh	3.98E+0
	limestone, milled, packed, at plant	CH	0	kg	1.98E-1
	electricity, hydropower, at run-of-river power plant	RER	0	kWh	0
	blasting	RER	0	kg	1.57E-1
	diesel, burned in building machine	GLO	0	MJ	7.94E-3
	chromium steel 18/8, at plant	RER	0	kg	1.17E-1
	chemicals inorganic, at plant	GLO	0	kg	1.21E-1
	sodium cyanide, at plant	RER	0	kg	5.49E-3
	chemicals organic, at plant	GLO	0	kg	3.54E-2
	conveyor belt, at plant	RER	1	m	1.19E-5
	aluminium hydroxide, plant	RER	1	unit	1.32E-9
	non-ferrous metal mine, surface	GLO	1	unit	1.73E-9
	non-ferrous metal mine, underground	GLO	1	unit	7.53E-10
	disposal, sulfidic tailings, off-site	GLO	0	kg	2.70E+2
resource, in water	Water, river			m3	2.32E-1
resource, land	Occupation, mineral extraction site			m2a	8.18E-3
	Transformation, to mineral extraction site			m2	2.73E-4
	Transformation, from unknown			m2	2.73E-4
resource, in ground	Stibnite, in ground			kg	7.00E-1
air, low population density	Antimony			kg	1.44E-8
	Arsenic			kg	1.09E-7
	Cadmium			kg	7.94E-9
	Carbon dioxide, fossil			kg	8.70E-2
	Chromium			kg	7.24E-6
	Copper			kg	3.61E-6
	Heat, waste			MJ	1.43E+1
	Lead			kg	1.01E-6
	Manganese			kg	6.89E-5
	Mercury			kg	3.61E-9
	Nickel			kg	5.78E-6
	Particulates, < 2.5 um			kg	3.67E-2
	Particulates, > 10 um			kg	3.55E-3
	Particulates, > 2.5 um, and < 10um			kg	3.19E-2
	Selenium			kg	3.61E-9
	Zinc			kg	1.37E-5
	Fluorine			kg	6.89E-5
	Cobalt			kg	1.44E-6
	Carbon disulfide			kg	1.57E-2
	Boron			kg	7.24E-7
	Beryllium			kg	1.88E-7
water, river	Arsenic, ion			kg	6.83E-7
	Cadmium, ion			kg	7.36E-8
	Chromium, ion			kg	1.27E-7
	Copper, ion			kg	1.83E-6
	Lead			kg	6.48E-7
	Mercury			kg	8.76E-9
	Nickel, ion			kg	5.65E-6
	Zinc, ion			kg	1.76E-5
	Aluminum			kg	2.00E-5
	BOD5, Biological Oxygen Demand			kg	2.42E-3
	Calcium, ion			kg	1.59E-1
	Cobalt			kg	1.81E-7
	COD, Chemical Oxygen Demand			kg	2.42E-3
	Cyanide			kg	6.07E-4
	DOC, Dissolved Organic Carbon			kg	9.46E-4
	Iron, ion			kg	6.72E-5
	Manganese			kg	5.72E-6
	Nitrogen, organic bound			kg	5.28E-3
	Dissolved solids			kg	1.20E-3
	Sulfate			kg	5.47E-1
	TOC, Total Organic Carbon			kg	9.46E-4
Outputs	stibnite ore, 70% stibnite, at mine	CN	0	kg	1.00E+0

Comparison with dataset "molybdenum concentrate, couple production Cu" (logarithmic scale)



Extraction and Refining

Database: ecoinvent v2.1 (Classen and colleagues 2009)

Process name: antimony, at refinery

Explanations	Name	Location	Infrastructure-Process	Unit	antimony, at refinery
	Location				CN
	InfrastructureProcess				0
	Unit				kg
Technosphere	electricity, medium voltage, at grid	CN	0	kWh	1.53E-1
	limestone, milled, packed, at plant	CH	0	kg	6.47E-1
	disposal, lead smelter slag, 0% water, to residual material landfill	GLO	0	kg	4.10E-1
	hard coal, burned in industrial furnace 1-10MW	RER	0	MJ	6.74E+0
	heavy fuel oil, burned in industrial furnace 1MW, non-modulating	RER	0	MJ	2.75E-1
	iron ore, 65% Fe, at beneficiation	GLO	0	kg	6.15E-2
	stibnite ore, 70% stibnite, at mine	CN	0	kg	1.79E+0
	natural gas, burned in industrial furnace >100kW	RER	0	MJ	5.58E-1
	nitrogen, liquid, at plant	RER	0	kg	2.00E-2
	oxygen, liquid, at plant	RER	0	kg	2.03E-1
	silica sand, at plant	DE	0	kg	6.08E-1
	transport, freight, rail	RER	0	tkm	5.28E+0
	transport, lorry >16t, fleet average	RER	0	tkm	9.31E-1
	resource correction, PbZn, silver, negative	GLO	0	kg	0
	resource correction, PbZn, lead, positive	GLO	0	kg	0
air, unspecified	Carbon dioxide, fossil			kg	2.85E-1
air, low population density	Antimony			kg	2.19E-6
	Arsenic			kg	3.92E-6
	Cadmium			kg	3.15E-6
	Lead			kg	3.02E-4
	Mercury			kg	8.04E-8
	Particulates, < 2.5 um			kg	1.60E-4
	Particulates, > 10 um			kg	4.57E-5
	Particulates, > 2.5 um, and < 10um			kg	1.14E-4
	Sulfur dioxide			kg	3.19E-2
	Dioxins, measured as 2,3,7,8-tetrachlorodibenzo-p-dioxin			kg	4.84E-11
water, river	Arsenic, ion			kg	9.67E-7
	Cadmium, ion			kg	2.51E-6
	Copper, ion			kg	4.84E-6
	Lead			kg	1.74E-5
	Mercury			kg	4.16E-8
	BOD5, Biological Oxygen Demand			kg	3.76E-4
	COD, Chemical Oxygen Demand			kg	5.64E-4
	DOC, Dissolved Organic Carbon			kg	2.20E-4
	TOC, Total Organic Carbon			kg	2.20E-4
	antimony, at refinery	CN	0	kg	1.00E+0