The Global Biogeochemical Cycle of Arsenic

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Abstract Direct exploitation and use of arsenic resources has diminished in recent years, but inadvertent mobilizations of As from mineral extractions (metal ores, coal, and phosphate rock) are now as much as ten-fold greater (1,500–5,600 × 10⁹ g/yr) than the As released by the natural rate of rock weathering at the Earth's surface (60–544 × 10⁹ g/yr). Although some As from mining activities enters global cycling through leaching and spills, the amount of dissolved As in rivers (23 × 10⁹ g/yr) is similar to the theoretical mobilization of As from chemical weathering. Anthropogenic emissions to the atmosphere (17–38 × 10⁹ g As/yr) are double the natural background sources (10–25 × 10⁹ g As/yr), largely as a result of the smelting of Cu and other non-ferrous ores. This results in increased atmospheric deposition near regions with high mining and industrial activities, with potential consequences to human health, natural ecosystems and agriculture. Using median values for As, the ratio of anthropogenic to natural emissions to the atmosphere (1.57) suggests a human impact on the global As cycle that rivals those for V, Hg and Pb.

Plain Language Summary This paper compares the human mobilization of arsenic at the Earth's surface to the underlying natural flux of arsenic from rock weathering, volcanoes and other processes. Humans have roughly doubled the emission of As to the atmosphere and substantially increased the As moving in freshwaters to the sea.

1. Introduction

History and literature are replete with stories of acute arsenic poisoning, often from inadvertent exposure and sometimes for murder. Long-term human exposure to As is associated with cancers and various skin, neurological and cardiovascular diseases (e.g., Rahaman et al., 2021). Exposure of humans and ecosystems to elevated As levels can result from geogenic processes or anthropogenic activities, or combinations of the two. Today, in the developed world, many of the human activities that once mobilized As to the environment have been curtailed, including its widespread use in agricultural chemicals and wood preservatives. Globally, about 45,000 metric tons (=45 × 10⁹ g) of As are currently recovered for commercial use each year, primarily as a by-product of mining and refining activities (USGS, 2022). Production and emissions of As have declined during the past several decades, owing to concerns for its toxicity and to the development of substitute materials (e.g., Meharg & Meharg, 2021; USGS, 2022). However, renewed interest grows from a potential role for As in electronics and photovoltaics as a gallium-arsenide compound.

Arsenic is found in the Earth’s upper continental crust at an average concentration of 4.8 μg/g (ppm; Rudnick & Gao, 2014), but in areas of soil contamination, concentrations >300 μg/g have been reported (Michopoulos, 2021). Arsenic often co-occurs with Cu- and S-bearing minerals. In soils and rocks, it occurs as both arsenite (As³⁺), which is highly toxic and mobile, and arsenate (As⁵⁺), which often binds to various Fe oxide minerals (Smedley & Kinniburgh, 2002). The concentrations of inorganic As species in aquatic solution are in equilibrium with their oxidized forms (As₂O₃ and As₂O₅, respectively), as determined by redox potential and pH. In low redox conditions, such as suboxic groundwater in deltaic aquifers, arsenate is reduced to arsenite, whereas in oxic and typically also alkaline groundwater, arsenate is the predominant species. Elevated levels of As in groundwater pose major health risks to an estimated 200 million people who depend upon groundwater as their major source for drinking water and irrigation (Bundschuh et al., 2012; Harvey et al., 2002; Mukherjee et al., 2020; Nordstrom, 2002; Podgorski & Berg, 2020; Shaji et al., 2021).

Arsenic plays no essential role in biochemistry, yet because it lies directly below the biologically essential element P on the periodic table, the two share a number of chemical properties. Arsenic has been explored as a proxy to investigate P-limitation in seawater (Wurl et al., 2013), and it is a trace constituent in marine phosphate rock, which is the main source of P in fertilizers applied to croplands (Smedley & Kinniburgh, 2002). It also serves as

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a metabolic electron acceptor, and can be reduced to several methylated forms known as methylarsine gases that are volatilized to the atmosphere from wet soils and seawater (Zhu et al., 2016). An intriguing recent report that As could substitute for P as one of the essential elements in biochemistry, especially in DNA, has been discounted (e.g., Erb et al., 2012).

This paper derives new estimates of the fluxes of As in the environment from both natural processes and human activities, the transport and circulation of As in rivers and the atmosphere, and the fate of As in the oceans (Figure 1). Drawing on data that have more recently become available, we provide an update of previous treatments of the global biogeochemistry of As by Chilvers and Peterson (1987), Matschullat (2000), Matschullat and Deschamps (2011), and Wenzel (2013), and incorporate the comprehensive evaluation of As in soils by Meharg and Meharg (2021). We standardize all flux estimates in the units of $10^9$ g As/yr, and attempt to provide estimates of uncertainty, particularly for the larger values.

2. Anthropogenic Mobilization of Arsenic

During the first half of the 20th century, As production and imports in the United States increased rapidly to $\sim 22 \times 10^9$ g/yr, largely for use in the manufacture of glass and agricultural insecticides and herbicides (Brooks, 2010; W. Q. Chen et al., 2016; Loebenstein, 1994). With growing concern about its environmental and health impacts and increasing environmental regulations (e.g., Jones, 2007; NTP, 2021), the use of As in these industries declined, and domestic As production ended in 1985. This was followed, however, by a sharp increase in its use primarily for the manufacture of chromated copper arsenide (CCA) wood preservatives, which in the 1990s accounted for $>85\%$ of As consumption in the US. A voluntary phase-out of CCA-treated wood for residential purposes led to a rapid decline in As use after 2003. As of 2021, apparent As consumption in the US was $6.8 \times 10^9$ g/yr (all imported), for manufacture of non-residential CCA-treated wood, some herbicides and pesticides, lead-acid batteries, metal alloys, and semiconductor technologies (USGS, 2022). Essentially none of the arsenic in these uses is recovered and recycled (Poncelet et al., 2022).

In developed countries, airborne As emissions, primarily from the production of glass and copper, have been curtailed by strict emissions standards (e.g., USEPA, 1986). Longitudinal studies show declining As deposition from the atmosphere in North America (Wiklund et al., 2020) and Europe (Kyllönen et al., 2009), and lower concentrations in recent deposits in peatbogs and mosses in these areas (Meharg & Meharg, 2021). Spatial
heterogeneity in As deposition persists (Jovan et al., 2022), with high concentrations of As in drinking water associated with low-income communities (Nigra et al., 2022). In other world areas, mining and other activities have increased As mobilization, accounting for the large differences in atmospheric deposition in South America and Asia compared to North America and Europe (Table 1; L. Zhang et al., 2020). In 2020 world production of As, mostly in Peru (45% of global production), China (40%) and Morocco (13%), was ~45,000 mt/yr (45 × 10^6 g/yr), largely derived from As recovered during refining of Cu and other ores (USGS, 2022).

### 2.1. Arsenic Mobilized by Processing of Copper and Other Non-Ferrous Metal Ores

#### 2.1.1. Copper

Copper production has long been cited as the dominant anthropogenic source of As in the environment, with particular attention focused on atmospheric emissions during copper smelting. Arsenic boils at 613°C, making the melting of Cu a major source of gaseous (arsine) and particulate As in the atmosphere.

##### 2.1.1.1. Arsenic in Copper Ore: Gross Mobilization Estimate

Primary copper production begins with the extraction of ores containing copper sulfide and other copper-bearing minerals (Figure 2). Production involves a series of physical and chemical processes that vary from region to region based on factors such as the characteristics of the ore deposit, local industrial practices, and regulations (e.g., Haldar, 2018). Because ~80% of current primary (from ore) copper output is produced by pyrometallurgical processes (e.g., Terrones-Saeta et al., 2020), for the purpose of estimating global As mobilization, we focus on that process, but note that hydrometallurgical processing (e.g., solvent extraction and electrowinning, or SX-EW) contributes ~20% to refined production from ore.

About 20.4 × 10^12 g of copper was produced in 2019 (USGS, 2022) from virgin ore with an average Cu grade of ~0.6 wt.% (e.g., Dong et al., 2020; Northey et al., 2014). Copper losses during beneficiation and production are estimated at ~16% (Glöser et al., 2013; Lifset et al., 2002), from which we estimate annual extraction of 24.3 × 10^12 g of Cu from 4.05 × 10^15 g of ore (Figures 1 and 2). This estimate of Cu extraction is consistent with the value of 15 × 10^12 g/yr calculated by Rauch and Pacyna (2009) for production in the year 2000, adjusting for increased production in recent years. The relatively few published estimates of As concentrations in copper ores vary widely — from 40 to >2,000 μg/g (Bruckard et al., 2010; Edelstein, 1985; Renman et al., 2006; M. O. Schwartz, 1995; Sokić et al., 2015; Tayebi-Khorami et al., 2017; Tylecote et al., 1977). Moats et al. (2021) note that the As/Cu ratio of typical ores range from about 0.03 to 0.2. Using this range, and the average Cu ore grade and masses above, we estimate 180–1,200 μg/g As in copper ores, and gross As mobilized by copper mining of 729–4,860 × 10^9 g/yr. Note that for simplicity, we assume that refining of recycled copper, about 3.9 × 10^12 g in 2020 (World Copper Factbook, 2021), does not mobilize significant additional As.

##### 2.1.1.2. Arsenic in Copper Concentrate (See Supporting Information S1)

Copper ores are normally beneficiated at the mine site to produce copper concentrates with 10%–40% Cu (USGS, 2022) and a current global average of ~27% (ICSG, 2021a, 2021b). A recent global compilation of copper concentrates for 2016–2019 (ICSG, 2021a) reported average annual production of ~61.3 × 10^12 g concentrate, containing at least 16.5 × 10^12 g Cu (27 wt.%) and 173 × 10^6 g As (average As concentration of 2,800 μg/g).

We can independently estimate the amount of As mobilized during smelting and refining because reliable data are available for pyrometallurgical processing of copper concentrate (Figure 2). Copper concentrate is smelted and processed to produce copper anode of ~99.2 wt.% Cu. Analyzing a selection of global anode samples, Moats et al. (2021) reported a weighted average As concentration of 1,239 μg/g, from which they estimate that globally ~25 × 10^6 g/yr of As is embodied in anode. Electrorefining of copper anode produces high-purity copper cathode (>99.99 wt.% Cu) with typical As contents of ~0.2 μg/g (Moats et al., 2019). Assuming 20.4 × 10^12 g/yr of Cu cathode produced, which includes hydrometallurgical as well as pyrometallurgical production, As in copper cathode amounts to a trivial flux of ~4 × 10^6 g/yr. Thus, essentially all of the 173 × 10^6 g/yr of As in copper concentrate ultimately ends in the wastes from smelting and refining (see below).

##### 2.1.1.3. Airborne Emissions During Copper Smelting

To estimate current global As emissions to the atmosphere from Cu smelting, we calculated global Emission Factors (EFs) weighted for the main copper refining countries (USGS, 2022). Currently, China and developed
<table>
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<th>Mean annual deposition (μg/m²/year)</th>
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countries produce approximately 60% of worldwide refined copper, while Chile, Congo and other countries produce about 40% (USGS, 2022). Recent estimates of EFs for developed countries range from about 0.006 to 0.03 kg As/t Cu (Pacyna et al., 2019; J. Zhang et al., 2022). To our knowledge, no recent estimates of EFs for developing countries have been published; we therefore use the range of EFs (1–3 kg As/t Cu) that was typical of the 1980s (e.g., Chilvers & Peterson, 1987; Nriagu & Pacyna, 1988), yielding a weighted EF of 0.6 kg As/t Cu.

Using these values and global production of refined mined copper in 2019 (20.4 × 10^12 g Cu; USGS, 2022), we estimate current airborne As emissions of about 8.2–24.8 × 10^9 g/yr from Cu smelting. Interestingly, our estimate of current global atmospheric As emissions from Cu smelting is at most double estimates from decades ago (8.5–13.0 × 10^9 g/yr; Chilvers & Peterson, 1987; Nriagu & Pacyna, 1988; Walsh et al., 1979), despite the almost 3-fold increase in annual copper production, declining copper ore grade, and increasing As content of copper concentrate (Yamazaki, 2018). The relatively moderate increase in As airborne emissions over time can be attributed to significantly improved As capture technologies and greater regulation implemented by China and other developed nations (e.g., Meharg & Meharg, 2021). Nevertheless, despite

<table>
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<th>Location</th>
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*In most cases the concentration of As in precipitation samples reflects dissolution of the accumulated dry deposition in an open funnel by the collected rainwater. Deposition includes both wetfall and dryfall, for which Savage et al. (2019) indicate that dryfall typically accounts for about one-third of the total. *Recalculated from original source.
well-documented improvements in the capture of airborne emissions, atmospheric arsenic emissions during copper production remain a significant challenge in a number of countries (e.g., Aminiyan et al., 2021; Pérez et al., 2021; Serbula et al., 2017; L. Zhang et al., 2020).

2.1.1.4. Arsenic in Solid and Aqueous Wastes From Copper Production

We estimate above that globally 729–4,860 × 10^9 g/yr of As is mobilized from copper mining. It is likely that a large fraction of the 45 × 10^9 g As/yr recovered globally for commercial purposes (USGS, 2022) comes from copper production; in the absence of published estimates, we assume that 75% (~34 × 10^9 g As/yr) is recovered during copper production. In addition, 8.2–24.8 × 10^9 g/yr is dissipated as airborne emissions, as described above; and a trivial amount ends in refined copper (Figure 1). Thus, we estimate that approximately 670–4,820 × 10^9 g/yr of As appears to reside in solid and aqueous wastes, such as mill tailings (gangue), leachates, slags (dross), dusts, anode slime, and electrolytes. While a number of these wastes are reprocessed to recover Cu and other metals of economic value (e.g., Falagán et al., 2017; Moats et al., 2021), the remainder is primarily disposed of in tailing ponds, slag ponds, and landfills (e.g., W. Q. Chen et al., 2016; Kalisz et al., 2022; Nazari et al., 2017; Shi et al., 2017), which pose a risk of As mobilization from these residual materials to the environment (e.g., Bortnikova et al., 2021; M. A. Taggart et al., 2006). We see no way to provide an estimate of this leakage with the available data.

2.1.2. Other Non-Ferrous Metals

Arsenic is also mobilized by the production of non-ferrous metals, particularly Pb and Zn, and other sulfide-hosted metals (e.g., Ni, Sn, Au, Ag and Hg). Previously published estimates of atmospheric As emissions vary widely and are based decades-old data (e.g., Chilvers & Peterson, 1987; Pacyna & Pacyna, 2001). Unfortunately, current mass flow data and information on production practices for these metals are even more sparse than for copper. Acknowledging these uncertainties, we attempt to estimate As mobilization during the mining and production of Pb and Zn—the two non-ferrous metals (after copper) believed to contribute most to As mobilization (e.g., Chilvers & Peterson, 1987; Pacyna & Pacyna, 2001).
Global Pb and Zn extracted in ores in 2020 are estimated as $4.4 \times 10^{12}$ and $1.2 \times 10^{13}$ g/yr, respectively (USGS, 2022). Sparse available data suggest average As/metal (wt.%) ratios in these ores of 0.037 and 0.011, respectively (Gul et al., 2013; Mikulski et al., 2020). From these, we estimate combined As mobilization in Pb and Zn ores of $292 \times 10^9$ g/yr. This would add an additional $\sim 6$–40% As to the range we estimated above for Cu ore ($729$–$4.860 \times 10^9$ g/yr). It should be noted, however, that because these metals are often mined from the same ore deposit, our approach may overestimate embodied As. As for Cu, most of the As mobilized through mining is presumed to accumulate in mine waste and mill waste tailings, as only a small fraction resides in the beneficiated metal concentrate (e.g., Blowes et al., 2014; Shi et al., 2017).

Some data are publicly available on the compositions of Pb and Zn concentrates, from which we can estimate As fluxes during concentrate processing and atmospheric emissions during smelting. Ratios of As/metal (wt.%) in Pb and Zn concentrates average 0.0026 and 0.0015, respectively (W. Q. Chen et al., 2016; Gashi et al., 2017; Gul et al., 2013). We estimate the average metal contained in each concentrate using typical percentages of each metal in concentrate (60% and 50% for Pb and Zn; W. Q. Chen et al., 2016; Gashi et al., 2017; Gul et al., 2013) and 2020 primary metal production values ($4.4 \times 10^{12}$ and $1.2 \times 10^{13}$ g/yr, respectively; USGS, 2022), yielding estimates of the Pb and Zn in each concentrate of $7.33 \times 10^9$ and $2.40 \times 10^9$ g/yr, respectively. With these values, we calculate combined As mobilization of $\sim 55 \times 10^9$ g/yr from these metals. The limited available data on airborne As emissions during processing of Pb and Zn concentrates vary widely, averaging 0.23 and 0.19 kg As per metric ton metal produced (Chilvers & Peterson, 1987; Pacyna & Pacyna, 2001; Sha et al., 2019; Skeaff & Dubreuil, 1997), suggesting combined airborne As emissions of $\sim 3 \times 10^9$ g/yr. This is $\sim 20\%$ of the mean of our range of As emissions from Cu smelting—consistent with previous work suggesting that smelting of these non-ferrous metals adds about 20% to the airborne emissions released by copper (e.g., W. Q. Chen et al., 2016; Shi et al., 2017). Further, in contrast to the findings of Chilvers and Peterson (1987), our calculations suggest that atmospheric emissions from Zn processing now dominate (69%) over in those from Pb, consistent with the steeper increase in Zn primary production compared to that for Pb in recent decades (e.g., Grandell & Höök, 2015).

### 2.1.3. Iron

Arsenic contents in iron ores vary widely, from trace amounts to $>1,000$ μg/g (e.g., Bergman & Kolesov, 2012; Swartjes & Janssen, 2016). To calculate the gross mobilization of As associated with Fe ore extraction, we use a typical concentration of 200 μg/g, and 2020 annual Fe ore production of $\sim 2,500$ million metric tons (USGS, 2022). This suggests gross mobilization of $\sim 500 \times 10^9$ g As/yr through mining of Fe ore (Figure 3). As for Cu, to estimate the amount of As released to the atmosphere during the processing of Fe ore, we estimate a global EF weighted by country of production. China currently dominates (~63%) world production of pig iron and steel, followed by India (~5%) and a mix of developed and developing countries (USGS, 2022). EFs for China are ~0.1 g As/t metal produced (Tian et al., 2010); in the absence of published EF data for the other countries, we use the average value of 2.0 g As/t metal produced reported by Nriagu and Pacyna (1988), yielding a global weighted EF of 0.8 g As/t metal produced. This, combined with 2020 steel and pig iron production of 2,500 million metric tons (USGS, 2022), suggests global atmospheric emissions of $\sim 2 \times 10^9$ g As/yr. For comparison, estimates of airborne As emissions from Fe processing based on data from 40 years ago suggest values ranging from $0.06 \times 10^9$ g As/yr (Chilvers & Peterson, 1987) to $4.2 \times 10^9$ g As/yr (Nriagu & Pacyna, 1988; Walsh et al., 1979).

### 2.2. Coal Combustion

The average concentration of As in coals is estimated as 8.3 μg/g (Ketris & Yudovich, 2009; Yudovich & Ketris, 2005), with lower average values in coals from China (3.8 μg/g; Dai et al., 2012), and higher values from the US (14 μg/g; Palmer et al., 2015). To evaluate the global As flux from coal combustion, we use the As contents in coals and the relative coal production in different countries (Table 2). China, for example, produced...
Table 2

<table>
<thead>
<tr>
<th>Country</th>
<th>Coal production (million tons)</th>
<th>As (mg/kg)</th>
<th>Percent ash yield</th>
<th>Enrichment factor</th>
<th>Expected as in fly ash (mg/kg)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>3,846</td>
<td>4</td>
<td>21</td>
<td>4.8</td>
<td>19</td>
<td>M. Wang et al. (2006); Dai et al. (2012)</td>
</tr>
<tr>
<td>India</td>
<td>756</td>
<td>4</td>
<td>30</td>
<td>3.3</td>
<td>13</td>
<td>Tewalt et al. (2010)</td>
</tr>
<tr>
<td>USA</td>
<td>640</td>
<td>14</td>
<td>11</td>
<td>9.1</td>
<td>127</td>
<td>Palmer et al. (2015)</td>
</tr>
<tr>
<td>Indonesia</td>
<td>610</td>
<td>4</td>
<td>7</td>
<td>14.3</td>
<td>54</td>
<td>Tewalt et al. (2010)</td>
</tr>
<tr>
<td>Australia</td>
<td>507</td>
<td>1</td>
<td>9</td>
<td>10.8</td>
<td>11</td>
<td>Tewalt et al. (2010)</td>
</tr>
<tr>
<td>Russia</td>
<td>440</td>
<td>2</td>
<td>10</td>
<td>10</td>
<td>15</td>
<td>Tewalt et al. (2010)</td>
</tr>
<tr>
<td>S. Africa</td>
<td>254</td>
<td>2</td>
<td>20</td>
<td>5</td>
<td>12</td>
<td>Tewalt et al. (2010)</td>
</tr>
<tr>
<td>Rest of World</td>
<td>1,075</td>
<td>8</td>
<td>20</td>
<td>5</td>
<td>42</td>
<td>Dai et al. (2012)</td>
</tr>
<tr>
<td>Total or Mean</td>
<td>8,129</td>
<td>5</td>
<td>19</td>
<td>5.4</td>
<td>27</td>
<td></td>
</tr>
</tbody>
</table>

3,486 million tons in 2019, which is equivalent to 47% of global coal production (British Petroleum, 2020). Data on As in coals in China indicate relatively similar concentrations among the different coal basins (M. Wang et al., 2006). Based on As data from the major global coal producers, we estimate a mean global As content of 5 μg/g (Table 2). Given the increase in the global production of coal, up to 8,129 million tons in 2019 (British Petroleum, 2020), the global mobilization of As from coal combustion has doubled from ∼20 × 10^9 g/yr in the early 1980s to 38 × 10^9 g/yr in 2019 (Figure 4). These estimates are consistent with earlier estimates made by Han et al. (2003) of 25 × 10^9 g/yr in 2000.

Arsenic is readily volatilized in the furnace during coal combustion, but condenses downstream with condensation of flue gas on fly ash particles (Clarke, 1993; Meij, 1993; Meij & Te Winkel, 2009; Swaine, 1994). A comparison of the median As concentrations in coals from the three major basins in the US (Palmer et al., 2015) to As contents in corresponding fly ashes reported by R. K. Taggart et al. (2016) shows an approximate 8-fold enrichment, with As median values of 107, 98, and 24 μg/g in fly ash originated from coals of the eastern, central and western US basins, respectively (Figure 5). This enrichment is consistent with the theoretical As enrichment in fly ash, given that US coals typically have ash contents of 9%–10% (Palmer et al., 2015).

Similar dependence of the As enrichment in fly ash on the ash content of the feed coals has been reported for coal–fly ash comparisons from India (Pandey et al., 2011), which have an average fly ash As content of 47 μg/g (Sharma & Tripathi, 2008). But in other world regions the As content in fly ash was found to be lower than that expected based on the ash content of the coals (Dai et al., 2010; K. Luo et al., 2004; Zielinski et al., 2007), possibly as a result of lower rates of As adsorption onto fly ash during coal combustion.

K. Luo et al. (2004) investigated atmospheric emissions of As from various coal-fired power plants in China and found the proportion of the As emitted to the atmosphere relative to that in the combusted coal ranged from 3% (for low- or medium-temperature power plants) to 7.7% (for high-temperature plants). Using their integrated mean of 6.5% and global coal production (Figure 4), we estimate that global atmospheric As emissions from coal-fired power plants increased from 1.3 × 10^9 g/yr in the early 1980s to 2.5 × 10^9 g/yr in 2019. Yet this approach does not include the contribution from the industrial sector, which in China constitutes about 45% of coal consumption (You & Xu, 2010). Based on data for China in 2007, Tian et al. (2010) estimated the total atmospheric emission of As from coal combustion was 2.2 × 10^9 g/yr.
The annual worldwide production of coal combustion residuals (CCRs), including fly ash and bottom ash, is estimated at 1,222 million tons/yr, which corresponds to ~15% of the total global mass of coal burned (Harris et al., 2019). In order to calculate the expected As concentration in CCRs, we estimated the percentage contribution to global coal combustion for each of the major coal-producing regions (Table 2). For each region, we used averages of the As concentrations in their parent coals and their percentage ash yields, and assumed that As in their CCRs is proportionally enriched as a function of the percent ash yield (as demonstrated for US fly ash; Figure 5). This calculation yields a mean As concentration of 27 μg/g in global CCRs (Table 2).

In many countries, CCRs are repurposed, particularly for concrete, cement, and structural fill (Gollakota et al., 2019; Harris et al., 2019; L. Luo et al., 2020). The relative fraction of utilized CCR varies among countries, from 38% in India to 70% in China (Gollakota et al., 2019; Yao et al., 2015). Based on the differential reuse of coal ash in major countries, we estimate that in 2019, 64% of global CCRs (782 × 10^12 g) were reused, while the remaining 440 × 10^12 g of CCRs were disposed of in coal ash impoundments and landfills. Given that the reuse of CCRs has occurred only during the last few decades, one would expect that in the early 1980s the majority of As flux was contained in CCR disposal wastes, which would be equivalent to ~19 × 10^9 g/yr (calculated based on global coal production, coal ash yield, arsenic in CCRs, and ignoring the atmospheric emission). Recent CCR disposal, which amounts to only 36% of the global CCRs produced, contains an As flux of 14 × 10^9 g/yr, within which the industrial and power sectors represented respectively 61.2% and 25.9% of China’s total As emissions. Coal production in China in 2007 was 2,760 million tons, which has increased 1.4-fold to 3,902 million tons in 2020 (British Petroleum, 2020). Given that the atmospheric emission of As from coal combustion is directly tied to overall coal utilization, we extrapolate from the 2007 emissions data for China to estimate the total global As emissions from coal combustion, based on global coal production data (British Petroleum, 2020). We estimate that total global As emissions from coal combustion for combined power and industry sectors increased from 5.3 × 10^9 g/year in 2007 to 6.2 × 10^9 g/yr in 2020 (Figure 4). Since this estimate is based on data for China and the use of coal for the industrial or power sectors varies by country, we present two scenarios of global As atmospheric emissions: a lower estimate based on coal power plants alone, and an upper estimate that combines power and industrial sectors (Figure 4).

The capture of As from flue gas depends on the use and efficiency of electrostatic precipitators (ESPs) and fabric filters installed in coal plants. While in many countries the installation of these scrubber systems is mandatory to prevent the fugitive emission of fly ash particles, numerous studies have reported release of fly ash particles to the atmosphere and deposition on surface soils, for example, in India (Mandal & Sengupta, 2006; Praharaj et al., 2003), China (M. Huang et al., 2018; Lu et al., 2013; Tang et al., 2008; L. Zhang et al., 2020), and the US (Sears & Zierold, 2017; Z. Wang et al., 2021; Zierold & Odoh, 2020). In some areas of China, the prevalence of arsenicism in populations that live near coal power plants (J. Chen et al., 2014), suggests long-term transmission of As to the environment.

Laboratory experiments have shown that As is easily mobilized from CCRs into aqueous phases and becomes enriched in the CCR-leachates (Izquierdo & Querol, 2012; Kosson et al., 2002; Thorneloe et al., 2010). X-ray absorption spectroscopy indicates that the majority (92%–97%) of total As in fly ash occurred as arsenate [As(V)], while the remainder is present as arsenite [As(III)] (Deonarine et al., 2016). The magnitude of As mobilization from fly ash depends on the ambient redox and pH conditions, as well as the liquid to solid ratio (L/S) (Deonarine et al., 2016; Harkness et al., 2016; Pandey et al., 2011; G. E. Schwartz et al., 2016, 2018). Under anoxic conditions, reductive dissolution of As-bearing phases such as iron ferrihydrite results in high dissolved As concentration compared to oxic conditions that foster reprecipitation of iron arsenate (Deonarine et al., 2016). The high mobilization of As under reducing conditions has been demonstrated in reduced groundwater underlying leaking coal ash impoundments (Harkness et al., 2016) and porewater associated with lake sediments contaminated by coal ash discharges in North Carolina (Z. Wang et al., 2022). Due to the buffering capacity of CCRs, arsenic redissolution in the porewater is limited.
the interaction of fly ash with water would increase the pH in the leaching environment. Under alkaline (high-pH) conditions, the magnitude of As mobilization would increase, leading to water contamination (Nordstrom, 2002; Plant et al., 2009; Smedley & Kinniburgh, 2002). The mobilization of As from coal ash under alkaline conditions is one of the key limiting factors for the ability to use fly ash as a medium for neutralization of acid mine drainage (Weinberg et al., 2022).

The USEPA (2015) has analyzed the chemistry of CCR wastewater from 150 sites in the US and reported extremely high concentrations of As in wastewater from flue gas desulfurization (FGD) (median value of 507 μg/L), fly ash (36.4 μg/L), and bottom ash (17.4 μg/L). Consistently, elevated levels of As in CCR effluents discharged from coal ash ponds to the environment have been reported in North Carolina, with concentrations up to 90 μg/L (Ruhl et al., 2012). In 2009, the volume of wastewater discharged to CCR impoundments in the US was 2.5 × 10^6 m³, whereas the wastewater discharge from the coal ash impoundments to the environment was estimated as 543 × 10^6 m³ for fly ash wastewater (from 113 plants) and 802 × 10^6 m³/yr for bottom ash (283 plants), for a total of 1.3 × 10^9 m³ of CCR wastewater (USEPA, 2015). At that time, the US annual coal production was 975 × 10^6 tons, which is equivalent to 13.8% of global coal production (British Petroleum, 2020). While the practice of coal ash management varies by country, we calculate an estimate for the US for As flux to the environment (0.03 × 10^9 g/yr) as a reference for global discharge of CCR effluents. Given that US coal production was 13.8% of the global total in 2009, we estimate a global As flux to the hydrosphere from coal ash effluents as 0.24 × 10^9 g/yr. This flux may be an underestimation of the true mobilization of As to the environment through CCR effluent discharge, given that CCR management practices vary in different countries, and extrapolation from the US may not provide an accurate estimate of the global volume of CCR effluent flux.

In addition to the regular discharge of CCR effluents, numerous studies have demonstrated that leakage and spills of both effluent and solids from coal ash ponds cause further As fluxes to the hydrosphere (Brandt et al., 2018; Harkness et al., 2016; Ruhl et al., 2009, 2010, 2012; Vengosh et al., 2019). Seepage from the bottom of coal ash ponds is likely to occur under reducing conditions, in which As in the form of As^3+ is expected to be preferentially mobilized and enriched in the underlying groundwater (up to 600 μg/L; Harkness et al., 2016). Leaching experiments using the water-soluble As from fly ash originating from combustion of the major coal sources in the US yielded As concentrations of 0.3 μg/g to 0.7 μg/g (Z. Wang et al., 2020), which reflects mobilization of ∼1% of the total As in the fly ash (with ∼110 μg/g). Using the predicted As concentration in global CCRs (27 μg/g; Table 2) and the estimated global quantity of disposed CCRs (440 × 10^6 tons), we calculate that 14 × 10^9 g As/yr is temporarily stored in CCR impoundments or released to the environment. Assuming that 1% of fly ash As is mobilized into the aqueous phase, this suggests that 0.14 × 10^9 g As/yr is mobilized into aquatic systems. This estimate is consistent with our independent estimate above for As mobilized through disposal of CCR effluents (0.24 × 10^9 g/yr). It is important to emphasize, however, that these estimates refer only to mobilization of As in the liquid phase from CCRs in storage sites such as coal ash impoundments. Solid coal ash particles from storage sites can be transported during flooding events and accumulate in sediments of nearby lakes (Vengosh et al., 2019), and represent an additional route that As in CCRs may enter the hydrosphere.

2.3. Arsenic in Petroleum

Arsenic occurs in crude oil at concentrations of 0.1–0.9 μg/g with an average of 0.23 μg/g (Schreiber & Cozzarelli, 2021). Based on 2020 global crude oil production of ~5.2 × 10^15 g (British Petroleum, 2020), we estimate As flux from the combustion of petroleum as ~1.2 × 10^9 g/yr in 2020. This estimate is roughly consistent with the earlier estimate made by Han et al. (2003) of 0.9 × 10^9 g/yr for the year 2000, adjusting for subsequently increased oil production.

The production of oil and gas is accompanied by produced water that becomes oil and gas wastewater. Reported data for As concentrations in oil-produced water vary between 0.03 mg/L to 0.7 mg/L (average of 0.23 mg/L), whereas flowback waters from unconventional shale gas and tight gas wells range from 0.01 mg/L to 0.07 mg/L (Schreiber & Cozzarelli, 2021). Clark and Veil (2009) and Grubert and Sanders (2018) estimated an average produced water-to-oil ratio in the U.S of ~5:1 and 8:1, respectively, but global estimates are lower, typically 3:1 (Ahmadun et al., 2009). Using the global water-to-oil ratio and a mean As concentration of 0.23 mg/L in oil-produced water, and oil production of 5.1 × 10^9 m³ in 2020 (British Petroleum, 2020), we calculate an As flux in oil-produced water of 3.4 × 10^9 g/yr. Given that off-shore produced water comprises about 30% of global
produced water (Dal Ferro & Smith, 2007) and the absence of treatment of produced water generated offshore, we estimate the release of ~1 × 10⁹ g As/yr to the oceans and the remainder disposed of on land.

For natural gas, the volume ratio of produced water to conventional gas production in the US is estimated as 2.4 × 10⁻², using data from Grubert and Sanders (2018). Assuming that this ratio applies globally, and global natural gas production of 3.850 × 10⁹ m³ in 2020 (British Petroleum, 2020) suggests a volume of produced water of 0.77 × 10⁹ m³, approximately 17-fold less than that of oil-produced water. Using the same As concentration of 0.04 mg/L reported for flowback waters from shale gas (Schreiber & Cozzarelli, 2021), the As flux from produced water co-extracted with natural gas is negligible (1.5–4.2 × 10⁷ g/yr) and thus insignificant among anthropogenic contributions.

Schreiber and Cozzarelli (2021) highlighted the risk of As mobilization to the environment from oil spills. In the early 2000s, about 800,000 m³ of petroleum entered the sea each year from the extraction, transportation, and consumption of crude oil and the products refined from it, with an additional 680,000 m³ derived from seepage (Board & Council, 2003), although the magnitude of spills at sea has been reduced in recent years (J. Chen et al., 2019). The transition to unconventional oil and gas exploration in the US has been associated with a higher frequency of oil spills, as occurred in the Williston Basin in North Dakota and the Permian Basin in New Mexico (Lauer et al., 2016). The US Office of Pipeline Safety estimated that an average of 83 crude oil spills occurred per year between 1994 and 1996 in the United States, with an annual spill volume of 3.4 million barrels (Delin et al., 1998). The infiltration of spilled oil into underlying aquifers, combined with associated low redox conditions, induces As mobilization from the host-aquifer sediments and rocks, and consequently indirect contamination of groundwater from oil spills (Ziegler et al., 2017).

2.4. Mobilization of Arsenic in Phosphorus Fertilizers

Most of the phosphorus in fertilizer is derived from phosphate rocks, with As concentrations ranging from ~3 to 100 µg/g (e.g., Boyle & Jonasson, 1973; Jiao et al., 2012; Macedo et al., 2009). Using a mean concentration of 20 µg/g and 2021 global phosphate rock mine production of 220 million metric tons (USGS, 2022), we estimate current annual As mobilization of 4.0 × 10⁹ g/yr. Given that most of the As from phosphate rock is incorporated into phosphate fertilizers (USGS, 2022), we assume that As from phosphate fertilizers is released directly on agricultural lands, causing some As accumulation in soils and release of As in runoff and potentially to underlying groundwater (Hartley et al., 2013; Jiao et al., 2012).

2.5. Groundwater Extraction

Inorganic As occurs in natural waters as an oxyanion, either as trivalent arsenite [As(III)] under reducing conditions or pentavalent arsenate [As(V)] under oxidizing conditions. At pH below ~9, the reduced arsenic species is chargeless (H₃AsO₄Ο⁻), and therefore highly mobile in the aquatic phase. Reductive dissolution of As-bearing iron oxides results in elevated As levels in groundwater from reduced aquifers, such as the deltaic aquifers of the major rivers of Southeast Asia (Charlet & Polya, 2006; Fendorf et al., 2008; Mukherjee et al., 2020; Polizzotto et al., 2008). The accumulation of organic matter and prevailing reducing conditions trigger microbial dissolution of As-bearing iron oxides and lead to high solubility of the chargeless As(III) in the shallow groundwater of these aquifers (Amini et al., 2008; Fendorf et al., 2008; Nordstrom, 2002; Plant et al., 2009).

At the same time, however, the adsorption of the oxic species arsenate in the form of H₃AsO₄Ο⁻ (pH <~7) and HAsO₄Ο₂⁻ decreases with increasing pH, and therefore elevated As levels can also occur in shallow, alkaline, and oxic groundwater induced desorption of As from iron and aluminum hydroxides (Charlet & Polya, 2006; Fendorf et al., 2008; Mukherjee et al., 2020; Nordstrom, 2002; Plant et al., 2009; Polizzotto et al., 2008; Smedley & Kinniburgh, 2002). Thus, elevated As concentration have been reported in a wide range of geographic settings and aquifer lithology (Mukherjee et al., 2020; Podgorski & Berg, 2020). Interestingly, the global occurrence of groundwater with As >10 µg/L is more prevalent in oxic and high-pH aquifers in the form of dissolved As(V) relative to anoxic aquifers with As (III) (Amini et al., 2008), such as the Chaco-Pampean Plain in Argentina (Bundschuh et al., 2004) and similar aquifers composed of volcanic rocks in Southern and Central America (Bundschuh et al., 2012).
The majority (>90%) of global groundwater withdrawal is used in the agriculture sector. However, given the high toxicity and carcinogenic effects of As, many surveys of the occurrence of As in groundwater have focused on domestic water supplies and the risks to populations (Bundschuh et al., 2012; Mukherjee et al., 2020; Nordstrom, 2002; Podgorski & Berg, 2020). Arsenic levels exceeding the health benchmark of 10 μg/L have been reported in numerous aquifers across southeast Asia and Southern and Central America, with an estimate of 94 million to 220 million people potentially exposed to high As in groundwater (Podgorski & Berg, 2020). While it has been demonstrated that the reduced As species (arsenite) is more toxic to human health than the oxidized (arsenate) species (Campbell & Nordstrom, 2014), drinking water regulations do not specify the As speciation but instead refer to the total As content in the water (e.g., the Maximum Contaminant Level standard in the US is 10 μg/L).

Based on the mean As concentrations in groundwater reported in large datasets from different countries (e.g., n = 50,625 for USA; n = 123,436 for India, n = 3,450 for China; Podgorski & Berg, 2020) and estimates of global annual groundwater extraction (900 × 10^9/yr; Margat & van der Gun, 2013; Mukherjee et al., 2020; Wada et al., 2010, 2012), we estimate a global As flux of 30 × 10^6 g/yr from groundwater extraction. Most (~90%) of the extracted As from groundwater is used for irrigation on agricultural soils and delivered to surface freshwater bodies.

Global groundwater recharge is estimated as 12,666 km^3/yr (Döll & Fiedler, 2008; Zektser & Loaiciga, 1993). Assuming steady-state, we can assume an equal amount is discharged to river systems, which would be equivalent to 30% of the annual river flow 3.74 × 10^8 km^3/yr (Berner & Berner, 2012). Other estimates have suggested groundwater baseflow to rivers as ~10% of the total river flow (~4,000 km^3/yr; Zektser & Loaiciga, 1993). Given that the dissolved As in global rivers is estimated as 23 × 10^6 g/yr (Gaillardet et al., 2014), 10%–30%, or 2.3 to 5.1 × 10^6 g/yr, of As may enter rivers from groundwater baseflow. However, given that extensive groundwater pumping has significantly reduced the natural discharge to rivers, demonstrated for example, by the ~60% reduction of baseflow to the Ganges River in India (Mukherjee et al., 2018), these estimates likely represent the upper limit for the possible As discharge to global rivers from groundwater.

2.6. Arsenic Release During the Incineration of Municipal Solid Waste

The World Bank (2021) estimates that 2 × 10^9 tons of municipal solid waste are generated annually, 11.1% of which is disposed of via incineration. The USEPA (1998) gives an emission factor during incineration of 6 × 10^-5 lbs As/ton when not subjected to pollution abatement, suggesting that 0.67 × 10^9 g As are emitted to the atmosphere each year globally. Most incinerators in the developed world, where about one-third of such wastes are generated (World Bank, 2021), are equipped with scrubbers, which would reduce the net emissions from this source to about 0.45 × 10^9 g As/yr.

3. Natural Biogeochemical Cycle of Arsenic

3.1. Natural Sedimentary Flux to the Oceans

A gross estimate of As mobilization by chemical weathering can be derived using estimates of the global transport of total dissolved solids in rivers (3.9 × 10^15 g/yr; Garrels & MacKenzie, 1971) and the mean concentration of As in the upper continental crust (4.8 μg/g; Rudnick & Gao, 2014), yielding a value of 18.7 × 10^9 g As/yr. For comparison, Gaillardet et al. (2014) calculated the global flux of 23 × 10^6 g/yr of As transported in the dissolved load of rivers based on their estimate of the average dissolved As concentration in rivers, 0.62 μg/L, and river discharge of 3.74 × 10^8 km^3/yr (Berner & Berner, 2012). Their value is only slightly larger than the theoretical mobilization of As from chemical weathering.

Using the mean concentration of As in the upper continental crust (4.8 μg/g) and estimates of the contemporary flux of suspended sediments to the ocean (12.6 × 10^15 g to 18.5 × 10^15 g/yr; Peucker-Ehrenbrink, 2010; Syvitski et al., 2005; Walling, 2006), we estimate that the flux of As to the oceans in the suspended load ranges from 60 × 10^7 to 89 × 10^7 g/yr. Chilvers and Peterson (1987) estimate this flux at 180 × 10^6 g As/yr, using a mean content of 14.5 μg/g in shales and clays, whereas Viers et al. (2009) estimate the average concentration of As in suspended sediment at 36.3 μg/g and a global flux of As in suspended sediments of 544 × 10^6 g/yr. This higher...
value may reflect adsorption of dissolved As from human activities on suspended sediments during transport to the sea.

3.2. Natural Fluxes to the Atmosphere

3.2.1. Volcanoes

Natural fluxes of As to the earth’s surface are believed to be dominated by terrestrial magmatism (e.g., Matschullat, 2000). Previous estimates of the global flux of As from subaerial volcanoes have typically focused on the portion of this flux to the atmosphere—extrapolating from measured As emissions from the relatively few well-studied volcanoes, despite wide global variations in volcanic As emissions. While acknowledging the uncertainties in this approach, Chilvers and Peterson (1987) suggested an atmospheric flux of $17 \times 10^9$ g As/yr, but more recently Meharg and Meharg (2021) suggested lower values of $0.2–8.5 \times 10^9$ g As/yr. Here we provide a new range of values for both subaerial and submarine volcanic systems.

3.2.1.1. Subaerial Volcanism

Subaerial volcanism transports As to the Earth’s surface in volcanic plumes, fumaroles, and magma (e.g., Henley & Berger, 2013; Mather, 2015; Signorelli, 1997). To estimate the total As flux from subaerial volcanism, we separately calculate the fluxes associated with volcanic plumes/fumaroles and those resulting from extrusive and intrusive magmatism.

Volcanic plumes are complex mixtures of solids, gases and aerosols produced by explosive eruptions that inject material into the atmosphere, leading to regional or worldwide dispersal. As a volatile element, As is released from the magma during ascent, and upon cooling within the plume is transformed by gas-to-particle conversion and condensation reactions to various gas and particulate aerosol compounds (e.g., Arndt et al., 2017; Henley & Berger, 2013; Mather, 2015). Plumes also transport As in the form of silicic ejecta (e.g., ash), and we therefore separately estimate volatile and silicic As fluxes.

Fluxes of volatile metals or semi-metals elements in volcanic plumes and fumaroles are often calculated using estimates of the ratio of the element to the well-studied flux of SO$_2$ (e.g., Hinkley et al., 1999). Using this approach, we draw on the small but growing body of plume and fumarole As/SO$_2$ (mass ratio) analyses, and extrapolate to global scale based on estimates of global volcanic SO$_2$ fluxes. Previous estimates of volcanic SO$_2$ emissions suggest values between $(13–21 \times 10^{12}$ g SO$_2$/yr; Andres & Kasgnoc, 1998; Halmer et al., 2002; Stoiber et al., 1987), but more recent multi-decadal satellite measurements suggest a higher value of $25 \times 10^{12}$ g SO$_2$/yr (Carn et al., 2016), which includes a significant contribution from passively degassing emissions. The relatively sparse As/ SO$_2$ emissions data vary widely ($2.3 \times 10^{-6}$ to $1.2 \times 10^{-3}$), with mean and median values of $2.6 \times 10^{-4}$ and $4.0 \times 10^{-5}$, respectively (Edmonds et al., 2018; Henley & Berger, 2013; Hinkley et al., 1999). While some of these studies identified contrasting As/SO$_2$ between arc and intraplate volcanoes, and between eruptive versus passively degassing emissions, these differences do not appear to be consistent across studies and we therefore do not distinguish among them. Using the range of SO$_2$ and mean and median As/SO$_2$ emissions, we estimate subaerial volcanic atmospheric flux of As as $0.5 \times 10^9$ g/yr to $7 \times 10^9$ g/yr. This range is quite similar to that suggested by Meharg and Meharg (2021), despite the different approaches used to arrive at each estimate.

Silicate ash and other ejecta also transport As to the atmosphere in volcanic plumes. To our knowledge, there are no published estimates of global annual volcanic ash emissions. Olgun et al. (2011), however, suggest a conservative value of $\sim 1.75 \times 10^{14}$ g/yr volcanic ash deposition in the Pacific Ocean, which is surrounded by most of the Earth’s explosive active volcanoes. These authors also note that Pacific ash compositions are dominated by subduction zone eruptions, and As contents in a large suite of circum-Pacific subduction zone samples suggest an average As concentration of $\sim 5.0 \mu g/g$ (Noll et al., 1996). Using these values, we estimate a global arsenic flux in volcanic ash of $\sim 0.9 \times 10^9$ g/yr. When added to the volatile atmospheric As flux determined above (based on As/SO$_2$), this suggests a total subaerial volcanic atmospheric As flux of $1.4 \times 10^9$ g/yr to $7.9 \times 10^9$ g/yr. It should be noted, however, that apart from the most explosive eruptions, much of the atmospheric As emitted by volcanism appears be deposited within tens to a few hundreds of km from its source (e.g., Ilyinskaya et al., 2017; Mather, 2015; Meharg & Meharg, 2021).
Arsenic is also transported from depth in magmas, which solidify as extrusive or intrusive igneous rocks. Concentrations of As in subaerial igneous rocks vary widely, with generally higher concentrations in arc than in intraplate volcanics (e.g., Edmonds et al., 2018; Noll et al., 1996). To estimate the flux of As partitioned into subaerial igneous rocks, we assume average As concentrations in arc and intraplate rocks of 2.3 μg/g and 1.0 μg/g, respectively (Edmonds et al., 2018; Noll et al., 1996). Combining these with estimates of magma production for arc and intraplate volcanoes (4.8 and 0.12 km³/yr, respectively; Hawkesworth et al., 2019), and an assumed average rock density of 2.9 g/cm³, we estimate a flux of 3.2 × 10⁹ g As/yr, dominated by magmatic Arsenic. The ratio of intrusive to extrusive magmatism is estimated at about 5:1 (Hawkesworth et al., 2019), so most As remains at depth (~160 × 10⁹ g As/yr), where under appropriate conditions it may be scavenged by magmatic and hydrothermal fluids, concentrated in metal ores (e.g., Henley et al., 2015; Lee & Tang, 2020), and mobilized at the surface by mining or terrestrial hydrothermal circulation (See Sections 3.1 and 3.2.1.2). In addition, biogeochemical weathering of volcanic and plutonic rocks is believed to be the primary source of natural As-enriched sedimentary aquifers and groundwaters (Mukherjee et al., 2020).

### 3.2.1.2. Submarine Volcanism and Hydrothermal Vents

A number of studies have noted that As is enriched in seawater (1.7 μg/L) relative to river water input (0.62 μg/L; e.g., Gaillardet et al., 2014), and some have suggested that submarine emissions of As-rich hydrothermal fluids may contribute to this enrichment (e.g., Breuer & Pichler, 2013). In deep water, basalt-hosted, sediment-poor hydrothermal systems (conditions along most of the mid-ocean ridge axis), cold, dense seawater percolates into the ocean crust, is heated in proximity to magma at depth, and water-rock reactions release As from the crust into the buoyant fluid that rises to the seafloor (see Breuer & Pichler, 2013, and references therein).

Elderfield and Schultz (1996) suggest As input to the oceans from axial high-temperature hydrothermal vents of 0.0067–1.05 × 10⁹ g/yr. More recently, Breuer and Pichler (2013) compiled a large data set of As concentrations in shallow- and deep-water hydrothermal fluids, including back arc, island arc, and mid-ocean ridges sites. Using an average hydrothermal fluid As concentration of 50 μg/L, these authors estimate a global As flux of 0.003–125 × 10⁹ g/yr from MOR hydrothermal systems - the wide range of which results from uncertainties in global hydrothermal fluid flow. Here, we use a more recent estimate of global axial hydrothermal fluid flow, 5.6 × 10¹⁶ to 3.75 × 10¹⁸ g/yr (German & Seyfried, 2014), and an average hydrothermal fluid As concentration of 20 μg/L (closer to mid-ocean ridge values reported by Breuer and Pichler [2013]), and estimate annual axial hydrothermal As input to the oceans of about 1.1–75 × 10⁹ g/yr. It should be noted, however, that this estimate does not include As potentially emitted through off-axis diffuse flow because data for As and other trace metals in these fluids are lacking (e.g., Baker et al., 2016). Because the fluid volume emitted as diffuse flow is believed to be orders of magnitude greater than that of axial flow (e.g., Schultz & Elderfield, 1997), even at very low As concentrations the As flux in diffuse flow could be substantial.

More important to our estimate of global As fluxes, a number of studies have shown that the vast majority of As emitted in submarine hydrothermal fluids is precipitated near or within hydrothermal vent fields (e.g., Breuer & Pichler, 2013; Fang & Wang, 2021; Feely et al., 1991). As noted by Breuer and Pichler (2013), however, data are lacking to evaluate the extent to which even a small hydrothermal input, particularly from shallow-high-As submarine vents, may contribute to the higher As concentration in seawater than in global rivers.

It is interesting to compare our estimate of As emitted in submarine hydrothermal fluids (1.1–75 × 10⁹ g/yr) with an estimate of the flux of As transported in magma from the mantle—which, at least for sediment-poor mid-ocean ridges, represents the source of As scavenged during hydrothermal circulation. About 5.6 × 10¹⁶ g of ocean crust is generated each year (calculated from Hawkesworth et al. [2019]), and basalt glasses have an average As concentrations of ~0.23 μg/g (Jenner & O’Neill, 2012), suggesting a magmatic As flux of ~13 × 10⁹ g/yr, which solidifies to form the extrusive and plutonic portions of the ocean crust. That this estimate is lower than our upper limit for As released during hydrothermal venting may be due to the various uncertainties involved in these calculations (e.g., global hydrothermal fluid flux, average hydrothermal fluid composition, etc.). There is also a possibility, however, that our use of As concentrations in erupted glasses may underestimate the true magmatic As flux from the mantle due to sulfide-melt partitioning of chalcophile elements during magma transport and cooling (e.g., Keith et al., 2017; Z. Wang & Becker, 2015).
3.3. Biomass Burning and Forest Fires

In areas remote from contamination, plant tissue contains 0.02–0.1 μg/g of As (Michopoulos, 2021). Based on the analysis of Chilvers and Peterson (1987), Matschullat (2000) estimated that 3.34 × 10^9 g/yr of As were released to the atmosphere by biomass burning worldwide. We have recalculated this estimate, using recent data for the annual consumption of plant biomass by fire (5 × 10^15 g/yr; Randerson et al., 2012) and the EF for As during combustion. For the latter we use an estimate of 8.8 × 10^-5 lbs As/ton (=4.4 × 10^-5 g As/g; USEPA, 1998) for wood combustion, resulting in an estimate for the As release from biomass burning of ~0.22 × 10^9 g/yr. We calculate an alternative estimate (0.06–0.3 × 10^9 g As/yr) using the As content of plant biomass, the amount of biomass burned globally, and an emission factor of 60% of the As in biomass, assuming that this percentage is similar to that from the combustion of coal (C. Wang et al., 2018). Both estimates are much lower than the value calculated by Matschullat (2000; Table 4). We assume that the flux from biomass burning is largely a natural process, inasmuch as fires from natural and human origins were widespread before the advent of the Industrial Revolution (Marlon et al., 2013; Ward et al., 2018).

3.4. Eolian Dusts

We calculate the atmospheric transport of As in eolian dust by multiplying the recent estimate for the transport of soil particles in the atmosphere (1.600 × 10^12 g/yr; Andreea & Rosenfeld, 2008) by the abundance of As in the upper continental crust (4.8 μg/g; Rudnick & Gao, 2003), to yield a global transport of 7.68 × 10^9 g As/yr from this process. By contrast, Chilvers and Peterson (1987) suggest a lower value for global transport of As in soil dust of 1.98 × 10^9 g As/yr.

3.5. Sea Spray

Seawater contains about 16–25 nmol/L of As (Bruland et al., 2014; Cutter et al., 2001). Thus, for seawater of average salinity (35‰), the As content of sea salt is 0.034–0.054 μg As/g. Each year about 5–10 × 10^15 g of sea salt enters the atmosphere (Andreea & Rosenfeld, 2008; Lewis & Schwartz, 2004), carrying 0.171 to 0.535 × 10^9 g of As. By contrast, Matschullat and Deschamps (2011) calculate a lower value of 0.027 × 10^9 g As/yr for this process.

3.6. Methylation and Volatilization of Arsenic From Wetlands and Rice Paddies

A variety of microorganisms can convert inorganic arsenic to arsines, including arsine (AsH3) and mono-, di-, and trimethylarsines (TMAs), with the latter often dominating the emission from reducing environments. These are analogous to methylated forms of Hg and Sn that are produced in anoxic environments (Gilmour et al., 1992; Hallas et al., 1982; Munson et al., 2018). Under reduced conditions that characterize rice paddies, soluble As in the form of the reduced As(III) is often methylated to form dimethylarsinic acid (DMA) species (Stolz et al., 2006). Both the inorganic and DMA As species are accumulated by rice, although the proportion of the two As species in rice vary geographically, with a higher proportion of inorganic As in southern eastern Asia rice (Reid et al., 2017; Zhao et al., 2013).

There are few measurements of the emission of arsines from wetlands to the atmosphere (Table 3), so any estimate of the global flux is necessarily suspect. Mestrot et al. (2011) suggest a global flux of arsine ranged from 0.42 to 1.25 × 10^9 g As/yr from wetlands, of which 0.1 × 10^9 g/yr may stem from aquifers (Maguffin et al., 2015). We estimate the flux from bogs, fens, and mires, using the global area of these ecosystems (708 × 10^6 m^2; Lehner & Doll, 2004) and a flux of 0.5 μg/m^2/day from Vriens et al. (2014) and Mestrot et al. (2011), assuming for the temperate zone that the daily flux pertains only to half of the year. The resulting global flux is 0.07 × 10^9 g As/yr. This flux is about 20% of that calculated by Meharg and Meharg (2021; 0.34 × 10^9 g As/yr), who used a much larger global surface area of peatlands (4,000 × 10^6 m^2). Rice paddies add little to the global flux of arsines from wetlands, owing to their lower emissions (Table 3), despite covering a large area (1,475 × 10^9 m^2; Matthews et al., 2012).
et al., 1991). Inasmuch as the volatilization of arsines may increase with global warming, further work on the emission of forms of methylated arsenic is urgently needed (Mueller et al., 2022).

### 3.7. Volatilization of Arsenic From Seawater

Lantzy and MacKenzie (1979) postulated a large release of As from seawater, stemming from arsines produced by microbial biomethylation in the surface ocean. Subsequently, Andreae (1980) reported limited As deposition from the atmosphere over the oceans, and thus limited emissions of gaseous arsenic from seawater (Walsh et al., 1979). Based on the measurements of Savage et al. (2018), Meharg and Meharg (2021) estimate the global volatilization of arsines from seawater as $0.70 \times 10^9$ g As/yr. Calculating a mean annual rate of volatilization from Savage et al. (0.9 nmol/m$^2$/day = 1.648 μg/m$^2$/yr), we estimate global emissions could approach $8 \times 10^9$ g/yr from the entire area of the world's oceans (∼326 × 10$^{12}$ m$^2$; Knauer, 1993). This value seems too high given the low rates of deposition of As from the atmosphere on remote islands and mid-ocean sites (Andreae, 1980; Cutter, 1993; Wurl et al., 2015, see Table 1). Savage et al. (2019) indicate the atmospheric deposition of arsines is 20% of the total over marine environments, or $3.6 \times 10^9$ g/yr (See Section 4.1). We suggest that the volatilization of arsine is likely confined to coastal areas of high marine productivity, totaling $36 \times 10^{12}$ m$^2$ and yielding $0.88 \times 10^9$ g As/yr, which is close to the estimate of Meharg and Meharg (2021). The wide range of these available estimates begs for further investigation of the volatilization of arsenic gases from seawater.
3.8. Circulation in the Biosphere

Arsenic in the biogeochemical cycle of land plants is estimated at 2.4 to 12 × 10⁹ g/yr, based on the net primary productivity (NPP) of land vegetation (∼120 × 10⁹ g/yr; Schlesinger & Bernhardt, 2020) and the As content of forest biomass (0.02–0.10 μg/g; Michopoulos, 2021). Thus, the annual uptake of As by land plants is a small fraction of the global atmospheric deposition on land (Table 4) and up to 60% of the transported As in rivers. The annual release of As to the atmosphere by forest fires is <10% of the amount of As circulating in land vegetation. The natural biogeochemical cycle of As on land is dwarfed by the activities of humans (Figure 1; Table 4).

Marine NPP is estimated at 100 × 10⁹ g/yr (Schlesinger & Bernhardt, 2020). With an average body concentration of 4 μg As/g (Chilvers & Peterson, 1987), marine phytoplankton would cycle 400 × 10⁹ g As/yr. This amounts to 0.003% of the arsenic pool in the surface waters, yielding a mean residence time of 300 years in that pool. In the oceans, the biogeochemical cycle of As is greater than the new inputs of dissolved As from the atmosphere (18 × 10⁹ g/yr) and river flow (23 × 10⁹ g As/yr). Most organic carbon is remineralized in the surface ocean, but about 15% of marine NPP sinks to the deep ocean (Falkowski, 2005). Ultimate burial of organic carbon in marine sediments is <1% of NPP, so we estimate As incorporated into biogenic sediments and phosphorites at 4 × 10⁹ g/yr.

4. Global Mass Balances

4.1. Atmospheric Mass Balance

Estimated emissions of As to the atmosphere from anthropogenic sources are dominated by emissions during the smelting of metals, especially Cu (Table 4). Total anthropogenic emissions have nearly doubled natural emissions to the atmosphere, yielding high airborne concentrations and human health effects in industrial regions (L. Zhang et al., 2020).

As a first approximation, deposition of As from the atmosphere is estimated by assuming a nominal value of 50 μg As/m²/yr (Table 1) over the area of the oceans (362 × 10¹² m²) and 200 μg/m²/yr (Table 1) on land (150 × 10¹² m²), yielding values of 18 × 10⁹ g/yr and 30 × 10⁹ g/yr, respectively. The mean residence time for As in the atmosphere is about 10 days (Matschullat, 2000), so deposition on land is regionally heterogeneous, with much higher values over Asia, Chile, and Peru (L. Zhang et al., 2020). If we assume that the deposition of As over India, China, Japan, Chile and Peru (13 × 10¹² m²) is 2,000 μg/m²/yr (Table 1), then the global deposition on land is 48 × 10⁹ g As/yr. Even these values are rough approximations; they do not recognize that high deposition in Asia is likely to extend over a considerable distance of the Pacific Ocean (Wai et al., 2016), that considerable smelting of metallic ores occurs in Africa (Congo), and that deposition in polar regions is likely to be lower than the mean value for land due to their distance from anthropogenic sources. Our estimate of As deposition from the atmosphere lies at the upper end of our estimate of total atmospheric emissions (Table 4).

4.2. Sources of Arsenic in Freshwaters

Dissolved As is found in freshwaters from the weathering of continental rocks and from the natural deposition of As from the atmosphere. These contribute to the total dissolved transport of As to the oceans of 23 × 10⁹ g/yr (Section 3.1). Groundwaters extracted by humans are the largest anthropogenic source of As in freshwater, estimated at 30 × 10⁹ g/yr (Section 2.5); inadvertent mobilizations to freshwaters from mine tailings, coal combustion, and coal ash disposal, fertilizers, and petroleum extraction are additional, but poorly quantified sources. Despite the potential for As pollution of rivers, they carry approximately the load of dissolved As that is predicted by the natural chemical weathering of continental rocks (18.7 × 10⁹ g/yr). It is possible that much of the dissolved input of As to rivers is adsorbed to particulate minerals and carried to the sea in suspended or bedload materials (Bowell, 1994; Cai et al., 2022).

Some of the arsenic in the load of suspended sediments in rivers is derived from mechanical weathering. Estimates of the transport of As in suspended sediments are poorly constrained, ranging from 60 to 544 × 10⁹ g As/yr (Section 3.1), most of which is likely deposited in estuarine, near-shore and continental shelf sediments. Here it is noteworthy that the mobilization of As from the Earth’s crust through the mining of metallic ores, coal and phosphate rock totals between 1,500 and 5,600 × 10⁹ g/yr, dwarfing the natural rate of As mobilization by chemical
weathering. Not all of this anthropogenic removal is mobilized to freshwater, but even a small percentage would represent a large increment to the natural flux of As to the sea. The accumulation of As in sediments of delta aquifers of the major river systems of southeastern Asia is associated with mobilization of As from the organic-rich sediments to the aquatic phase, induced by reduced conditions, leading to significant contamination of groundwater in these aquifers (Nordstrom, 2002; Plant et al., 2009; Smedley & Kinniburgh, 2002; Winkel et al., 2011).

4.3. Sources and Fate of Arsenic in the Oceans

The surface waters of the oceans receive dissolved As from riverflow (18–23 × 10⁹ g/yr) and atmospheric deposition (18 × 10⁹ g/yr). Inputs of dissolved As from marine hydrothermal vents are poorly constrained (1–75 × 10⁶ g As/yr; Section 3.2.1.2), and while it is believed that most is deposited near the venting sites, this also is not quantified. The mean residence time for dissolved As in the entire oceanic reservoir is >20,000 years, so As is a well-mixed conservative element in seawater (Whitfield & Turner, 1979).

Of the 60 to 544 × 10⁹ g As/yr (Section 3.1) delivered to the oceans in the riverine suspended sediments and deposited on continental margins, some is subducted. The flux of As that undergoes subduction has been previously estimated as 38.2 × 10⁹ g/yr (Matschullat & Deschamps, 2011); however, this is significantly less than our estimate of the As content of the magma that forms arc volcanic and plutonic rocks (∼192 × 10⁹ g As/yr).

To provide a revised estimate of the As flux in subducted sediment, we draw upon a calculation of the average Fe content of sediment entering the subduction zone (56,700 mg/kg; Plank, 2014) and an estimate of the average As/Fe ratio in deep sea sediments (0.0013; Neal et al., 1979), to calculate an average As concentration of 74 μg/g in subducting sediment. This is somewhat greater than the 40 μg/g suggested by Boström and Valdes (1969). With a subduction sediment rate of 11.3 × 10¹⁵ g/yr (Plank & Langmuir, 1998), we suggest that 790 × 10⁹ g/yr of As is removed from the marine sedimentary reservoir by subduction. Unfortunately, available data do not allow us to provide a better mass balance for sedimentary As cycling in the oceans.

5. Conclusions

Due to concerns for human health, direct exploitation and use of arsenic resources has diminished in recent years, but inadvertent mobilizations of As from mineral extractions (metal ores, coal and phosphate rock) are now as much as 10 times higher than As released by the natural rate of rock weathering at the Earth’s surface. Not all of the As is lost from these wastes: the amount of dissolved As in rivers shows no significant increase in recent decades (Lettenmaier et al., 1991), perhaps due to the adsorption of As to Fe minerals during transport (Bowell, 1994; Cai et al., 2022). Airborne emissions have roughly doubled as a result of the smelting of Cu and other non-ferrous ores (Table 4). This results in excess deposition in certain regions (L. Zhang et al., 2020), with potential consequences to human health and agriculture. Using median values, the ratio of anthropogenic to natural emissions of As to the atmosphere (1.57) shows human impact on its global cycle that rivals that for V (0.59–1.71), Hg (1.56), and Pb (1.48) (Schlesinger et al., 2002; Sen & Peucker-Ehrenbrink, 2012). Future studies should further investigate the occurrence and impact of the apparent As excess derived from the increasing anthropogenic sources to the environment.

Data Availability Statement

This paper is a review and compilation of published open access data in the scientific literature, with each cited value coupled to a source entry in the reference list. Other than the calculation of means, no statistical or other software was used in data synthesis.

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