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Anthropogenic arsenic cycles: A research framework and features

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ABSTRACT

Arsenic is a trace element and a global contaminant. There are currently large uncertainties associated with our understanding and quantification of the arsenic cycles in the global environment. This study proposes a research framework where the major anthropogenic processes affecting anthropogenic arsenic cycles (AACs) are identified. A characteristic of this framework is that it divides AACs into two parts: one related to intentional uses, and the other driven by unintentional uses. Several significant features of AACs are summarized as follows: (1) existing studies reveal that AACs at Earth's surface is at the same order of magnitudes as its natural cycles; (2) arsenic mostly enters modern anthroposphere as a companion element of nonferrous metal ores or fossil fuels, and currently there is abundant arsenic reserves relative to the limited intentional use of arsenic; (3) China owns the majority of arsenic reserves and is the biggest producer of arsenic for the present day, while U.S. was the biggest user of arsenic in the whole 20th century; (4) there were several waves of rise and fall of intentional arsenic use in the 20th century of U.S., with the rises driven by various applications of arsenic in agriculture and industry (such as glass making in the 1900s, agricultural applications in the 1920s, and wood preservatives in the 1970s), and the falls mainly resulting from the regulations in response to its toxicity; (5) the majority of intentional arsenic uses are in the form of chemical compounds rather than single substance, and almost all intentional uses of arsenic not only are unrecyclable but also result in emissions that may last years or decades after being used.

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1. Introduction

Studies on anthropogenic cycles of an element concern stocks and flows of the element within anthropogenic systems (e.g., the anthroposphere of a country or a city), and exchange flows of the element between anthropogenic systems and natural systems (e.g., atmosphere, hydrosphere, biosphere, or pedosphere) or among different anthropogenic systems (Chen and Graedel, 2012a). For an element, the anthropogenic cycles are an indispensible part of its global anthrobiogeochemical cycles (Rauch and Graedel, 2007; Rauch and Pacyna, 2009); and its anthropogenic emissions, if defined as the amount of the element emitted from anthropogenic systems to non-anthropogenic systems, are part of its anthropogenic cycles.

Arsenic (As) is a ubiquitous element known for its toxicity to biota (Capitani, 2011; Mandal and Suzuki, 2002) and it naturally occurs in several oxidation states between -III and +V (Wenzel, 2013). It is widely distributed but relatively scarce in Earth's crust, with its abundance usually in the range of 2-10 parts per million (ppm), although higher concentrations up to 60 ppm or more are found in some sulfide deposits (Edelstein, 1985; Grund et al., 2012; Mandal and Suzuki, 2002). The existence of arsenic in air, water, and soil is of global concern because many of its compounds are poisonous and can be a serious threat to human health. There have been many episodes of arsenic poisoning reported worldwide, e.g. (Bundschuh et al., 2010; Mandal and Suzuki, 2002). Although many of these episodes are due to arsenic from geogenic sources (Bundschuh et al., 2010), in particular arsenic-rich ground water (e.g., the widely known cases in Bangladesh (Bhattacharya et al., 2010) and Taiwan (Jean et al., 2011)), the contamination of air, water, soil, food, and beverage by arsenic from anthropogenic sources has led to increasing environmental concerns (Bhattacharya et al., 2007; Mandal and Suzuki, 2002). It is







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estimated that nowadays anthropogenic processes, which include coal burning, petroleum burning, mining, biomass burning, human apportionment of terrestrial net primary productivity, and construction, are as important as natural processes (i.e. sources from wind erosion, volcanic emissions, and volatilization from soil and water surface) in affecting the arsenic cycles at Earth's surface (Klee and Graedel, 2004; Sen and Peucker-Ehrenbrink, 2012). However, there are large variations in the anthropogenic activities and hence the anthropogenic cycles of arsenic around the world, so it is important to (both qualitatively and quantitatively) characterize the anthropogenic cycles and emissions (as part of cycles) of arsenic at the national level.

Anthropogenic cycles of an element can result from both intentional and unintentional uses of the element (Elshkaki et al., 2009; Lifset et al., 2012). Intentional uses refer to those applications of the element itself that provide services or functions for modern human society, such as the use of aluminum for manufacturing cars and the use of arsenic for producing pesticides or wood preservatives. Unintentional uses refer to those applications of other elements or resources in which the concerned element is just an unavoidable (and in many cases unwanted) impurity, such as the mining of arsenic and other trace metals contained in coals during coal mining. Thus, studies on anthropogenic cycles of an element resulting from intentional uses mainly concern how the element enters, passes through, accumulates in, and leaves an anthroposphere (e.g., (Chen and Graedel, 2012b; Chen et al., 2010; Reck et al., 2008; Wang et al., 2007b)), while studies on anthropogenic cycles of an element resulting from unintentional uses mainly concern how the element is moved into an anthroposphere together with other elements or resources and how it is lost or emitted from anthroposphere to other non-anthropogenic systems (e.g., (Pacyna and Pacyna, 2001; Tian et al., 2014; Zhang et al., 2015)).

Unlike some bulk metals such as iron (Müller et al., 2006) or aluminum (Chen and Graedel, 2012b) of which the anthropogenic cycles are dominantly driven by their intentional uses or some organic toxic by-products such as dioxins for which there is no intentional use, anthropogenic arsenic cycles (AACs) are driven by both intentional and unintentional uses. Especially, the dissipative arsenic emissions resulting from intentional uses are at the same order of magnitude as atmospheric emissions resulting from coal combustion, which is an important unintentional arsenic use (Shi et al., 2016). However, one on hand, there are few publications that provide analysis on AACs resulting from intentional uses. (Lindau, 1977) investigated arsenic input and output of Sweden economy but did not analyzed arsenic flows and uses inside the economy. Some other studies characterized AACs driven by intentional uses inside an economy, but only provided one-year snapshot results and were either too old (Loebenstein, 1994) or just for an isolated island (Chen et al., 2013). On the other hand, it seems studies aiming at quantifying arsenic emissions mainly determined atmospheric emissions of arsenic resulting from unintentional uses, and these studies are usually conducted together with studies for other heavy and/or toxic elements such as cadmium, chromium, or selenium (Cheng et al., 2015; Tian et al., 2010, 2014; U.S. Environmental Protection Agency, 1998). Therefore, it is necessary to develop a research framework that can be used to quantify the cycles driven by both intentional and unintentional uses for arsenic and several other elements with similar features, such as mercury, cadmium, and chromium.

Therefore, with a longer-term plan of quantitatively characterizing AACs for major countries and the global, this study seeks to achieve the following goals: (1) to propose a research framework that can be used to characterize AACs driven by (or related to) both intentional and unintentional uses; (2) to qualitatively characterize anthropogenic processes and their relevant arsenic stocks and flows that constitute the proposed research framework; (3) to identify key parameters and data sources for quantitatively characterizing AACs at the national level (for example, China); and (4) to summarize several features of AACs that are different from the anthropogenic cycles of other elements and that can be observed from existing studies and available data.

2. The research framework

The framework we propose to characterize AACs is shown in Fig. 1. The red dashed lines define the spatial boundary of the system being studied (such as mainland China). In this target system, arsenic can cycle within and among various reservoirs such as anthroposphere, lithosphere, atmosphere, hydrosphere, pedosphere, and biosphere (Matschullat, 2000, 2011). The anthropogenic cycles of arsenic comprise two parts: (1) the anthropogenic cycles that are related to intentional uses; and (2) the anthropogenic cycles that result from unintentional uses. 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 atmosphere, hydrosphere, biosphere, pedosphere, and lithosphere. Some of the transfer processes are dissipative and usually referred as emissions (e.g. emissions of arsenic to the atmosphere from metal smelting), and some others are not dissipative (e.g. the arsenic mining process is simply transferring the arsenic from one place to another) (Chen et al., 2010: Kapur and Graedel, 2006: Lifset et al., 2012). However, losses resulting from most anthropogenic processes illustrated in Fig. 1 are probably dissipative and should be regarded as emissions, especially for those processes resulting from unintentional uses resulting in emissions to atmosphere. For a target domain that is smaller than the global system, there almost always exist trade of arsenic-containing resources and products between the target system and other anthropogenic systems (illustrated in Fig. 1 as "import and export").

Following the Stocks and Flows (STAF) framework developed by the Yale Center for Industrial Ecology that is used to characterize anthropogenic cycles of many metals such as iron and aluminum (Chen and Graedel, 2012b; Wang et al., 2007a), AACs related to intentional uses are depicted in the upper part of Fig. 1 and consist of several processes: (1) mining of both arsenic ores and other metal ores containing arsenic, (2) dressing of ores to produce concentrates, (3) processing of arsenic and other metal concentrates, (4) production of As₂O₃, (5) production of arsenic metal and arsenic chemical compounds, (6) manufacturing of various arseniccontaining final products, (7) use of these final products, and (8) end-of-life management and recycling of arsenic. Both the physical and chemical forms of arsenic change along these processes. Unlike iron or aluminum of which the cycles are almost completely driven by intentional uses and thus the cycles won't occur from the beginning mining process if there are not intentional uses for them, the AACs are just partly driven by its intentional uses (agricultural chemicals, wood preservatives, etc.) and the mining and dressing of ores will still occur even though there is not any intentional use for arsenic, because arsenic is mostly mined as a by-product of other metal ores (e.g., copper and gold ores). This means that it is the combination of intentional and unintentional uses of arsenic that drives the AACs depicted in the upper part of Fig. 1, and thus we just call them AACs "related to" rather than "resulting from" intentional uses.

Similar to some other toxic metals such as mercury, cadmium, and chromium, arsenic widely exists as a trace element in metal ores and fossil fuels (Grund et al., 2012). Consequently, many anthropogenic processes involving fossil fuels, metal ores, metal



Fig. 1. A research framework for characterizing anthropogenic arsenic cycles related to intentional uses and resulting from unintentional uses in national or global anthropogenic systems.

concentrates, metal products, and wastes result in unintentional AACs by either bringing it into anthroposphere or emitting it into non-anthropogenic systems (as demonstrated in the lower part of Fig. 1). Therefore, when doing research on arsenic cycles driven by unintentional uses, it is necessary to identify a full list of these anthropogenic processes, evaluate the existence and concentration of arsenic in resources entering these processes, estimate the emissions of arsenic from these processes, and explore the corresponding regulation and control policies. Unlike the AACs related to intentional uses, the AACs associated with unintentional cycles of arsenic are not step-by-step linked so as to form a life cycle chain. In contrast, they are separate and independent from one another (e.g., waste incineration and coal burning), or are just weakly linked (e.g., metal production and coal mining).

3. Anthropogenic arsenic cycles related to intentional uses

3.1. Geological occurrence, mining, and ore dressing

There are more than 200 mineralogical species known to contain arsenic, of which about 60% are arsenates, about 20% are sulfides and sulfosalts, and the remaining are arsenides, arsenites, oxides, silicates, and arsenic in its native form (Bligh, 2012; Mandal and Suzuki, 2002). However, only in a few minerals arsenic occurs in abundance high enough to be worked economically, and the most recoverable forms of arsenic are found in various types of metalliferous deposits, such as enargite-bearing copper-zinc-lead deposits, arsenical pyritic copper deposits, native silver, nickel-cobalt arsenide deposits, and arsenical gold deposits (Edelstein, 1985; Mandal and Suzuki, 2002). The most important minerals from which arsenic may be directly extracted (namely, not as a byproduct of metals production) are arsenopyrite (FeAsS), orpiment (As₂S₃), realgar (AsS), and native arsenic. The average

concentration of arsenic in ore deposits varies between <0.1% and 4.0% in the world outside China (Mandal and Suzuki, 2002; Tanaka, 1988). Around 15% of all commercial copper ores are classified by U.S. Bureau of Mines as arsenical, with an average Cu/As ratio of 50:1 for arsenical copper ores (in non-arsenical copper ores the ratio is 500:1) (Ayres et al., 1996). Because the average Cu/As ratio in all U.S. copper reserves is about 170 (13 pounds of As per ton of Cu) (Edelstein, 1985), this means that the average concentration of arsenic in copper ores in the United States may be even much lower than 0.1% (the average copper concentration in copper ores is lower than 1% now but much higher some decades ago (Graedel et al., 2002)).

China owns the majority of arsenic reserves and the average arsenic concentrations of ores in China seem higher than those in other areas (Xiao et al., 2008). According to the latest available data (Xiao et al., 2008), arsenic reserves explicitly listed in the Minerals Reserves Tables (thereafter MR Tables, compiled by the Chinese provincial governments) in China was about 2.8 million metric tons (MMTs) at the end of 2003, and there were about 1.5 MMTs of arsenic reserves not listed in the MR Tables due to their relatively low arsenic content (Table S1). For those listed in the MR Tables, about 67% has the arsenic concentration of more than 1.0%, with the arsenic concentration of the remaining probably more than 0.1%; while for those not listed in MR Tables, about 90% has the concentration of more than 0.1%. The geographical distribution of arsenic reserves in China is quite uneven, with more than 50% located in only three provinces in south China, and most of the remaining located at some other provinces in the southwest (Table S1). There were about 360 thousand metric tons (TMTs) of arsenic reserves existing in ores in which arsenic is the host element rather than a companion element of other metals (Table S1). However, the majority of arsenic ores exist as a companion element of nonferrous metal ores. For example, in the 84 ore

deposits listed in China's provincial MR Tables as arsenic reserves, tin occurs in 24 ore deposits, lead occurs in 30 ore deposits, copper occurs in 26 ore deposits, and gold occurs in 49 ore deposits as the host element (Table S2).

Most arsenic raw materials are by products from the dressing and smelting of complex ores mined for nonferrous metals such as gold, silver, lead, copper, nickel, tin, and cobalt (Grund et al., 2012). There are three types of arsenic ores (realgar, orpiment, and arsenopyrite) directly used for producing arsenic trioxide in China, which is reported as the only country doing so (Grund et al., 2012; Xuan, 1998). However, not that the majority of arsenic mined in China is by-product of the mining of nonferrous metals ores too (Xiao et al., 2008). Due to its relatively low demand compared to supply and its toxicity, arsenic in most cases is regarded as an undesirable element in metals mining, smelting, and refining (Edelstein, 1985; Grund et al., 2012). The loss rates of arsenic in the mining and dressing of nonferrous metals ores are pretty high. In the ore dressing process, it is reported that the percentage of arsenic entering metal concentrates ranges from only 2% to 41% and the remaining is lost to waste, depending on the type of ores and technologies (Grund et al., 2012). The average loss rates of arsenic in China's ore mining and dressing processes were reported to be 36% and 30% (Xiao et al., 2008; Yin, 1991), respectively.

Globally, the average arsenic contents in metal concentrates generated from ore-dressing processes vary considerably (from <1% to, in some extreme cases, 10%; copper concentrate may contain 0.5–1.0% arsenic and concentrates of the complex ores may have up to 5–8% arsenic (Grund et al., 2012)), depending on both arsenic concentrations in the initial metal ores and technologies that distribute arsenic between metal concentrates and wastes. The large variations of arsenic concentrations in different nonferrous metal concentrates produced in China are shown in Table S3. Chinese government has set standards on the highest limit of arsenic content in various metal concentrates that are imported into the Chinese market or are domestically mined and then used for nonferrous metals production in China. For example, arsenic content in imported copper concentrate should be less than 0.5% as of June 1st, 2006 (PRC, 2006). Due to the decline of grades of metal ores, there is a trend occurring in both China and the rest of the world that metal concentrates are becoming dirtier, which implies higher arsenic content (Grund et al., 2012; PRC, 2012).

3.2. Processing of concentrates and production of refined As_2O_3

The existence of arsenic in metal concentrates may result in challenges such as increases in production costs, decreases in product purity and quality, and environmental hazard for metal industries. Therefore, arsenic should be separated from metal concentrates as early as possible and be stabilized for safe disposal (Grund et al., 2012; Piret, 1999). The dearsenifying pretreatment technologies can be categorized into pyro- and hydro-metallurgical processes (Flynn and Carnahan, 1989; Jorgensen et al., 2007; Mihajlovic et al., 2007). Pyrometallurgical technologies are more widely used (for example, in copper and lead industries) and may comprise roasting, smelting, blowing, and refining processes. For certain applications, some hydrometallurgical protesses such as oxidative pressure leaching or biochemical pretreatment are applicable alternatives (Wei et al., 2003; Grund et al., 2012).

Arsenic may end up in flue dusts, emitted gases, slag, slurry, wastewater, and metal products (e.g., copper matte or crude lead) after dearsenifying pretreatment (Grund et al., 2012). The ratios by which arsenic are distributed into these sinks depend on metal concentrates, pretreatment technologies, equipments, and operations, but most arsenic is probably concentrated in the gas phase (flue dusts) during roasting or smelting operations due to the

volatility of arsenic sulfides and oxides. An estimate of typical distribution patterns of arsenic in Chinese nonferrous metal industries is listed in Table S4. Currently, only a small share (e.g., in China, less than 10%) of arsenic entering nonferrous metal industries is recovered from the flue dust and slurry to produce arsenic trioxide of commercial purity, and most of them come from copper, lead, tin, gold, silver, and cobalt smelters (Grund et al., 2012: Loebenstein, 1994: PRC, 2012). High-purity arsenic oxide. which is marketed as white arsenic, can then be obtained by either dry or wet refining process. In the dry sublimation process, crude arsenic is heated, filtered, collected, and separated. The low-purity products have to be returned to the process, and the high-purity products will be sold. In the wet process, crude arsenic is dissolved, crystallized, separated, washed, and then dried to get highpurity products. The mother liquor can be continuously recycled in the system.

3.3. Production of arsenic metalloid and compounds

The major use of arsenic trioxide is the precursor to arsenic metalloid and various arsenic compounds that are used to produce final products such as electronics or pesticides (Grund et al., 2012). There are two grades of arsenic metalloid: the commercial-grade arsenic and the high-purity arsenic. For the production of commercial-grade arsenic, the starting material is mostly white arsenic (arsenic trioxide), which is normally reduced with carbon and in some cases with carbon monoxide or ammonia. In addition. commercial-grade arsenic can be directly obtained from arsenopyrite and lollingite by thermal dissociation (Grund et al., 2012). Commercial-grade arsenic produced from arsenic trioxide contains more than 99% of arsenic and is primarily used for the production of alloys. In order to make arsenic metalloid applicable for semiconductors and some other applications, it has to be further purified to obtain high-purity arsenic that may contain up to 99.99% or 99.999% of arsenic (Grund et al., 2012).

There are a number of arsenic compounds, all of which can be mainly grouped into inorganic compounds, organic compounds, and arsine gas from both the biological and the toxicological point of view (WHO, 2000). Inorganic compounds mainly include oxides (trioxide and pentoxide), acids (arsenous acid and arsenic acid) and their salts, sulfides, halides, and arsenides. Almost all arsenic compounds are produced from arsenic oxide. Especially, arsenic acid is obtained solely by the oxidation of arsenic trioxide and it is used as a starting material for important inorganic and organic arsenic compounds (Grund et al., 2012).

3.4. Manufacturing and use of arsenic-containing final products by end-use sector

Arsenic, in the form of As₂O₃, has been used both as a medicine and a poison for several hundreds of years, and is famous as Pi-Shuang in Chinese. However, the medicinal application is not its major use in modern world. According to the U.S. Geological Survey (Kelly et al., 2005; Loebenstein, 1994), there are five end-use sectors of arsenic as listed in Table 1 and Fig. 2. Each specific application of arsenic relies on one or several special functions provided by arsenic and there is more than one application in each end-use sector (Table 1). Although the classification of arsenic applications into five end-use sectors is relatively rough, it is enough to investigate the main features and changes of arsenic uses over the past century. For the United States where almost half of global arsenic was used during the 20th century, there were several significant transitions of arsenic use during the period 1901-2010 (Fig. 2), and the decline of arsenic use for a major application mainly resulted from its toxicity and the regulation in response to its toxicity (Kelly

Table 1

End-use ^a	Specific applications	Estimated lifespan ^b	Chemical forms or functions ^b
Agricultural chemicals	Insecticides Herbicides Plant desiccants Animal feed	Less than 1 year	As_2O_3 and various compounds produced from As_2O_3 used for cotton, coffee, and rice.
Glass production	Fining agent Decolorizing agent In glass ceramics In red glass	5—20, or 10 years	As ₂ O ₃ for removing air bubbles. Arsenic acid for reducing dusting. As compounds for controlling crystal growth rate. As ₄ S ₄ for its red color.
Nonferrous alloys and electronics	l Lead alloys for batteries Lead alloys for ammunition Copper alloys Electronic products	5—20, or 12 years	Metallic form for increasing battery's endurance and corrosion resistance, for improving bullet's sphericity, and for improving copper alloys' corrosion resistance and tensile strength. High-purity arsenic metal and gallium arsenide for semiconductors, integrated circuits, and other electronics.
Wood preservatives	Decks, fences, and landscaping High way and marine uses Poles	10—40 years	i 1940s–1960s: mainly used as Wolman salts. 1970s–now: as Chromated copper arsenate (CCA). 2003: U.S. industries volunteer to stop using CCA.
Other	Feed additives for poultry Chemical catalysts Veterinary medicines Pharmaceuticals	12.5 years	_

^a These five end-use sectors are classified in accordance to a method developed by U.S. Geological Survey (Edelstein, 1985; Loebenstein, 1994). ^b Data sources: (Edelstein, 1985; Grund et al., 2012; Khan et al., 2006a, 2006b; Loebenstein, 1994; Nassar et al., 2012; Shibata et al., 2007).





Fig. 2. Historical evolution of U.S. arsenic apparent consumption by end-use sector, Gg: thousand metric tons. Data source: U.S. Geological Survey (Kelly et al., 2013).

et al., 2013). The U.S. historical evolution of arsenic apparent consumption (namely, flows entering use) by end-use sector demonstrates the following features (Fig. 2):

- a) 1901–1920s. The early use of arsenic trioxide since its first reported production in 1901 in the United States was principally in glassmaking (about 50%) (Edelstein, 1985). However, the use of arsenic in glass is at a much lower percentage after 1920s and the chemical form of its major application in glassmaking changed from powdered arsenic trioxide to the more environmentally friendly liquid arsenic acid (Loebenstein, 1994).
- 1920s-1970s. A sharp increase in demand for arsenical inb) secticides began in 1917 (Edelstein, 1985) and arsenic was

then used to produce more agricultural chemicals such as herbicides, plant desiccants, and defoliants, making U.S. arsenic apparent consumption peak in 1940s and agriculture chemicals the dominating end-use until the 1970s. The development of organic pesticides following the World War II led to the gradual phase-out of inorganic arsenical pesticides since the late 1940s; and following the implementation of regulations by the U.S. Occupational Safety and Health Administration and U.S. Environmental Protection Agency, the application of arsenic compounds in agriculture dramatically declined since the 1970s (Edelstein, 1985).

- c) 1970s–2000s. With the introduction of chromated copper arsenate (CCA) that contains arsenic in the less toxic pentavalent form in about 1972, arsenical wood preservatives became more and more prevalent, making wood preservatives the dominating end-use of arsenic since the 1980s (Edelstein, 1985; Loebenstein, 1994). However, due to concerns of the environment and public health, a voluntary ban on the use of arsenic trioxide for the production of CCA wood preservatives in 2003 resulted in the sudden sharp decrease of arsenic use in the United States (U.S. Geological Survey, 2012) (note, however, that many countries or regions except the United States and Malaysia have prohibited the use of CCA as wood preservatives). Since then there have been no arsenic end-use statistics reported by USGS (data on the share of each end-use after 2003 as shown in Fig. 2 were assumed to be the same as those in 2003).
- d) It is only in the end-use Nonferrous Alloys and Electronics that arsenic is used in the metallic form and this end-use sector only accounted for less than 5% of arsenic use in the United States prior to 2003. However, although the use in this sector is minor compared to other end-use sectors, it has existed for many decades and is critical for each of its specific application. Commercial-grade arsenic metalloid is mainly

used for alloys, batteries, and ammunitions, while its application in semiconductors and other electronics requires high-purity arsenic metalloid (Edelstein, 1985; Loebenstein, 1994; U.S. Geological Survey, 2012).

Unfortunately, except the United States, there are no data on apparent consumption of arsenic by end-use sector for other countries or territories available to us at this point. It is said that about 70–80% of arsenic trioxide in China is used in the glass industry (Jiang, 2002; PRC, 2012). However, there is no convincing statistics supporting this conclusion. Therefore, it is necessary to perform bottom-up analyses (namely, by identifying a detailed list of arsenic-containing products and calculating their production/ use and average arsenic concentrations) so as to estimate arsenic uses and to infer arsenic emissions, in-use stocks, and end-of-life flows by product/sector (a case is developed in (Shi et al., 2016) for China).

3.5. In-use stocks

In-use stock of a material is the amount of the material that is in active use (Chen and Graedel, 2015; Gerst and Graedel, 2008). It is only for materials or the applications of a material that require the physical retention of the material in the use status that this concept applies. For some arsenic applications (such as insecticides), because the use of arsenic results in the dissipated loss of arsenic itself, there is no in-use stock accumulated in them. For other applications (such as wood preservatives), because arsenic is embedded and stored in wood products that can be used for years or decades, there are in-use arsenic stocks accumulated in them.

The loss or emission of arsenic immediately occurs when arsenic is used for the former type of applications; while the loss or emission may occur during the whole use period of arseniccontaining products or when these products reach their ends of life from use. Because data on end-use are only at the resolution of one year, we classify those end-uses of which the residence time is less than one year into the former type, while those end-uses of which the residence time is longer than one year into the latter type (Table 1). In-use stocks of arsenic in those applications belonging to the second type can then be estimated using the residence time model, which consists of three steps: (1) estimate outflows from use in each year by taking into account historical annual inflows before that year and the residence time of each year's inflows in the use stage; (2) calculate the stock changes in each year as the difference between that year's inflows and outflows; and (3) infer the in-use stocks in a certain year by cumulating stock changes before that year (Chen and Graedel, 2015; Gerst and Graedel, 2008).

3.6. EOL management and recycling

An element may have three fates after used: in-use dissipated, currently unrecyclable, and potentially recyclable (Ciacci et al., 2015). Only those that are not in-use dissipated will enter the stage of end-of-life Management and Recycling (EM&R). More than 17% of arsenic use is dissipated when used and the rest will enter the EM&R stage (Ciacci et al., 2015). More than 64% of arsenic is currently unrecyclable because recycling end-of-life arsenic-containing products to recover the arsenic content is of no economical interest presently due to its low price and hazardous nature (Grund et al., 2012; Loebenstein, 1994). Both in-use dissipation and the failure of recycling arsenic at the EM&R stage result in its loss and emissions back to the environment. Because the intentional uses of arsenic bring arsenic from mining spots to vast area (e.g., agricultural lands), these loss and emissions are widely distributed and thus become non-point emissions.

There were possible recycling of arsenic reported, two as "new scrap", and two as end-of-life scrap. The recycling of "new scrap" occurs during the production of pressure-treated wood and the manufacturing of gallium-arsenide electronic devices (Loebenstein, 1994). The recycling of old scrap occurs when arsenic used as a minor additive (0.01%–0.5%) to lead in lead acid storage batteries is collected and reused in new storage batteries, or when electronic devices containing gallium arsenide are recycled to recover gallium and arsenic due to gallium's (rather than arsenic's) high price and scarcity (Grund et al., 2012; Loebenstein, 1994). However, due to its poor recycling potential as well as toxicity, the major aim of the arsenic end-of-life management is the stabilization and subsequent secure and long-term disposal.

3.7. Trade of arsenic

Trade flows make arsenic enter (import) or leave (export) an anthropogenic system and can be directly calculated by multiplying trade of arsenic-containing products by their arsenic contents. Trade of arsenic at the national level should be calculated from a life cycle perspective, meaning that trade of all arsenic-containing products generated from every anthropogenic process should be considered. Data on trade of arsenic-containing products for a country can be obtained from its customs statistics. However, there are at least two challenges: (1) identifying those products that contain significant amount of arsenic and matching them with relevant anthropogenic arsenic processes; and (2) obtaining data to determine average arsenic contents in those products. By taking into account these, we identify a list of arsenic-containing products and collect data on their average arsenic contents (Table S5). Using national customs statistics, this list enables researchers to estimate trade of arsenic among countries, e.g., the trade between China and the rest of the world is provided in (Shi et al., 2016).

4. Anthropogenic arsenic losses and emissions

Both the upper and the lower parts of AACs demonstrated in Fig. 1 result in the losses of arsenic from anthroposphere to the environment. Similar to aluminum and other metals (Chen et al., 2010), these losses can be divided into two main categories: (1) the deposited losses that are deposited in either mining residues, tailing ponds, slag ponds, or landfills, and that will result in the formation of deposited stock and maybe re-exploited in the future; (2) the dissipated losses (or termed dissipative losses) that will be dissipated into the environment, and that have almost no possibility to be reused or recycled in the future. Determining whether a loss is deposited or dissipated is a dynamic process because the standard of differentiating them is not always distinct and some deposited stocks can result in further dissipated losses if they are not well stabilized. Note that although emissions can always be regarded as losses, not all losses are emissions, because only dissipative losses can be regarded as emissions (Chen et al., 2010; Kapur and Graedel, 2006; Lifset et al., 2012).

Despite various differences, the estimation of arsenic losses and emissions share the same procedures: (1) the identification of anthropogenic processes such as copper production; (2) the determination of anthropogenic activity levels such as the amount of copper produced; (3) the determination of loss rate or emission factor, which can be defined as the loss or emission of arsenic per activity level (e.g., production of one ton of copper); and finally, (4) the calculation of arsenic losses or emissions by multiplying activity levels by loss rates or emission factors.

A list of anthropogenic processes belonging to arsenic cycles related to intentional uses is shown in Table S6, and a list of anthropogenic processes that are identified for determining atmospheric arsenic emissions in China is shown in Table S7 (Cheng et al., 2015). A comparison between these two lists demonstrates the following features: (1) a complete list in Table S6 can only be identified from the perspective of elemental life cycle as demonstrated in the upper part of Fig. 1; (2) almost all activities listed in Table S7 result from unintentional uses of arsenic: (3) there are only a few processes (nonferrous metals smelting and lead-acid batteries production) existing in both lists, meaning that existing studies may have underestimated atmospheric arsenic emissions without considering many activities related to intentional uses of arsenic; (4) the list for arsenic losses and the list for arsenic emissions (only dissipated losses) have a big overlap, but are not the same. Besides these two lists that enable bottom-up estimation of arsenic losses or emissions activity by activity, we note that official statistics in China report arsenic emissions from various economic sectors (Fig. 3), for which the classification method is different from the way of classifying anthropogenic processes listed in Tables S6 and S7. These different sources of data can thus either be compared with or complement one another in generating a more comprehensive and detailed determination of arsenic losses and emissions. For example, the official statistics on emissions by economic sectors (Fig. 3) provide atmospheric emission data on food production and textiles sectors that are usually ignored by bottom-up investigation, which focuses on some most important sectors such as coals and power plants (Tian et al., 2014).

Determining loss rates and emission factors is an important but usually challenging task, and it is necessary to take into account the following aspects: (1) Arsenic can be lost or emitted in different physical and chemical forms with different oxidation states between –III and +V, each of which has different impacts on human health and ecosystem (Pacyna and Pacyna, 2001; Pacyna et al., 1995; U.S. Environmental Protection Agency, 1998). Thus, a comprehensive determination of arsenic losses and emissions should estimate loss rates and emission factors for at least some specific oxidation states of arsenic. However, no existing studies have done so as far as we know. (2) Arsenic can be lost or emitted into different environments such as atmosphere, hydrosphere, biosphere, and pedosphere, making arsenic emissions termed air emissions, atmospheric emissions, aquatic emissions, emissions to water, emissions to soil, and so on in different references (Cheng et al., 2015; Nriagu, 1979; Nriagu and Pacyna, 1988; Pacyna et al., 1995; Parviainen et al., 2006). However, almost all existing studies only estimate atmospheric emission factors and atmospheric emissions; probably because atmospheric emissions can be easily transported to vast areas, result in direct impacts on human health and ecosystem, and thus draw much more attentions. (3) The loss rate and the emission factor from a same process could be very different, because some measures such as the collection and stabilization of generated waste can prevent part of losses from emitting to atmosphere or water, thus making emissions lower than losses from production processes (Tian et al., 2010, 2014).

5. Summary

This study proposes a research framework in which AACs are divided into two parts (Fig. 1): (1) the part that is related to intentional arsenic uses; and (2) the other that results from unintentional arsenic uses. Anthropogenic processes constituting the AACs are identified and described qualitatively with suitable details. In order to quantitatively characterize AACs based on the proposed framework, stocks and flows relevant to each anthropogenic process have to be considered. For the first part of AACs, all flows can be classified into four groups: (1) the trade flows, (2) the loss flows, (3) the transformation flows that transform arsenic from natural ores through to arsenic trioxide, metalloid, various intentionally used compounds and final products, and (4) the end-of-life discard and recycling flows after arsenic is put into use. The arsenic stocks can be categorized into four groups: (1) the natural stocks that are also termed as arsenic reserves; (2) the in-use stocks that are embedded in products such as furniture and building materials treated with arsenic-containing wood preservatives, (3) the deposited loss stock that are deposited in mining residues, tailing ponds, slag ponds, or landfills, and (4) the dissipated loss stock that has dissipated into the environment which is almost impossible to be reused or recycled in the future.

Unlike base metals such as iron or aluminum, the economy scale of arsenic industry (the part related to the intentional use of arsenic) is so small that there is no special arsenic industry association dedicated to compiling arsenic statistics, making much more efforts needed in collecting data for characterizing AACs. The



Fig. 3. China's atmospheric and aquatic emissions of arsenic by economic sector in 2010. Data sources: The supporting information of Liang et al. (2013) that compiles various Chinese official statistics on emissions.

arsenic data we can collect and compile are roughly grouped into the following categories: (1) data on production, consumption, trade, and arsenic contents of arsenic-containing ores and products, (2) data on loss or emission rates of arsenic from different anthropogenic processes, and (3) data on lifespans of intentionally used arsenic final products in the Use stage. Several methods can be applied for estimating arsenic stocks and flows: (1) analysis based on statistical data of arsenic compounds; (2) analysis based on data for other element (X) by applying an As-X correlation coefficients; (3) modeling to estimate discard flows and in-use stocks; and (4) deduced by mass balance.

There are some significant features of AACs that can be summarized: (1) existing studies reveal that AACs at Earth's surface is at the same order of magnitudes as its natural cycles and are driven by both intentional and unintentional uses; (2) arsenic can be mined and extracted from natural ores as a desired host element, but mostly is mined as a companion element (namely, a by-product) of other metals or fossil fuels; and there is enough supply of arsenic, because arsenic in many cases is an unwanted impurity; (3) China owns the majority of arsenic reserves and is the biggest producer of arsenic today, while U.S. was the biggest user of arsenic in the whole 20th century; (4) there were several waves of rise and fall of intentional arsenic use in the 20th century of U.S., with the rises driven by different applications of arsenic (such as glass making in the 1900s, agricultural applications in the 1920s, and wood preservatives in the 1970s), and the falls mainly resulting from the regulations in response to its toxicity: and (5) the majority of arsenic intentional uses are in the form of chemical compounds instead of single substance, and almost all intentional uses of arsenic not only are unrecyclable but also result in emissions that may last years or decades after being used.

We note that the current studies of arsenic emissions mainly focus on atmospheric emissions resulting from unintentional uses but do not pay enough attention to emissions along the life cycle related to intentional uses. We believe that filling this research gap by accounting for the AACs associated with intentional arsenic use will help identify a more complete list of arsenic emissions, to better understand the drivers and suppliers of arsenic use, and to promote more effective management and reduction of arsenic in the environment. It is both necessary and feasible that similar research framework be developed for several other elements, such as mercury, chromium, and cadmium, of which the anthropogenic cycles are also driven by both intentional and unintentional uses.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jclepro.2016.08.050.

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