

Anthropogenic Cycles of Arsenic in Mainland China: 1990–2010

Ya-Lan Shi,^{†,‡} Wei-Qiang Chen,^{*,‡,§} Shi-Liang Wu,^{§,||} and Yong-Guan Zhu[‡]

[†]College of Tourism, Huaqiao University, Quanzhou, Fujian 362021, China

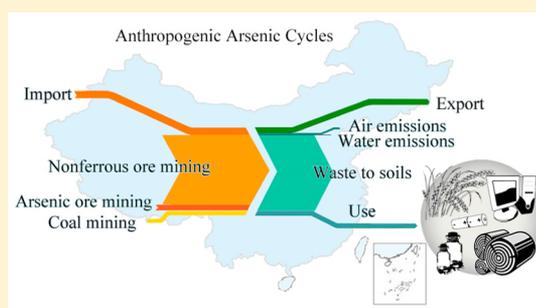
[‡]Key Lab of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, Fujian 361021, China

[§]Department of Geological and Mining Engineering and Sciences, Michigan Technological University, Houghton, Michigan 49931, United States

^{||}Department of Civil and Environmental Engineering, Michigan Technological University, Houghton, Michigan 49931, United States

Supporting Information

ABSTRACT: Arsenic (As) is a trace element in the global environment with toxicity to both humans and ecosystem. This study characterizes China's historical anthropogenic arsenic cycles (AACs) from 1990 to 2010. Key findings include the following: (1) the scale of China's AACs grew significantly during the studied period, making China the biggest miner, producer, and user of arsenic today; (2) the majority of arsenic flows into China's anthroposphere are the impurity of domestically mined nonferrous metal ores, which far exceeds domestic intentional demands; (3) China has been a net exporter of arsenic trioxide and arsenic metalloid, thus suffering from the environmental burdens of producing arsenic products for other economies; (4) the growth of arsenic use in China is driven by simultaneous increases in many applications including glass making, wood preservatives, batteries, semiconductors, and alloys, implying the challenge for regulating arsenic uses in multiple applications/industries at the same time; (5) the dissipative arsenic emissions resulting from intentional applications are at the same order of magnitude as atmospheric emissions from coal combustion, and their threats to human and ecosystem health can spread widely and last years to decades. Our results demonstrate that the characterization of AACs is indispensable for developing a complete arsenic emission inventory.



1. INTRODUCTION

Arsenic (As) is a trace element with toxicity to both human and ecosystem.^{1,2} There have been many arsenic poisoning episodes and millions of people are at risk of arsenic-induced diseases.^{1,3} Besides geogenic sources, the contamination of air, water, soil, food, and beverage by arsenic resulting from anthropogenic sources are now getting more and more concerns, and the characterization of anthropogenic arsenic cycles (AACs) can help to identify the sources and pathways of anthropogenic arsenic pollutions.^{4,5}

The anthropogenic cycle of an element refers to the stocks and flows of the element within a given anthropogenic system plus its exchange flows between the given system and other anthropogenic or natural systems.⁶ Anthropogenic elemental cycles result from both intentional and unintentional uses of the element.^{5,7} Intentional uses refer to the applications of the element itself that provide services for human society; and the cycles driven by intentional uses usually form stage-by-stage life cycles (e.g., the four-stage life cycle of iron⁸). Unintentional uses refer to the applications of other elements or resources in which the concerned element is just an unavoidable impurity; and those cycles driven by unintentional uses usually take place in separate and independent processes (e.g., mercury emissions occurring in cement production and copper smelting⁹). The

systemic and quantitative studies on anthropogenic cycles are very helpful for the sustainable management of materials in various aspects, such as promoting secure supply and improving use efficiencies of valuable materials and resources, as well as reducing losses and emissions of those that are harmful for the environment.

Like many other elements, the anthropogenic cycles of arsenic are driven by both intentional uses and unintentional uses. There have been some studies on air emissions of arsenic driven by unintentional uses.^{10–13} However, little has been done in characterizing historical AACs driven by intentional uses, except a few publications that provide one-year snapshots and that are either outdated¹⁴ or just for an island.¹⁵ In order to fill in this gap, we proposed an AACs framework at the national level that divides arsenic cycles into two parts, one part resulting from intentional uses and the other driven by unintentional uses, in a relevant study.⁵ This AACs framework is well constructed based on material flow analysis and emission

Received: September 4, 2016

Revised: December 30, 2016

Accepted: January 2, 2017

Published: January 2, 2017

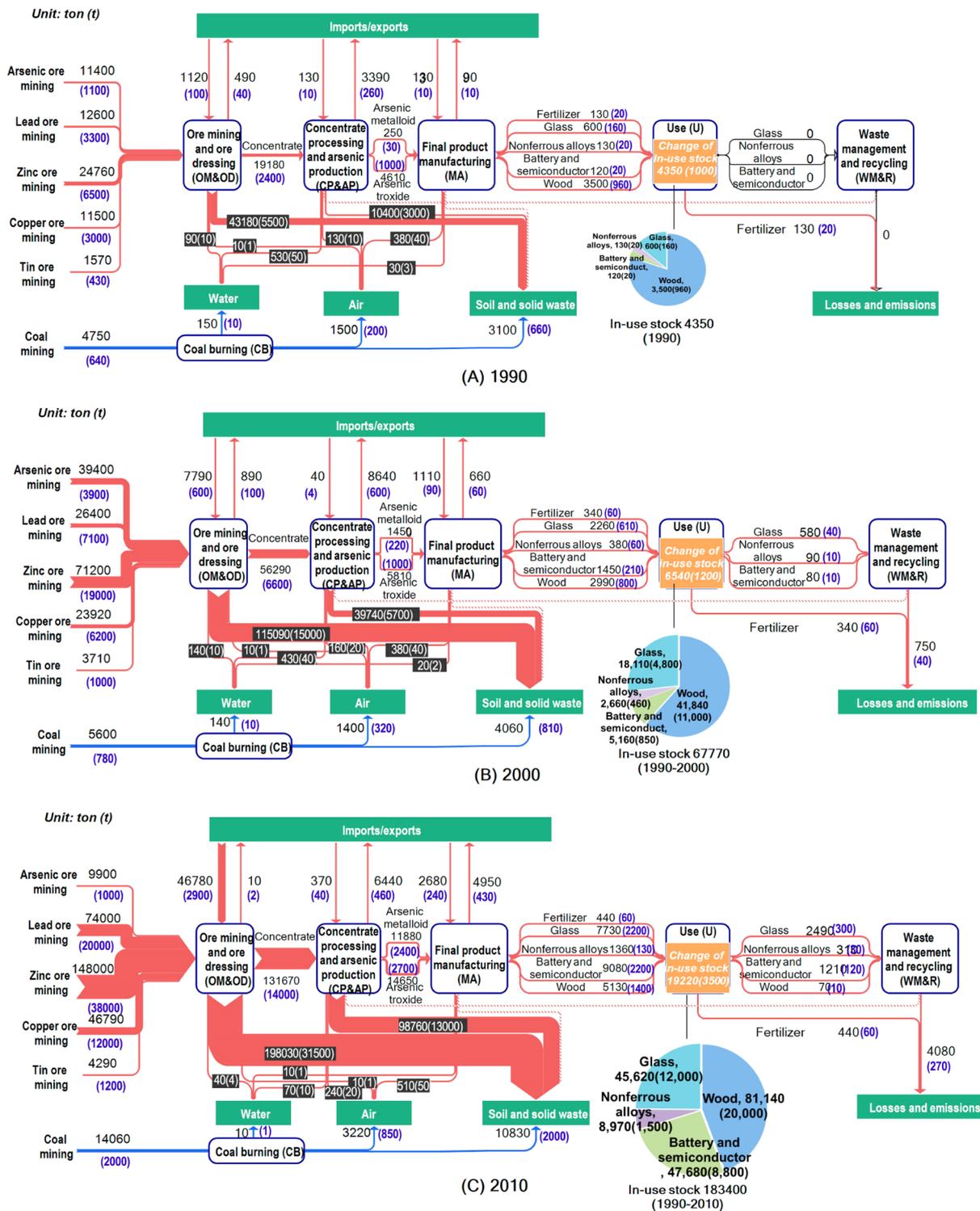


Figure 1. Anthropogenic arsenic cycles related to intentional uses in China for 1990, 2000, and 2010. The water and air losses were obtained from official statistics;^{25,27} while other flows and stocks were calculated by this study. The values are expressed as mean value (standard deviation). Please note that although some values have 3 or more significant digits, they are showed here mainly for the convenience of illustration and for keeping mass balance. In most cases, these values are reliable enough only when rounded to 1 or 2 significant digits.

inventory analysis, forming an improved conceptual model of national arsenic cycles.

With the major use of arsenic gradually banned in most developed countries, especially Europe, Japan, and the United States,^{16,17} the role of developing countries in global arsenic production and consumption are becoming more and more

important. China is currently the biggest producer of arsenic trioxide and other arsenic containing compounds, with its global share growing dramatically from less than 20% in 1990 to almost 65% in 2003 and remaining stable at about 50% after 2005 (Figure S2 in the Supporting Information (SI-1)). Although it is reported that a significant share of China's

arsenic production has been exported to other economies such as the United States,¹⁸ its position as the biggest producer indicates that China is now playing an important role in the global AACs. Therefore, this study applies the AACs framework to provide a historical analysis of arsenic stocks and flows in China's anthroposphere from 1990 to 2010, aiming at quantifying how much arsenic has entered, left, passed through, and ultimately accumulated in China's anthroposphere during this period. AACs driven by the mining and combustion of coals (which is an unintentional arsenic use) are also taken into account because coals contribute a significant amount of atmospheric arsenic emissions in China.

2. MATERIALS AND METHODS

2.1. System Definition. AACs at the national level comprise two parts (Figure 1): (1) the part that is related to intentional uses (such as the use of arsenic for producing pesticides or wood preservatives); and (2) the other that results from unintentional uses (such as coal mining and burning). Both parts of AACs begin with the mining of arsenic-containing natural resources (ores or fuels) from lithosphere and/or biosphere, and result in the transfer of arsenic from anthroposphere to air, water, or soil.

2.1.1. AACs Related to Intentional Uses. A major focus of this study is to examine the AACs driven by intentional uses with the stage-by-stage cycle analysis, which allows us to better keep track of the material stocks and flows, and to apply mass conservation in deriving missing information based on available data. The Stocks and Flows Analysis framework developed by the Yale Center for Industrial Ecology¹⁹ is applied to simulate the whole AACs related to intentional uses (SI-1 Figure S1), which consist of the following processes: (1) Mining of both arsenic ores and other metal ores containing arsenic. The majority of arsenic is mined as a byproduct of nonferrous metal ores (e.g., copper and lead ores). China owns the majority of global arsenic reserves and it is the only country that excavates ores in which arsenic, rather than other metals, is the main targeted material and also known as the host metal. (2) Dressing of ores to produce concentrates. Nonferrous metal ores containing arsenic have to be dressed to produce concentrates, and it is in this process that the majority of arsenic coexcavated with nonferrous metal ores is removed from ores and then is deposited in tailings.¹⁶ (3) Processing of arsenic and other metal concentrates. Nonferrous metal concentrates are then dearsenified so that the metal industry can reduce production cost, improve product purity, and avoid environmental hazards. After this dearsenifying pretreatment, arsenic may end up in flue dusts, emitted gases, slag, slurry, wastewater, and metal products (e.g., copper matte or crude lead). (4) Production of arsenic trioxide. Part of the flue dust and slurry is used as raw materials for producing arsenic trioxide. Arsenic trioxide plays a key role in forming the life cycle of AACs by linking arsenical ores to the intentional uses of arsenic-containing products. (5) Production of arsenic metalloid and arsenic compounds. Arsenic trioxide is not only directly used in some applications, but also the precursor to arsenic metalloid and other various arsenic compounds that are intentionally used. Arsenic metalloid can be divided into commercial-grade and high-purity arsenic, while arsenic compounds can be categorized into inorganic compounds, organic compounds, and arsine gas. (6) Manufacture of various arsenic-containing final products. There are five end-use sectors of intentionally used arsenic according to the U.S. Geological

Survey:^{14,20} agricultural chemicals, glass making, alloys, and electronics, wood preservatives, and other. Note that we classify arsenic end-use sectors in a way that is a little different from that of the U.S. Geological Survey^{13,20} by distinguishing batteries, semiconductors, and alloys. (7) Use of the final products. It is only for the alloys and electronics that arsenic is used in the metallic form, and the commercial-grade is primarily used for the production of alloys while the high-purity arsenic is used for electronics. The use of arsenic as agricultural chemicals is dissipative, meaning that the losses or emissions of arsenic immediately occur when it is put into use in this application. For other applications such as wood preservatives, the retention time of arsenic in the use stage reach years or decades; therefore arsenic is accumulated in the anthroposphere to form in-use stocks. (8) End-of-life management and recycling of arsenic. Due to its low price and toxicity, the recycling of arsenic from end-of-life arsenic-containing products is very rare, thus the major aim of arsenic management in the end-of-life stage is stabilization and subsequent disposal.¹⁶

A detailed description of the AACs related to intentional uses has been provided in a relevant study.⁵ Note that for the convenience of quantitative material flow analysis, some adjacent processes are combined together in this study, therefore only five processes are shown in the upper part of Figure 1: (1) ore mining and ore dressing (OM&OD), (2) concentrate processing and arsenic production (CP&AP), (3) final product manufacturing (MA), (4) use of final products (Use), and (5) waste management and recycling of arsenic (WM&R).

For an anthropogenic system at the national level, trade of arsenic in different forms occurs between the studied system and other systems. Losses of arsenic from anthroposphere to the environment take place along its life cycle, and can be classified into two types: the deposited loss and the dissipative loss.^{5,21} The deposited losses refer to the losses mainly to soil or water in mining residues, tailing ponds, slag ponds, or landfills. The dissipative losses refer to the losses to the atmosphere and hydrosphere, which will be widely dispersed in the environment and can be regarded as emissions.

2.1.2. AACs Resulting from Coal Use. Besides metal ores, arsenic can be extracted from lithosphere together with fossil fuels, such as coal and oil. During the burning of coals, the contained arsenic is distributed into bottom ash, fly ash, and fuel gas. Part of arsenic is directly volatilized into atmosphere in the gas phase because arsenic is volatile, and part of arsenic tends to concentrate in fine particles.²² Therefore, coal burning is one of the most significant unintentional processes resulting in atmospheric emissions of arsenic, especially in China where the annual use of coals reaches up to 4 billion metric tons, which accounts for nearly half of global coal use.^{23–26}

2.2. Data Compilation and Analysis. The quantitative characterization of AACs is done by analyzing the arsenic flows and stocks, which are indicated in weight of arsenic in pure form per year in the period 1990–2010. Details on identifying and calculating the stocks and flows, as well as the data collection and compilation are described in the sections S1-2 of the SI-1. The flows of each process in the stage-by-stage cycle include the input from the previous process, the output to the next process, the trade with other anthropogenic systems, and the loss to domestic environment (Figure S1 in the SI-1). According to the mass conservation rule, the total input of each process equals to its total output plus the net addition to the stock in this process.

Table 1 classifies all concerned flows and stocks into four groups. (1) The trade flows. A list of traded products is

Table 1. Four Ways for Estimating Flows and Stocks

ways	types			
	statistical data	direct calculation	modeling	mass conservation
trade flows		×		×
loss flows	×	×		×
transformation flows		×	×	×
in-use stocks			×	×

identified according to the life cycle framework of arsenic and are coded by the Harmonized Commodity Description and Coding System (HS).²⁶ Most of the trade flows are directly calculated by multiplying the mass of traded products containing arsenic (from United Nations Comtrade database²³) by their average arsenic concentrations (Table S2). (2) The loss/emission flows. Atmospheric and aquatic emissions from OM&OD, CP&AP, MA, and WM&R stages are directly obtained from official statistics;^{25,27} and the losses to soil and solid wastes in OM&OD and CP&AP stages are calculated based on mass conservation (Table S3), with the loss to soil from MA stage not distinguished due to the lack of data. In addition, the atmospheric emissions of arsenic from coal consumption are calculated based on information including China's total coal consumption,²⁸ the arsenic content of coal, the release rate, and the removal rate of arsenic (detailed parameters in Table S6 and Table S7). (3) The transformation flows that include arsenic from natural ores through to arsenic trioxide, metalloid, various intentionally used compounds, final products, and end-of-life discards. The quantification of transformation flows mostly relies on the direct calculation method that multiplies arsenic product flows by arsenic concentrations. Statistical data on arsenic product flows are collected and used in this study (e.g., data on the mining of arsenic ore and nonferrous metal ores are from the *China National Land and Resources Statistical Yearbook*²⁹ and *Minerals Reserves Tables*,³⁰ the arsenic trioxide production data are from U.S. Geological Survey,¹⁸ and data for the production of final products are from the *China Statistical Yearbook*³¹), while the arsenic concentration data are from existing studies or reports (Table S4 and Table S5). (4) In-use stocks. At a given time (year), the annual change in in-use stock is derived as the balance of input and output flows, and the in-use stock is deduced by accumulating its annual change from the initial year, 1990, to the given year.

As summarized in Table 1, four different ways are used to quantify the flows and stocks based on their specific types: (1) Using statistical data, for example, some atmospheric and aquatic emissions of arsenic are directly obtained from official statistics compiled in the Chinese Environmentally Extended Input-Output (CEEIO) database.^{25,27} (2) Direct calculation, for example, some trade flows are calculated by multiplying trade of arsenic-containing products by their average arsenic concentrations; (3) Modeling, for example, the end-of-life arsenic flows from in-use stocks are calculated by the lifespan modeling method that is based on input flows and lifespan parameters;^{5,32,33} and (4) Mass conservation, for example, the annual change of in-use stock is calculated as the difference between input flows and end-of-life flows. More details on data

compilation, modeling and analysis are available in the SI-1 and SI-2.

2.3. Uncertainty Analysis. Monte Carlo simulation (10⁴ iterations) is performed to estimate uncertainties of flows. Most of the activity data are assumed to have a uniform coefficient of variation (CV: expressed as the standard deviation divided by the mean) that is 10%, and technical parameters are assumed to have a CV ranging from the lowest 5% to the highest 25% according to their max and min values, assumptions, uncertainties, and range. A beta distribution is used for some parameters with value between 0 and 1; a triangular distribution is used for the parameters with the max, min and most possible values (e.g., the release and removal rates of arsenic during coal burning); and a normal distribution is used for the activity data and other parameters with mean value and standard deviation.¹² Uncertainties and distributions of all variables are summarized in Table S8. As a result, the values and uncertainties in this study are expressed as the mean \pm standard deviation in the main text and Figure 1, Figure S4, and Table S9; whereas other figures only show the mean values for the convenience of visualization.

3. RESULTS

The majority of arsenic (79% by weight in 2010) entered China's anthroposphere as an impurity of domestically mined nonferrous metal ores. Arsenic ores mining, coal mining, and the import of nonferrous metal concentrates were also significant sources for arsenic input to China's anthroposphere (about 3%, 4%, and 14% by weight, respectively, in 2010). The import of arsenic metalloid, arsenic trioxide, and final products only brought a small percentage (less than 1% of the total arsenic input by weight in 2010). The majority (91% by weight in 2010) of all these arsenic inputs exited China's anthroposphere and got back to the environment by depositing in the tailing or releasing to the atmosphere and aquatic system. Ore dressing and dearsenifying processes were the most important pathways that arsenic exited China's anthroposphere (about 57% and 29% of total arsenic input by weight, respectively, in 2010). Only a small percentage (6% by weight in 2010) of total arsenic input to China's anthroposphere was used to produce arsenic trioxide and other intentionally used arsenic products, which may then be accumulated in China's anthroposphere as in-use stocks. The remaining 3% was exported as arsenic-bearing products to other anthropogenic systems.

The scale of AACs in China grew significantly from 1990 through 2000 to 2010, as indicated by the widths of flows in Figure 1 and Figure S5. Specifically, the amount of arsenic combined with nonferrous metal concentrates (Figure 2), the trade of arsenic contained in imported metal ores (Figure 3 (a), (b)), the amount of intentionally used arsenic (Figure 4 (a)), and the losses of arsenic back to the environment (Figure 5) grew by over 4, 73, 4, and 4 times from 1990 to 2010, respectively. This growing pattern is similar to that of other metals such as iron³⁴ and aluminum,³⁵ and is mainly driven by the growth of China's economy during this period.

China's domestic mining of arsenic increased from about 67 000 \pm 10 000 t in 1990 to about 300 000 \pm 57 000 t in 2010 (Figure 2). More than 95% of mined arsenic was extracted from China's lithosphere together with nonferrous metal ores and coals in 2010. The mining of zinc, lead, copper, and coal ores contributed 50%, 25%, 16%, and 5% of total arsenic mining in China in 2010, respectively. (Note, however, that arsenic is also combined with gold, tungsten, silver, sulfur, antimony, mercury,

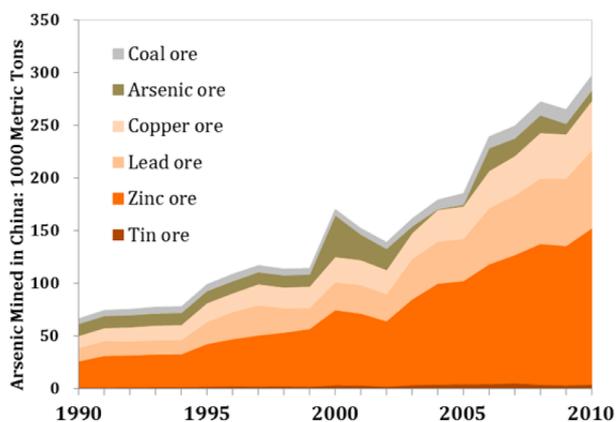


Figure 2. China’s domestic mining of arsenic from arsenic ores, coals, and nonferrous metal ores.

petroleum, and natural gas, although these flows are much smaller or negligible when compared to those combined with zinc, lead, and copper.) As the only country that was reported to process arsenic directly from arsenic ores, China did excavate arsenic ores in the period of 1990–2010, with the amount of mined arsenic ores staying relatively stable in this period at around 10 000 t per year.

China was a net importer of arsenic in the forms of ores and concentrates, and a net exporter of arsenic in the forms of metalloid and oxides from 1990 to 2010 (Figure 3). With all arsenic-containing products accounted for, China had an increasing net export of arsenic before 1994 and a decreasing net export of arsenic from 1995, and then it became a net importer of arsenic from 2004. The import of arsenic raw materials was mainly contained in the imported lead, zinc, and copper ores and concentrates, and increased from 1990 to

2010, especially after 2001 when China became a member of the World Trade Organization. The export of arsenic occurred mainly in the form of arsenic trioxide and metalloid, with the export of arsenic trioxide peaking around 2002. More than 50% of both arsenic trioxide and arsenic metalloid produced in China before 2005 were exported to other regions, but domestic uses have grown quickly after 2005 (only 24% of arsenic trioxide and 14% of arsenic metalloid were exported in 2010, Figure S11). As a fast-growing global manufacturing enter, China had an increasing net export of arsenic contained in several manufactured products including glass (from 1990 to 2010), batteries (after 1997) and semiconductors (after 2008); however, due to its shortage in many raw minerals, including copper, lead, zinc, tin, and wood resources,^{36,37} China had a net import of arsenic contained in nonferrous metal alloys and wood products in the same period.

China’s domestic intentional use of arsenic trioxide and metalloid increased from about 4600 ± 1000 and 250 ± 30 t in 1990 to about $14\,600 \pm 2700$ and $11\,900 \pm 2400$ t in 2010, respectively (Figure 1 and SI-1 Figure S12). The majority of these intentional arsenic uses were in the form of arsenic compounds, however, the percentage of metallic use increased from about 5% in 1990 to 45% in 2010 (Figure S12). With the adjustment of final products’ trade, the flows of intentionally used arsenic entering in-use stocks in China stayed stable and were dominated by the use in wood products from 1990 to 2001 (Figure 4 (a)). These flows then grew sharply from about 7700 ± 1000 t in 2001 to about $24\,000 \pm 3300$ t in 2010, because of the increasing use in glass, nonferrous alloys, batteries and semiconductors. The growth of flows entering use resulted in the growth of flows leaving in-use stocks (Figure 4 (b)), mainly in the form of end-of-life glass and the dissipative use of agricultural applications. Because the retention time of

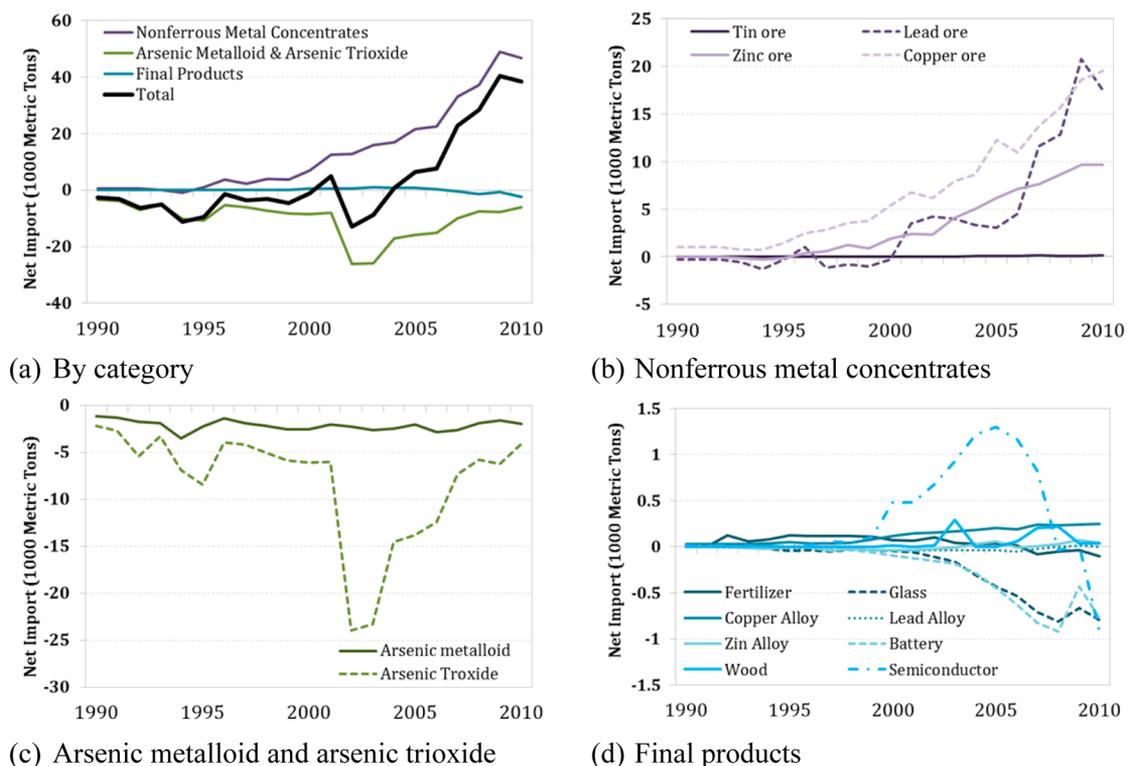


Figure 3. China’s net import of arsenic in different forms, 1990–2010. Unit: 1000 t of arsenic.

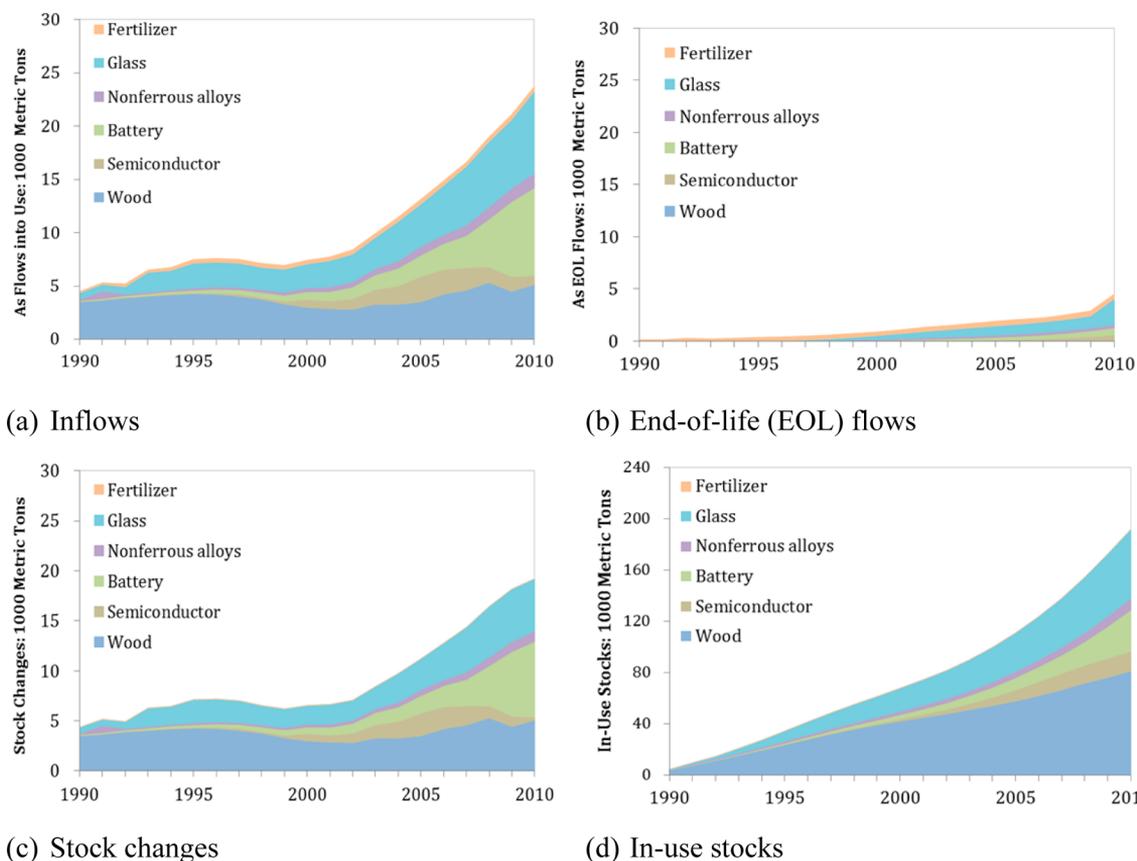


Figure 4. Arsenic in-use stocks and their inflows, outflows, and changes in China, 1990–2010. Unit: 1000 t of arsenic.

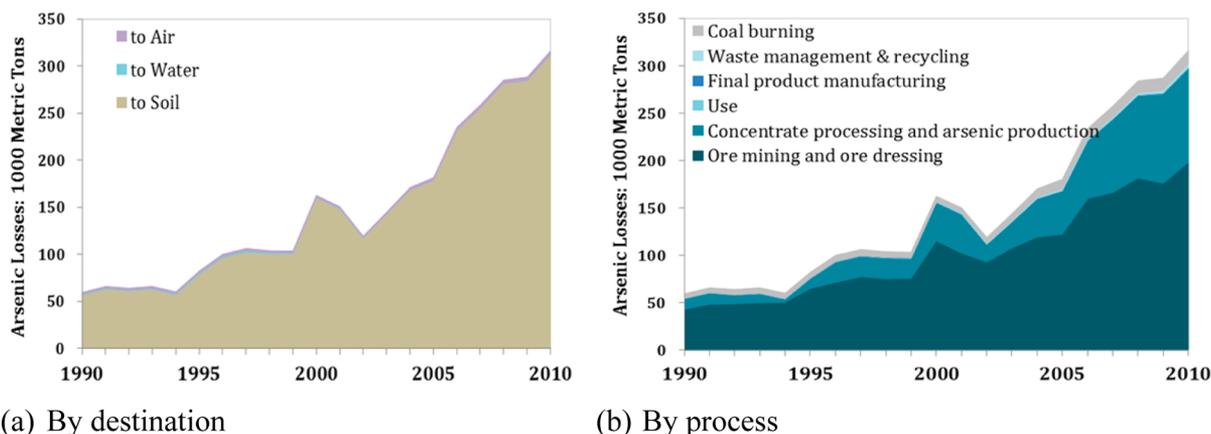


Figure 5. China's anthropogenic arsenic losses to the environment (a) by destination and (b) by process, 1990–2010.

most arsenic uses is more than one year (some may reach up to several decades), the majority of arsenic flows entering use were accumulated in its in-use stocks (Figure 4 (c)), which increased by 40 times, from about 4400 ± 1000 t in 1990 to $183\,000 \pm 27\,000$ t in 2010 (Figure 4 (d)). In 2010, wood products, glass, nonferrous alloys, batteries and semiconductors accounted for 44%, 25%, 5%, and 26% of arsenic in-use stocks in China, respectively.

The losses of arsenic from China's anthroposphere to natural environment grew from about $60\,000 \pm 7400$ t in 1990 to more than $320\,000 \pm 42\,000$ t in 2010 (Figure 5). The destination of the dominant majority (about 98.7% in 2010) of these losses was soil; only about 1.25% was directly dissipated into the atmosphere and only less than 0.05% was directly emitted into

the hydrosphere (Figure 5(a)) in 2010. More than half (e.g., 73% in 1990 and 63% in 2010) of arsenic losses occurred in the process of ores dressing. Other significant processes of arsenic losses included the processing of arsenic-containing nonferrous metal concentrates plus the production of arsenic trioxide and metalloid (accounting for about 18% of total arsenic losses in 1990 and 31% in 2010), as well as the coal burning process (about 5% of the total arsenic loss in 2010). The losses from the processes of Use and WM&R, which completely resulted from intentional uses, only accounted for about 1% of total arsenic loss in 2010.

4. DISCUSSION

Our results demonstrate that China has not only become the biggest miner of arsenic-containing ores, but also remained the biggest producer of arsenic trioxide (which is directly used and is the precursor to almost all intentionally used arsenic products) since the mid 1990s. It has replaced the United States to be the biggest user of arsenic trioxide since early 2000s (Figure S2). Mainly mined as a companion material of copper, lead, tin, and zinc,³⁸ there is no supply shortage of arsenic in mainland China. In contrast, the demand for arsenic is much less than the amount of arsenic comined with nonferrous metal ores, which results in the problems of arsenic oversupply and challenges of dealing with arsenic-containing byproducts, tailings, slag, flue dust, and wastewater. The oversupply also leads to the low market price of arsenic, making it uneconomical to recycle arsenic at the end-of-life stage and the lack of economic incentive to develop arsenic recycling technologies.^{16,38}

China's growing domestic use of arsenic since the 2000s was mainly driven by the growing manufacture of batteries and semiconductors, glass making, and alloys (Figure 4 (a)). Compared to the historical waves of rise and fall in arsenic use in the United States,⁵ of which the rises were successively driven by the growing demand in glass making (1900s), agricultural applications (1920s), and wood preservatives (1970s), respectively, and the falls were mainly driven by the environmental regulations, it seems China is now seeing a rise of arsenic use simultaneously driven by all applications. Thus, unlike the United States that had quite a long period for regulating arsenic use, China is facing the challenge of regulating arsenic uses in many applications at the same time in just a short period. Recently, China's Ministry of Environmental Protection released a *Technological Policy on Arsenic Pollution Prevention and Treatment*³⁹ that aims at restricting arsenic use or promoting alternative materials and technologies in agricultural applications, glass making, and wood preservatives. However, it is still uncertain whether these regulations will result in the fall of arsenic use in China in the coming years or not.

Similar to several other metals including iron,³⁴ aluminum,³⁵ and nickel,⁴⁰ China's anthropogenic cycles of arsenic in the studied 1990–2010 period has two features: (1) the scale of almost all flows grew significantly, which corresponds to and probably results from the simultaneous growth of China's economy; and (2) China was a net importer of natural ores but a net exporter of primary products such as unwrought aluminum ingot,³⁵ arsenic metalloid, and arsenic trioxide. China's net export of arsenic products, similar to many other low value-added but energy and/or emissions intensive primary products, implies that China suffers from the environmental burdens embodied in its export to other economies. Our results demonstrate that about half of the production of arsenic metalloid and trioxide, as well as their associated emissions, were driven by the export during 1990–2010. Especially, the United States significantly relied on China in importing arsenic metalloid (about 85%) and arsenic trioxide (about 50%) during this period (Figure S3), meaning that the United States transferred more than half of the environmental burdens of producing primary arsenic products to China. In fact, Chinese central government had realized this situation and therefore took some measures to optimize its trade composition after 2004, such as restricting the export of so-called *Energy,*

Emissions, and Resources Intensive products, which include some arsenic-containing products.⁴¹

The mismatch between the intentional use and unintentional mining of arsenic results in a challenge that the majority of arsenic entering China's anthroposphere is released back into the environment in the same year it is mined, and these flows are 2 orders of magnitude higher than the atmospheric arsenic emissions resulting from coal combustion¹² (10^5 vs 10^3 after 2000, Figure 1 and Figure S4). However, note that these flows back to the environment should not be simply regarded as emissions. As we have pointed out in a relevant study,⁵ they are deposited (but not dissipated) losses that mainly go back to soils (Figure 1 and Figure 5) and are deposited in either mining residues, tailing ponds, slag ponds, or landfills. If these deposited losses are not safely dealt with, they may lead to slow and long-term dissipated emissions of arsenic to the soils, water, and air, thus result in significant threats to human and ecosystem health. Yet, because nonferrous metal ores with high arsenic concentration are concentrated in only a small number of provinces including Guangxi, Yunnan, and Hunan,⁵ these deposited losses, as well as the threats to human and ecosystem health they pose, are unevenly distributed in these few provinces too. Unfortunately, currently it seems impossible to stop these unwanted arsenic flows entering and leaving China's anthroposphere, because arsenic is an inevitable impurity in mined nonferrous metal ores, and still China has to produce a large amount of copper, zinc, lead, tin, and other nonferrous metals for its ongoing industrialization and urbanization.

Two significant consequences of the intentional arsenic uses are (1) the formation of arsenic in-use stocks and (2) the dissipated emissions of arsenic. These dissipated arsenic emissions may occur over various time scales, for example, right after arsenic is put into dissipative use (agricultural pesticides or fertilizers), or over a long period in which arsenic is used (leaching from in-use wood products⁴²), and when arsenic is discarded at the end-of-life stage.⁴³ Compared to the unintentional flows of arsenic mining, these arsenic dissipative emissions resulting from intentional uses are 2 orders of magnitude smaller. However, their spatial distribution can be very wide and scattered, the leaching and emissions from in-use stocks are slow and can last several decades, and these emissions can be released into not only atmosphere but also hydrosphere and pedosphere. Therefore, the threats to human and ecosystem health posed by these emissions can be spread more widely and last longer than those posed by the unintentional mining-related flows. To our knowledge, except some small spatial scale analysis of arsenic leaching from wood products^{42–44} or arsenic air emissions,^{10–13} no study has provided a systemic analysis of arsenic emissions into various systems resulting from intentional uses. This research gap may have resulted in the underestimate of arsenic emissions, which is similar to a former situation for mercury.⁴⁵

There are significant uncertainties associated with the values of arsenic flows or stocks, which may result from three sources: (1) the uncertainties associated with the original data, (2) the estimation and modeling methods, and (3) the assumptions on some parameters, especially the assumption that the arsenic concentrations in some final products are assumed to be constant over time. However, the Monte Carlo simulation demonstrates that these uncertainties do not affect the major findings from this study (e.g., the most important pathways for arsenic entering and exiting China's anthroposphere as well as the temporal trends in the past decades, Figure S14).

Therefore, despite several limitations of assumptions and data uncertainties, this study provides some new and valuable findings in characterizing China's anthropogenic arsenic cycles, in understanding the interactions between China and the rest of the world on arsenic demand and supply, and in developing a more accurate arsenic emission inventory resulting from both intentional and unintentional uses. According to these findings, we suggest that Chinese policy makers pay more attention to the ores mining and dressing industries in controlling arsenic losses to soils, reduce or restrict the export of arsenic-containing primary materials, and regulate the use as well as prevent the dissipative emissions of arsenic from some growing applications such as glass, batteries, and semiconductors. We also expect that our approach be applied to more regions, countries, or at the global scale to quantitatively determine arsenic cycles and emissions with higher spatial and temporal resolution, thus help to better regulate arsenic uses and minimize the threats of arsenic to human and ecosystem health resulting from its anthropogenic cycles.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.est.6b01669](https://doi.org/10.1021/acs.est.6b01669).

Details on estimation method, data compilation and complementary figures are listed in SI-1 (PDF)

A database used for this study is provided in SI-2 (XLSX)

■ AUTHOR INFORMATION

Corresponding Author

*Phone/fax: +86-592-6190-763; e-mail: wqchen@iue.ac.cn, wqchen.thu@gmail.com.

ORCID

Wei-Qiang Chen: [0000-0002-7686-2331](https://orcid.org/0000-0002-7686-2331)

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study is sponsored by the CAS Pioneer Hundred Talents Program. We thank Pi-Cheng Chen, T. E. Graedel, Sai Liang, Hong-Wen Ma, William Schlesinger, Xi-Yuan Xiao, the editor, and the anonymous reviewers for providing relevant literature/data or for helpful comments.

■ REFERENCES

- (1) Mandal, B. K.; Suzuki, K. T. Arsenic round the world: a review. *Talanta* **2002**, *58* (1), 201–235.
- (2) Capitani, E. M. D. Arsenic toxicology—a review. In *Arsenic: Natural and anthropogenic*; Deschamps, E.; Matschullat, J., Eds.; CRC Press: London, UK, 2011.
- (3) Bundschuh, J.; Litter, M. I.; Bhattacharya, P.; Hoinkis, J. The global arsenic crisis—a short introduction. In *The Global Arsenic Problem: Challenges for Safe Water Production*; Kabay, N.; Bundschuh, J.; Hendry, B.; Bryjak, M.; Yoshizuka, K.; Bhattacharya, P.; Anaç, S., Eds.; CRC Press: London, UK, 2010.
- (4) Bhattacharya, P.; Welch, A. H.; Stollenwerk, K. G.; McLaughlin, M. J.; Bundschuh, J.; Panaullah, G. Arsenic in the environment: biology and chemistry. *Sci. Total Environ.* **2007**, *379* (2), 109–120.
- (5) Chen, W. Q.; Shi, Y. L.; Zhu, Y. G. Anthropogenic Arsenic Cycles: A Research Framework and Features. *J. Cleaner Prod.* **2016**, *139*, 328–336.

- (6) Chen, W. Q.; Graedel, T. E. Anthropogenic Cycles of the Elements: A Critical Review. *Environ. Sci. Technol.* **2012**, *46* (16), 8574–8586.

- (7) Lin, Y.; Wang, S. X.; Wu, Q. R.; Larssen, T. Material Flow for the Intentional Use of Mercury in China. *Environ. Sci. Technol.* **2016**, *50* (5), 2337–2344.

- (8) Wang, T.; Muller, D. B.; Graedel, T. E. Forging the anthropogenic iron cycle. *Environ. Sci. Technol.* **2007**, *41* (14), 5120–5129.

- (9) Zhang, L.; Wang, S. X.; Wang, L.; Wu, Y.; Duan, L.; Wu, Q. R.; Wang, F. Y.; Yang, M.; Yang, H.; Hao, J. M.; Liu, X. Updated Emission Inventories for Speciated Atmospheric Mercury from Anthropogenic Sources in China. *Environ. Sci. Technol.* **2015**, *49* (5), 3185–3194.

- (10) Tian, H.; Wang, Y.; Xue, Z.; Cheng, K.; Qu, Y.; Chai, F.; Hao, J. Trend and characteristics of atmospheric emissions of Hg, As, and Se from coal combustion in China, 1980–2007. *Atmos. Chem. Phys.* **2010**, *10* (23), 11905–11919.

- (11) Tian, H.; Liu, K.; Zhou, J.; Lu, L.; Hao, J.; Qiu, P.; Gao, J.; Zhu, C.; Wang, K.; Hua, S. Atmospheric Emission Inventory of Hazardous Trace Elements from China's Coal-Fired Power Plants: Temporal Trends and Spatial Variation Characteristics. *Environ. Sci. Technol.* **2014**, *48* (6), 3575–3582.

- (12) Cheng, K.; Wang, Y.; Tian, H.; Gao, X.; Zhang, Y.; Wu, X.; Zhu, C.; Gao, J. Atmospheric emission characteristics and control policies of five precedent-controlled toxic heavy metals from anthropogenic sources in China. *Environ. Sci. Technol.* **2015**, *49* (2), 1206–1214.

- (13) *Locating and Estimating Air Emissions from Sources of Arsenic and Arsenic Compounds*; U.S. Environmental Protection Agency: Research Triangle Park, NC, 1998.

- (14) Loebenstein, J. *The Materials Flow of Arsenic in the United States (Information Circular No. IC 9382)*; Bureau of Mines, U.S. Department of the Interior: Denver, 1994.

- (15) Chen, P. C.; Su, H. J.; Ma, H. W. Trace anthropogenic arsenic in Taiwan-substance flow analysis as a tool for environmental risk management. *J. Cleaner Prod.* **2013**, *53*, 13–21.

- (16) Grund, S. C.; Hanusch, K.; Wolf, H. U. Arsenic and arsenic compounds. In *Ullmann's Encyclopedia of Industrial Chemistry: Metals and Alloys*; Library, W. O., Eds.; Wiley-VCH: Weinheim, Germany, 2012; pp 199–234.

- (17) USGS. *Arsenic Mineral Commodity Summaries*. <http://minerals.usgs.gov/minerals/pubs/commodity/arsenic/mcs-2012-arsen.pdf>; 2012.

- (18) U.S. Geological Survey Arsenic Statistics and Information. <http://minerals.usgs.gov/minerals/pubs/commodity/arsenic/> (accessed November 1, 2015).

- (19) Graedel, T. E.; Bertram, M.; Fuse, K.; Gordon, R. B.; Lifset, R.; Rechberger, H.; Spataro, S. The contemporary European copper cycle: The characterization of technological copper cycles. *Ecological Economics* **2002**, *42* (1–2), 9–26.

- (20) Kelly, T. D.; Matos, G. R.; Buckingham, D.; DiFrancesco, C.; Porter, K.; Berry, C.; Crane, M.; Goonan, T.; Sznopce, J. *Historical Statistics for Mineral and Material Commodities in the United States*. U.S. Geological Survey Data Series, VA, 2010.

- (21) Chen, W.-Q.; Shi, L.; Qian, Y. 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* **2010**, *54* (9), 557–570.

- (22) Yudovich, Y. E.; Ketris, M. Arsenic in coal: a review. *Int. J. Coal Geol.* **2005**, *61* (3), 141–196.

- (23) United Nations Comtrade. United Nations Commodity Trade Statistics Database. 1990–2010. <http://comtrade.un.org/db/>.

- (24) Chen, J.; Liu, G. J.; Kang, Y.; Wu, B.; Sun, R. Y.; Zhou, C. C.; Wu, D. Atmospheric emissions of F, As, Se, Hg, and Sb from coal-fired power and heat generation in China. *Chemosphere* **2013**, *90* (6), 1925–1932.

- (25) Liang, S.; Liu, Z.; Crawford-Brown, D.; Wang, Y.; Xu, M. Decoupling analysis and socioeconomic drivers of environmental pressure in China. *Environ. Sci. Technol.* **2013**, *48* (2), 1103–1113.

- (26) United Nations. *United Nations International Trade Statistics Harmonized Commodity Description and Coding System (HS)*, 2015.
- (27) Liang, S.; Feng, T.-T.; Qu, S.; Chiu, A. S. F.; Jia, X. P.; Xu, M. Developing the Chinese Environmentally Extended Input-Output (CEEIO) Database. *J. Ind. Ecol.* **2016**, *0* (0), 1–13.
- (28) National Bureau of Statistics (NBS) and National Development and Reform Commission (NDRC). *China Energy Statistical Yearbook*; China Statistics Press: Beijing, China, 1990–2010.
- (29) *China National Land and Resources Statistical Yearbook*; Ministry of Land and Resources of PRC, 1999–2010.
- (30) *Minerals Reserves Tables*; Division of Mineral Reserves, Ministry of Land and Resources of PRC, 1990–2010.
- (31) National Bureau of Statistics of China. *China Statistical Yearbook*. China Statistics Press: Beijing, China, 1990–2010.
- (32) Melo, M. Statistical analysis of metal scrap generation: the case of aluminium in Germany. *Resources, Conservation and Recycling* **1999**, *26* (2), 91–113.
- (33) Gerst, M. D.; Graedel, T. In-use stocks of metals: status and implications. *Environ. Sci. Technol.* **2008**, *42* (19), 7038–7045.
- (34) Pauliuk, S.; Wang, T.; Müller, D. B. Moving Toward the Circular Economy: The Role of Stocks in the Chinese Steel Cycle. *Environ. Sci. Technol.* **2012**, *46* (1), 148–154.
- (35) Chen, W. Q.; Shi, L. Analysis of Aluminum Stocks and Flows in Mainland China from 1950 to 2009: Exploring the Dynamics Driving the Rapid Increase in China's Aluminum Production. *Resources Conservation and Recycling* **2012**, *65*, 18–28.
- (36) USGS. *China Minerals Yearbook*; United States Geological Survey, 1994–2011.
- (37) Yang, H. Q.; Nie, Y.; Ji, C. Y. Study on China's Timber Resource Shortage and Import Structure: Natural Forest Protection Program Outlook, 1998 to 2008. *Forest Products Journal* **2010**, *60* (5), 408–414.
- (38) Nassar, N. T.; Graedel, T. E.; Harper, E. M. By-product metals are technologically essential but have problematic supply. *Science Advances* **2015**, *1* (3), e1400180.
- (39) *The Technological Policy for Arsenic Pollution Prevention and Treatment*; Ministry of Environmental Protection of PRC, 2015.
- (40) Reck, B. K.; Rotter, V. S. Comparing Growth Rates of Nickel and Stainless Steel Use in the Early 2000s. *J. Ind. Ecol.* **2012**, *16* (4), 518–528.
- (41) *Catalogue of Prohibited Good for Export*; Ministry of Commerce, General Administration of Customs of the People's Republic of China, 2015.
- (42) Khan, B. I.; Solo-Gabriele, H. M.; Townsend, T. G.; Cai, Y. E. s. t. Release of arsenic to the environment from CCA-treated wood. 1. Leaching and speciation during service. *Environ. Sci. Technol.* **2006**, *40* (3), 988–993.
- (43) Khan, B. I.; Jambeck, J.; Solo-Gabriele, H. M.; Townsend, T. G.; Cai, Y. Release of arsenic to the environment from CCA-treated wood. 2. Leaching and speciation during disposal. *Environ. Sci. Technol.* **2006**, *40* (3), 994–999.
- (44) Shibata, T.; Solo-Gabriele, H. M.; Fleming, L. E.; Cai, Y.; Townsend, T. G. A mass balance approach for evaluating leachable arsenic and chromium from an in-service CCA-treated wood structure. *Sci. Total Environ.* **2007**, *372* (2), 624–635.
- (45) Horowitz, H. M.; Jacob, D. J.; Amos, H. M.; Streets, D. G.; Sunderland, E. M. Historical Mercury Releases from Commercial Products: Global Environmental Implications. *Environ. Sci. Technol.* **2014**, *48* (17), 10242–10250.