Use of Metallic Mercury in Artisanal Gold Mining by Amalgamation: A Review of Temporal and Spatial Trends and Environmental Pollution

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Abstract: The introduction of mercury (Hg) into the environment by anthropogenic activities has resulted in negative implications for ecosystem functions and human health. Unlike the legacy of huge environmental pollution left by historic gold rushes in several developed countries, gold-rich nations in the developing world are currently witnessing what could qualify as a “new gold rush”, conducted primarily by small-scale mining operators and characterized by the use of metallic Hg (Hg⁰) in the amalgamation process to extract gold from crude ores. Once introduced into the environment, Hg⁰ can undergo biogeochemical transformations to produce Hg species such as methyl-Hg, with well-established adverse impacts on living organisms. This review summarizes published data on both historical and recent trends of the use of Hg⁰ in artisanal gold mining (AGM) on a global scale and emphasizes the impacts of AGM on the environment. To achieve this, we used citations from research conducted in North and South America, Europe, Asia, Africa, Australia, and New Zealand, obtained from several search engines and databases. Our findings show that, in addition to the well-known environmental and human health adverse effects of gold mining with Hg⁰, gold extraction by the Hg amalgamation technique is boosting the economy in parts of Africa, South America, and Asia. Unfortunately, this appealing aspect of AGM may not be easily halted, pending the creation of alternative employment. Therefore, there is a clear need for the development of safe and affordable gold extraction and purification technologies. Ultimately, the growth of this specific economic sector should be regulated to help protect both the environment and human health. Information compiled in this review should help to (i) improve the mapping of AGM-impacted soil and aquatic systems on a global scale and (ii) stimulate discussions and research on how to take down current barriers to the development and implementation of safe AGM methods.

Keywords: gold; mercury; amalgamation; mining; developing nations; environmental pollution

1. Introduction

Throughout recorded history, mercury (Hg) has been considered a valuable resource with a varied and wide range of applications, despite its known poisonous properties. For instance, the literature focusing on the historic aspects of the adverse impacts of Hg points to mercurialism as one of the first industrial diseases known to the Romans, who sentenced slaves and prisoners to work in the mines at Almadén (Spain) [1–3]. Also, references to the toxicity of Hg salts such as Hg(NO₃)₂ used in the making of felt hats from rabbit furs have been described by Pliny the Elder, who died in 79 A.D. [1–3]. It has also been reported that Ulrich Ellenborg was one of the first investigators to adequately demonstrate the dangers of human exposure to Hg vapor around 1493 [1,2]. Later, in 1527, Theophrastus von Hohenheim, known as Paracelsus, wrote a book titled “Von der Bergsucht und anderen Krankheiten” that focused on occupational diseases and described in detail the effects of Hg on miners [2–4].
If the dangers of exposure to high doses of Hg have been known now for thousands of years, Hg toxicity resulting from exposure to trace levels, particularly via food consumption, was not noted until the incident of Minamata, Japan in the late 1950s. Additionally, if reports of health issues related to methylmercury (MeHg) poisoning date back to the 1860s [5–7], research on the environmental transformation of inorganic Hg species to produce organometallic compounds of Hg is rather recent. Knowledge on this specific aspect of the environmental cycling of Hg helped to shed light on the adverse effects of Hg exposure via diet, such as neurological disorders, visual constriction, brain damage, and paralysis [3,8–10]. Other recent incidents of Hg outbreaks resulting from the consumption of Hg-tainted foods were reported in Iraq, Pakistan, Ghana, and Guatemala, which resulted in numerous deaths [11–16].

Environmental pollution with Hg is still of significant concern today and human exposure to Hg via food consumption has become an increasingly problematic issue throughout the world [3,15,17,18]. There is a growing public awareness of the dangers associated with Hg pollution and its potential impacts on human health. This awareness has resulted in a high demand for information on background Hg levels in the environment, the parameters controlling the conversion of inorganic Hg species to the more toxic MeHg, and the degree to which Hg bioaccumulates and biomagnifies in food chains. Previously, global Hg emission into the atmosphere was blamed primarily on industrial and combustion sources from Europe and North America [15,19,20], while the mining sector, an important anthropogenic source of Hg emissions [19,21,22], was not always included among the dominant Hg polluters on a global scale. Today, however, and although considered as a minor but fast-growing contributor to the global Hg cycle [23–25], artisanal gold mining (AGM) by Hg amalgamation techniques is recognized as one of the sources of environmental pollution with Hg, with primarily local and regional implications [26,27]. This specific source of Hg pollution appears to be a consequence of socio-economic predicaments in many developing nations in Africa, Asia, and South America, where the use of Hg0 to mine gold has rebounded and heightened in spite of the introduction of much safer mining technologies, such as cyanidation and bacterial oxidation processes [28–30]. Resurgence of the gold rush in the 1970s and 1980s in gold-rich developing nations resulted in millions of people becoming partakers of this mining activity because of increasing poverty, the effects of natural disasters, particularly droughts, a lack of alternative employment, climate change and its impact on crop production, and, above all, the urge to escape social marginalization [15,31–35]. This informal mining activity supplies miners with quick income, and, though labor-intensive, it provides an answer to under-employment. In addition, it reduces rural-to-urban migration by providing work to rural people who would have left had this alternative not existed [36,37]. Moreover, miners involved in AGM seem to find the Hg amalgamation process inexpensive, reliable, easy to use, and effective in extracting gold. It requires only very simple tools and can be set up anywhere, absolving miners from non-affordable capital investment for equipment such as that used in large-scale mining operations [10,33,38].

As the price of gold has increased over time, the number of artisanal gold miners has increased substantially in rural areas all over the world. Around 16 million people are directly involved in this activity, producing 380–450 tons of gold, and releasing around 1400 tons of Hg per year [39–41]. Other sources, such as the UNEP, suggest that AGM contributes about 727 tons of Hg to global emissions per year [40]. Overall, while developed nations such as the U.S. and Canada have abandoned large-scale gold extraction by Hg amalgamation techniques and adopted more efficient but expensive processes such as the “cyanidation technique” [10,33,42], the current gold rush in developing tropical nations is, in a way, a simple depiction of an old tragedy [43]. Accordingly, the large number of studies conducted in historically Hg-impacted regions of developed nations has served as a foundation for Hg biogeochemical research in countries affected by the current gold rush, with fast growing efforts in the Amazon River basin [22,37,44–47] and in the tropical regions of Asia and Africa [48–54].
1.1. History of Gold Mining and Use of Mercury in Amalgamation Techniques

Gold has been known since antiquity and described as a lustrous, yellow, dense, soft, ductile metal that is inert in air, thus resisting corrosion \[15,55\]. Also called “chrysos” by the Greeks, gold appears to be the first precious metal used by man \[15,56\]. Because of its luster and durability, gold was used in ornamentation and coinage. Ultimately, it became the accepted financial basis of many societies. It is believed that gold has been mined, collected from alluvia, and separated from the ores of silver, copper, and other metals since prehistoric times \[55\]. It is a highly valuable metal and has been much sought after as a symbol of prosperity, wealth, and, above all, an asset since the Bronze Age \[46\]. Even today, gold remains one of the most influential mineral commodities in human history and an object of great human desire \[57\]. Originally, gold was recovered by swirling a mixture of auriferous sand and water in a shallow pan or separated using sluice boxes fitted with transverse riffles that retain the gold. Later, probably prior to 1000 B.C., gold recoveries were improved by adding \( \text{Hg}^0 \) to the system to wet the gold particles and bind them together \[10,23,58,59\].

Similar to gold, metallic mercury and cinnabar have also been known since antiquity \[60\]. Though \( \text{Hg} \) is one of the most pernicious toxic chemicals ever known, among all metals, \( \text{Hg} \) has been extensively used by man since the advent of civilization. In fact, even now, \( \text{Hg} \) is still used in medications, industry, and agriculture \[7,16,61,62\]. In Table 1, a summary of some of the key historic turning points of the use of \( \text{Hg} \) by human societies is presented. Overall, it can be noted that gold extraction by \( \text{Hg} \) amalgamation techniques, although not safe for both the environment and human health, has persisted throughout historic and present times.

1.2. Historic and Present Time Gold Rushes around the World

Summarized in Table 2 are the main gold rush events as reported in the literature. Briefly, a “gold rush” is a new discovery of gold that brings an onrush of miners seeking their fortune. Gold rushes were typically marked by a general buoyant feeling of a “free for all” in income mobility, in which any single individual might become abundantly wealthy almost instantly \[63–65\]. In the late 18th century, and mostly in the 19th century, gold rushes occurred in several parts of the world \[38,66–69\]. Major gold rushes took place in the 19th century in Australia, New Zealand, Brazil, Canada, South Africa, and the United States of America (USA), while smaller gold rushes took place elsewhere \[70\]. The first significant gold rush in the U.S. was in Cabarrus County, North Carolina, in 1799 at today’s Reed’s Gold Mine \[71,72\].

In this review, global trends in past and present gold mining by \( \text{Hg} \) amalgamation techniques commencing from ancient times to historic gold rushes in the 1800s to more recent gold rushes in the 1980s and the resulting environmental impacts in North and South America, Europe, Asia, Africa, Australia, and New Zealand are compiled and compared. Previous reports concluded that artisanal gold miners and their families are exposed to \( \text{Hg} \) vapor, while residents of nearby and downstream AGM sites are exposed primarily through the consumption of \( \text{Hg} \)-contaminated fish \[3,14–16,73\]. Given the fact that nearly 15 million people participate in current artisanal small-scale gold mining in developing countries \[27,73\], recommendations are formulated herein with regard to the potential adverse impacts of the ongoing AGM activities.
Table 1. Historic milestones of mercury (Hg) use throughout history.

<table>
<thead>
<tr>
<th>Timeline</th>
<th>Remarks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early 2700 B.C.</td>
<td>The Phoenicians and Carthaginians used Hg to amalgamate precious metals, recovered upon heating.</td>
<td>[15,58,59]</td>
</tr>
<tr>
<td>Before 4th Century B.C.</td>
<td>The Egyptians, Greeks, and Romans used Hg in the making of cosmetics and medicines and for amalgamation of gold and other precious metals.</td>
<td>[8,74]</td>
</tr>
<tr>
<td>In the 4th Century B.C.</td>
<td>Hg was used in religious ceremonies and to extract other metals—this was first documented by Aristotle.</td>
<td>[8,56,75]</td>
</tr>
<tr>
<td>2nd Century B.C.</td>
<td>Alchemists in China used Hg in processes that tried to convert base metals to gold.</td>
<td>[15,58]</td>
</tr>
<tr>
<td>From 50 to 68 A.D.</td>
<td>First application of amalgamation technique to mining gold in Bosnia under Emperor Nero (56–68 A.D.) This technology had a widespread application among the Romans in 50 A.D. Its environmental problems led the Romans to prohibit this activity in Italy after less than 100 years.</td>
<td>[8,76]</td>
</tr>
<tr>
<td>About 1400 A.D.</td>
<td>Gold mining was revived after the fall of the Roman Empire in the 11th century in Central Europe, around the Harz Mountains in Germany. ** Amalgamation and retorting processes were applied in gold extraction.</td>
<td>[8]</td>
</tr>
<tr>
<td>In 1500s A.D.</td>
<td>The use of Hg was launched in the Americas in the 16th century by the Spanish to amalgamate silver and gold in Mexico, Peru, and Bolivia by applying the “Patio” process. Later, the Patio amalgamation technique was industrialized and used for the recovery of gold and silver.</td>
<td>[10,21,33,38,43] [10,68,77]</td>
</tr>
<tr>
<td>1400–1600 A.D.</td>
<td>Gold was produced by the amalgamation technique using Cu plates in areas of European explorations.</td>
<td>[78]</td>
</tr>
<tr>
<td>In 1800s A.D.</td>
<td>Gold mining with Hg began in North America, New Zealand, Australia, and Russia.</td>
<td>[38,43,63,68–81]</td>
</tr>
<tr>
<td>End of 1800s</td>
<td>The use of the “Patio” process continued through the end of the 19th century. This process, in spite of its convenience, led to the discharge of unprecedented amounts of Hg to the American environment.</td>
<td>[21,33,38,43]</td>
</tr>
<tr>
<td>During the 1980s</td>
<td>An increase in gold price boosted a new gold mining boom using Hg for amalgamation occurring in South America, Africa, and Southeast Asia.</td>
<td>[21,82]</td>
</tr>
<tr>
<td>Today</td>
<td>Small-scale artisanal gold mining in gold-rich developing tropical nations continues to use the amalgamation technique intensively and often unrestrictedly, whereas larger companies in developed nations have long replaced Hg amalgamation practice with cyanidation and oxidation methods to extract gold from crude ores. The impact on biodiversity remains poorly studied.</td>
<td>[69,83,84]</td>
</tr>
</tbody>
</table>

** Retorting is a process that cools Hg vapor produced when the amalgam is heated in a sealed container to recover Hg in its liquid form for reuse.
Table 2. A summary of recorded main “gold rush” events throughout history.

<table>
<thead>
<tr>
<th>Gold Rush Events</th>
<th>Remarks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>North America from 1799 onwards</td>
<td>Gold mining commenced in USA with gold rushes spreading to several states, including North Carolina, Alabama, California, South Dakota, Colorado, Georgia, and Nevada. In 1896–1901, Klondike, Yukon, Canada experienced a gold rush. In all locations, gold was primarily concentrated using Hg amalgamation techniques.</td>
<td>[67–69,77]</td>
</tr>
<tr>
<td>In 1838</td>
<td>The discovery of gold in Siberia on the Ulderey River resulted in a gold rush, restricted only to the local population. Significant mining also took place in the Lena Basin from 1846, relying on Hg amalgamation techniques.</td>
<td>[85–90]</td>
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<td>In 1851</td>
<td>The Australian gold rush started at Bathurst (New South Wales) and Ballarat and Bendigo in Victoria. More gold was discovered in New South Wales, Queensland, Western Australia, and New Zealand subsequently, depending principally on gravity concentration and Hg amalgamation as the main gold extraction technique.</td>
<td>[68,79,81,91,92]</td>
</tr>
<tr>
<td>Between 1873 and 1886</td>
<td>South Africa experienced a gold rush following gold discovery in Lyndenburg, Witwatersrand and other localities. Similarly, Hg amalgamation was the method of choice for gold extraction.</td>
<td>[38,68,93]</td>
</tr>
<tr>
<td>Gold-rich developing nations</td>
<td>Gold mining by Hg amalgamation remains the method of choice used in small-scale mining (SSM) activities. SSM occurs primarily in South and Central America, Africa, and Asia. SSM by amalgamation is still practiced by a few placer miners in Australia, Canada, Russia, and USA.</td>
<td>[21,33,87,88,94–100]</td>
</tr>
</tbody>
</table>
2. Methods

Global trends in past and present AGM by Hg amalgamation techniques, starting from ancient times and moving to historic gold rushes in the 1800s and to present gold rushes in the 1980s, are reviewed, summarized, and analyzed. Several search engines and databases such as SCOPUS, PubMed, Google Scholar, ResearchGate, Copernic Basic, and MEDLINE were used. The key words used in the search process included a combination of “mercury use” and one or more of the following: “small scale” or “artisanal gold mining”, “past or historic and present mining sites”, “developed and developing nations”, “gold production”, “estimated mercury releases or discharges”, “mercury pollution”, “environmental fate”, “environmental impacts”, and “human health”. The bibliographic records of papers obtained through these literature searches were also reviewed for additional literature, particularly those that were regularly cited and had the relevant data for this review. Gray literature consisted of reports from governmental and non-governmental agencies, the United Nations Environment Programme (UNEP), and the United Nations Industrial Development Organization (UNIDO). In addition to past and present trends of Hg use in AGM, we also compiled and compared the environmental impacts of AGM in North and South America, Europe, Asia, Africa, Australia, and New Zealand.

More than 1000 papers focusing on gold rush events and mining through Hg amalgamation across recorded history were reviewed. Of these, just over 200 papers cited herein were retained primarily based on their relevance to this specific review. The information gathered from these papers primarily covers historic milestones in mercury usage, the various techniques employed for gold extraction via Hg amalgamation in both developed and developing nations, the quantities of mercury used in AGM, gold production figures, and estimated amounts of mercury released into the environment by AGM activities, categorized by geographical locations and mining periods.

Quantities of gold produced and of mercury used were reported by various sources, and tons herein refers to short tons (907.185 kg) and metric tons to tonnes (1000 kg). The correlation between gold production and mercury release into the environment was analyzed using data published for different countries/continents whenever available.

Furthermore, this review also examined the pathways of mercury after its introduction into various environmental compartments (such as soils, waters, sediments, and the atmosphere), as well as the potential for human exposure to Hg. In AGM locations, exposure primarily occurs through inhalation during both the amalgamation process and the burning of Au-Hg amalgams, as well as through the consumption of mercury-contaminated food. This contamination arises from the oxidation of released metallic mercury, which then becomes susceptible to biotransformation, bioaccumulation, and transfer up the food chain.

Finally, based on the synthesized information, recommendations were formulated concerning the current gold rushes and their anticipated impacts on the environment and human health.

3. Results and Discussion

3.1. Gold Mining Processes and Amalgamation Technology

The Hg amalgamation technique used in past gold mining activities differs very little from the present-day widespread amalgamation technique in developing nations (Figure 1 and Table 3).
Table 3. Comparative presentation of the sequence of processes used in the extraction of Au by Hg amalgamation in developed and developing nations.

<table>
<thead>
<tr>
<th>Developing Nations</th>
<th>Developed Nations</th>
</tr>
</thead>
<tbody>
<tr>
<td>• SSM mining operations are found in gold-rich African, Asian, and South American nations [101].</td>
<td>• Mining operations are on a large scale (e.g., North America and Australia)</td>
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<tr>
<td>• In these locations, rudimentary equipment (e.g., shovels, pick-axes, chisels, wooden mortar, etc.) is used in the mining process [48,96,102,103].</td>
<td>• Heavy machinery is used (shafts, dredgers, hydraulics, excavators) [38,43,77].</td>
</tr>
<tr>
<td>• Gold ores are primarily from alluvial/placer deposits/surface soils or rocks.</td>
<td>• Gold ore hard rock (lode, gold–quartz veins) or placer ore (e.g., alluvial) is focused on.</td>
</tr>
<tr>
<td>• Mined gold ores are ground in locally fabricated ball mills or designed metal/wooden mortars and pestles. The technique is widely used in African countries, Brazil, and China.</td>
<td>• Underground methods (audits and shafts) are used to mine hard rock gold ore deposits; hydraulic, drift, or dredging methods are used to mine riverbeds or placer deposits; water cannons are used to break placer ores [38,43,77,106].</td>
</tr>
<tr>
<td>• Gravity separation panning and washing on short, inclined sluices (shaped like stairs) are used to concentrate gold, which is then amalgamated with metallic Hg. In some cases, the bottom of the sluice is lined up with cloth, which is continuously impregnated with Hg(^0) to make gold particles agglutinate. Large amounts of Hg(^0) are used to prevent water from washing away gold particles. Powdered soap is used sometimes to allow for making float, enhancing the adherence of gold particles on the riffles.</td>
<td>• The ore is shipped to stamp mills and pulverized. The gold is recovered by mechanical settling in troughs/panning and mixed with water, salts, and Hg to produce gold/silver amalgam (amalgamation). Additionally, sluice boxes are also used on a large scale (made of long troughs with series of upraised riffles of Cu) in North America, Australia, and New Zealand; this involves pouring the ground ore into sluice impregnated with Hg by which gold particles adhere [79,97,107].</td>
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<td>• The ratio of Hg(^0) used and gold produced in most developing nations is about 2–4 kg Hg per kg gold produced. African and Brazilian miners sometimes use a 10 kg of Hg(^0) to 1 kg gold ratio. Usually, two-thirds are consumed in the amalgamation process in the riffles. The remainder eventually ends up in the terrestrial or river environments [38,96,99,104,105].</td>
<td>• Amalgam is squeezed via buckskin bag/strong cotton and excess Hg is recycled into a barrel. Substantial quantities of Hg are lost with the discarded milled fine tailings into the environment at every stage in the amalgamation process. Hg is discharged into waterways, and some is lost to flowing slurry and carried to downstream environments. [38,43,77,106].</td>
</tr>
<tr>
<td>• Amalgam is burned by roasting on bonfire/charcoal fire/crucible/frying pan in open air or in huts along rivers or homes to drive off Hg vapor, producing pure Au. Miners are exposed to noxious fumes of Hg. Some treat crude gold with borax, as in Indonesia, or nitric acid (e.g., Latin America and Africa) in subsequent steps to obtain pure gold. Others perform bullion smelting in gold shops sited in their homes/towns. Hg(^0)-containing wastes are discharged at or near the mining sites [3,35,54,76].</td>
<td>• Distillation of amalgam is carried out, Hg is condensed for recycling, and pure metal is recovered. Hydraulic mining destroys river- and bay-mobilized sediments and choke natural streambeds, spreading Hg contamination [38,57,67,109]. Hg losses during the processing of gold from panning to refining were exceptional at the historic sites because added salts formed insoluble Hg compounds [38].</td>
</tr>
<tr>
<td>• The distillation and recycling of Hg is not a popular practice—Hg is lost by volatilization during smelting/roasting and during the handling of metallic Hg. Also, Hg is introduced into the atmosphere from mine tailings [35,99,102,103], resulting in a legacy of mine tailings, standing waters, ponds, diverted rivers, destruction of farmlands, scattered trenches and pits, etc.</td>
<td>• Hg-containing tailings are left behind, forming “Hg hot spots”. Deposits of large mine wastes in many areas impact soils, waters, and biota [82,102,110,111].</td>
</tr>
</tbody>
</table>
In the past, gold or silver ores obtained from placer deposits (alluvial) or deep shaft mines were pulverized and mixed with water, and various salts and Hg were added to the mixture to produce gold/silver amalgam. Although the use of distillation techniques allowed for Hg condensation and recycling, substantial quantities were lost to different environmental compartments with the released gas and liquid effluents, as well as the discarded solid wastes [38,43,77,111]. For instance, calculations show that approximately 5715 to 6120 metric tons of Hg were released into the environment between 1860 and 1890 [106]. Small-scale gold mining, on the other hand, contributes a significant amount of Hg to the environment after the processing and isolation of gold by applying rudimentary techniques; the estimated annual input stands at about 405 metric tons, the main contributors being South America, Russia, and Asia, forming more than 50% of the total anthropogenic release on regional scales [112]. Thus, in the developing countries, small-scale mining (SSM) is the largest single source of Hg release into the environment. The sequence of processes used in gold extraction by Hg amalgamation techniques in developing and developed nations is summarized comparatively in Table 3.

3.2. Mercury Discharges into the Environment Due to Past and Present Gold Mining Activities

The use of Hg for gold amalgamation and its releases has varied among continents for centuries. Examples of trends in gold production and Hg consumption and releases are presented in Tables 4 and 5. However, it should be noted that estimates of the releases of total Hg into the environment are difficult to assess and generally poorly quantified, especially in the informal sector of gold production widespread in developing nations [21,40,113,114]. Figure 2 gives temporal trends of estimated tons of Hg released into the environment for
both historic sites and current SSM nations, comparing the different regimes of gold rushes as adapted from computations available in the literature [115].

Figure 2. Historical mercury (Hg) discharged into the environment as a result of gold mining activities plotted as a function of selected geographical locations and time of mining activities.

Gold produced and corresponding Hg discharge figures (i.e., calculated from numbers obtained during this review process or readily available from the literature) vary among continents and specific sites within each continent. For instance, Yoshimura et al. reported average ratios of Hg lost to Au produced of 1.96 in Africa, 4.63 in Latin America, and 1.23 in Asia for AGM [116]. However, it is likely that the reported figures for Hg release and Au production could be either under- or over-estimated. For instance, for most Au mining areas, Hg releases are estimated using gold production figures, and Hg used/released is deducted from such figures [112,117]. Overall, the more Au produced, the higher the levels of Hg released into the environment (Figure 3), and differences in Au production and Hg consumption levels have been linked to several factors. For example, numbers obtained from SSM nations are often not accurate due to factors such as smuggling, informal commercialization, and the typical social behavior of artisanal miners being “untruthful” in their production figures and processing techniques [59,112,118]. Nevertheless, the total amount of Hg used per year to extract Au in the historic sites is not comparable to the present-day amount used in SSM nations (Tables 4 and 5). Figures of Au produced in the SSM nations are lower, stemming from the scale of production. It appears that available Hg consumption data are less accurate than Au gold production numbers [59], and pre-industrial mining sites had no estimate of Hg consumption and corresponding gold production as reported by several authors reviewing AGM.
Figure 3. Relationship between gold (Au) production (in metric tons or tons/year) and mercury (Hg) released into the environment (in tons/year) using published numbers from different parts of the world. The 1:1 ratio is represented by the dotted line. The results show that, in all cases, the amount of Hg released into the environment is either equal to or in excess of the amount of Au produced. Overall, departure from the 1:1 line occurs with increasing rates of Au production, with China and Amazon countries having the highest Hg pollution rates.

Nriagu [43] estimated that, in the 18th century, the Hg to Ag recovery ratio was 1.5 to 1, which agrees quite well with estimates by others in the literature [112]. If such a ratio has been used as proxy for Hg/Au, it is well known that the amount of Hg applied to extract Au was exceptionally high in historic time. In fact, used Hg/Au ratios varied depending on the ore and Hg availability across regions. By this, we mean that at the historic sites, if twice Nriagu’s Hg amount was used in the amalgamation of gold [112], then it implies that 3.0 metric tons of Hg were required to produce 1 metric ton of Au, with about 50% Hg loss during Au production. If this assumption holds, then the unknown Hg amounts used in the past (historic sites) are calculated based on a 3 Hg metric ton to 1 Au metric ton ratio (see Table 4).

Again, the amount of Hg used per year to extract Au and Ag has decreased over time. This trend is in accordance with the observation by Pirrone et al. [20,83] in that the amount of Hg released during pre-industrial times in Au and Ag recovery is much higher than that released presently (Figure 2 and Tables 4 and 5). Therefore, it is believed that Hg losses were higher in the historic periods because of poor technologies and carelessness on the part of miners. Moreover, with advanced technological innovations available at that time, the loss of Hg in the mills, for instance, in western U.S. remained high and varied from about $2.7 \times 10^{-4}$ to $2.7 \times 10^{-3}$ metric tons of ore processed [38,43].
Table 4. Example historic sites of gold production by Hg amalgamation and estimated amounts of Hg used and lost into the environment.

<table>
<thead>
<tr>
<th>Countries and Mining Sites</th>
<th>Years</th>
<th>Au Production (Metric Tons)</th>
<th>Hg Consumption (Metric Tons)</th>
<th>Hg Release/Loss (Metric Tons)</th>
<th>Receptors</th>
<th>Remarks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spanish America</td>
<td>1550–1880</td>
<td>12,7006 *</td>
<td>34,2916 **</td>
<td>17,7808</td>
<td>Hg trapped in tailings/soils</td>
<td>Mercury is still present in mine tailings, soils, and sediments</td>
<td>[15,26,43,119]</td>
</tr>
<tr>
<td>Comstock Lode, Nevada (USA)</td>
<td>1859–1890</td>
<td>406 *</td>
<td>11,897 **</td>
<td>5761 to 6169</td>
<td>Carson River Basin. Hg lost to streams in both NV and CA</td>
<td>Contaminated milling tailings; Hg persists in water and sediments; mercurialism among miners</td>
<td>[106,112,123,124]</td>
</tr>
<tr>
<td>Dahlonega Mining District, North Georgia (USA)</td>
<td>1820–1900</td>
<td>9.7–20.7 *</td>
<td>26.2–55.9 **</td>
<td>13.6–29.0</td>
<td>Dahlonega Mining District</td>
<td>Hg pollution of both terrestrial and aquatic environments</td>
<td>[25,119,125]</td>
</tr>
<tr>
<td>Canada</td>
<td>1800s</td>
<td>20.1 *</td>
<td>54.2 **</td>
<td>28.1</td>
<td>Air, water, soil</td>
<td>Anthropogenic release</td>
<td>[28]</td>
</tr>
<tr>
<td>Goldenville, Nova Scotia (Canada)</td>
<td>1860–1940</td>
<td>4.4 *</td>
<td>11.9 **</td>
<td>6.2</td>
<td>Air, water, soil</td>
<td>2.72 × 10^8 metric ton tailings with 6.2 metric tons of Hg</td>
<td>[69]</td>
</tr>
<tr>
<td>Alaska and Klondike goldfields</td>
<td>1800s</td>
<td>1525 **</td>
<td>4119</td>
<td>2136 *</td>
<td>Processing sites</td>
<td>1.4 × 10^−3 metric tons of Hg lost for every kg of Au</td>
<td>[38]</td>
</tr>
<tr>
<td>Wales (Gold belt of Gwynedd)</td>
<td>1860–1916</td>
<td>3.40</td>
<td>9.2 **</td>
<td>4.8 *</td>
<td>High levels of Hg in Mawddach River</td>
<td>Hg pollution of a river system.</td>
<td>[126]</td>
</tr>
<tr>
<td>Australia</td>
<td>1850–1930</td>
<td>583.2 *</td>
<td>1575 **</td>
<td>817</td>
<td>Hg contamination of waterways and biota</td>
<td>Weight of Hg used was same as weight of Au recovered</td>
<td>[81,91,92,127,128]</td>
</tr>
<tr>
<td>New Zealand</td>
<td>1860–1870s</td>
<td>20–544.3</td>
<td>54–1470 **</td>
<td>28–762.0 *</td>
<td>Air, water, soil</td>
<td>Legacy of Hg impacted river systems</td>
<td>[79,97,129]</td>
</tr>
<tr>
<td>Former Soviet Union</td>
<td>1800s</td>
<td>6.2–14.5</td>
<td>16.7–39.1 **</td>
<td>31.0 to 73</td>
<td>Air, water, soil</td>
<td>High Hg levels in water, soil, and sediments; 0.38 MT Hg used on rugs of sluices; 5.4 MT Hg used on dredges</td>
<td>[85–90]</td>
</tr>
</tbody>
</table>

* 0.0014 metric tons of Hg lost is equivalent to 0.001 metric tons of Au produced ** 0.0027 metric tons of Hg consumed is equivalent to 0.001 metric tons of Au produced.
The types of ores played a role as the main factor in the release of Hg into the environment, while ore availability drove the abundance of Hg-polluted sites. Since heavy machinery was employed, it implied that more gold concentrate was retrieved, requiring larger amounts of Hg being utilized during the various stages of amalgamation observed in all sites. This was the case for Russia, where, before 1988, 5.4 metric tons of Hg were used on dredges (Table 4). On the contrary, for SSM nations, for example, an inventory reported for Tanzania and Zimbabwe in 2000 showed lower values of Hg release into the environment, at about 9–13.5 and 9–18 metric tons/year [105,112,129–131], respectively. Likewise, in the Philippines, Hg discharges varied from 13.5 to 42.3 metric tons/year [98,132,133].

The amount of Hg released during the pre-industrial period in recovering Au and Ag is also higher than current releases because of an inefficient or total lack of recovery technologies during that period (Table 4). These historic mining sites have a profound legacy characterized by adverse impacts of Hg on ecosystems. In present times, the largest Hg releases into the environment occur in South American countries, particularly the Amazonian nations, followed by Asian countries, Russia, and the Philippines, which are also considered large contributors [112]. However, the total amounts of Hg released by Regional/World SSM in the 2000s (Table 5) [40,59] remain far less than the total released per year from historic sites in North America and Spanish Colonial America (Figure 2, Table 4).

Table 5. Regional small-scale mining (SSM) sites and estimated environmental releases of mercury (Hg) in the 2000s [40].

<table>
<thead>
<tr>
<th>Regions</th>
<th>2000</th>
<th>2005</th>
<th>2010</th>
</tr>
</thead>
<tbody>
<tr>
<td>Africa</td>
<td>&gt;32.7 to &gt;51.7</td>
<td>40</td>
<td>200</td>
</tr>
<tr>
<td>Asia</td>
<td>&gt;294.8 to &gt;430.9</td>
<td>160</td>
<td>240</td>
</tr>
<tr>
<td>South America</td>
<td>&gt;96.2 to &gt;130.6</td>
<td>80</td>
<td>160</td>
</tr>
<tr>
<td>Former Soviet Union</td>
<td>18.1</td>
<td>* NA</td>
<td>NA</td>
</tr>
<tr>
<td>World Total</td>
<td>&gt;441.8 to &gt;631.4</td>
<td>NA</td>
<td>727</td>
</tr>
</tbody>
</table>

* NA: not applicable.

In 2010, AGM was a major contributor in Hg release into the environment, so the releases were more than double those of 2005 [40]. Environmental Hg in the Amazon originates initially from geochemical sources, and AGM adds to such natural inputs [134]. AGM contributed about 727 tons per year, which could be attributed to factors such as the rise in gold price at that period and rural poverty, which makes the business lucrative, hence the increase in Hg use and release into the environment. In the recent general trends of Hg release into the environment from AGM, China has been a major contributor, even though China banned AGM in 1996. South America and Sub-Saharan Africa have also been a factor in the global releases recently [14,40]. For instance, the amount of Hg released by AGM in 70 countries (93% of the countries using Hg in AGM) is around 1607.8 tons/year [135].

Numerous reports on past gold mining sites in developed nations show the significant contribution on Hg contamination and the persistence of Hg as an environmental pollutant [81,91,136,137]. From these reports, it is obvious that Hg pollution left behind during the first gold rushes remains evident and is a continuing hazard to the people and wildlife of the impacted regions. In developed nations, numerous studies have assessed Hg contamination in catchments with known historical mining activities, such as Victoria, Australia [25,81,91,136–138]. In this case, the Hg used by miners to amalgamate gold in stamp batteries and the rates of Hg lost in the process were analyzed based on the seven historical mining districts of Victoria from 1868 to 1888. The total volume of Hg lost in Victoria ranged between 121 and 585 tons of reported imports [92], resulting in elevated Hg levels in water, sediments, and biota downstream of old gold workings [17,18]. Other studies have reported a significant Hg contamination from the major centers of the 19th century gold mining sites in California [139–141], North Carolina [142,143], Nevada [144], and New Zealand [145]. For instance, sedimentary and historic records from the San Francisco Bay
Recent stringent Hg release controls in most developed nations have led to a substantial fall in global Hg inputs into the environment, unlike the gold-rich developing nations, where gold amalgamation is on the increase. As observed by Nriagu [148], North America Hg releases fell to values ranging from 5400 to 12,150 metric tons/year in the late 1980s thanks to the effectiveness of Hg control policies. In developing countries, the major setbacks common to all are probably the lack of regulations and the inefficiency of environmental protection agencies to raise concern about environmental quality [149].

More Hg has been lost per metric ton of gold extracted in historic times compared to recent mining activities. However, the decrease over time in the amount of Hg released into the environment by AGM does not reduce its environmental impacts.

Our current knowledge of the environmental biogeochemistry of Hg tends to suggest that the bioaccumulation and toxicity of Hg to aquatic organisms are not necessarily an issue of total quantity (i.e., total concentrations) but rather a qualitative one (i.e., speciation), leading to the methylation of Hg. Therefore, the current increase in AGM in gold-rich developing nations and the introduction of Hg into the environment in Africa, Asia, and South America could result in short- and long-term catastrophic effects, regardless of the actual amount discharged into river basins, where most gold mining activities occur (Figure 4). In addition, the lack of adequate equipment in the handling and processing of Au-Hg amalgam by miners leads to direct exposure to Hg vapor by inhalation.

![Figure 4. Main pathways of mercury (Hg) released into the environment by artisanal gold mining (AGM). On local to regional scales, AGM is a known source of Hg pollution in impacted soils, waters, sediments, and the atmosphere. Human exposure is primarily through inhalation (for miners) and via consumption of Hg-contaminated food as a result of the biotransformation of inorganic Hg species to methyl-Hg species.](image-url)

Unfortunately, AGM is driven primarily by several social predicaments, the lack of alternative employment, and many other factors that do not have foreseeable solutions.
Therefore, the development of efficient and affordable mining techniques/practices that can help to protect the environment and minimize the direct exposure of miners to Hg vapor is necessary. Past or present gold mining practices by Hg amalgamation would likely result in lingering adverse impacts on the environment and living organisms.

3.3. Fate of Mercury Introduced into the Environment

Figure 4 summarizes the pathways of Hg\(^0\) released into the environment because of gold mining by Hg amalgamation. Artisanal gold mining releases Hg\(^0\) directly to soil, water, and sediments during the amalgamation process and into the atmosphere during the torching of the obtained Au-Hg amalgam in the open environment, followed by gold purification, which takes place in gold shops. In each of these environmental compartments, Hg\(^0\) undergoes transformations ultimately to produce chemical species that are readily bioavailable, leading to Hg bioaccumulation. Hg\(^0\) released into the atmosphere from the different Au extraction stages can undergo atmospheric oxidation through reactions mediated by ozone, solar energy, and water vapor to yield divalent Hg ions (Hg\(^{2+}\)) (Figure 4). Particle reactive and soluble Hg(II) compounds are then returned to the terrestrial environments by wet/dry deposition [33,150,151]. Under hot tropical atmospheric conditions, Hg\(^0\) oxidizes quicker than in temperate atmospheres, and such oxidation is faster in the presence of ozone and soot emissions that come from forest burning [33,109,112,152]. As a consequence, and when compared to temperate regions, shorter residence times in the atmosphere and higher atmospheric deposition rates of Hg have been reported for the Brazilian Amazon [112,153,154], limiting the long-range transport of Hg and contamination of distant ecosystems. Once deposited on soil and/or aquatic landscapes, further transformations occur, including the reduction of atmospherically deposited Hg\(^{2+}\), catalyzed by biotic and/or abiotic processes, to Hg\(^0\) and the return to the atmosphere via volatilization. On a global scale, this cyclic behavior sustains the flux of Hg between the atmosphere and terrestrial landscapes [33,38,43].

The atmospheric portion of the Hg cycle is dominated by inorganic species, primarily Hg\(^0\). Despite the presence of methyl-Hg in rainwater samples [155], there are no known chemical pathways for atmospheric methyl-Hg production. It is believed that terrestrial sources (e.g., wetlands, landfills) release alkyl-Hg (mono- and di-methyl Hg) compounds into the atmosphere [156,157].

3.4. Gold Mining and Mercury Pollution of Terrestrial Landscapes

In the past, gold ores from placer deposits and deep shaft mines were pulverized at stamp mills before Hg amalgamation, while current gold miners depend mostly on ground gold-rich soils and active bottom or riverbank sediments [38,100]. Therefore, in addition to Hg contamination of terrestrial landscapes via atmospheric deposition, Hg\(^0\) enters aquatic and terrestrial systems directly during the stamping, grinding, sluicing, panning, and amalgamation processes. Mine wastes rich in Hg\(^0\) are usually left on riverbank soils, concentrated in mining ponds, or directed to nearby waterways, where they become dispersed through fluvial processes [158]. In AGM-impacted sites, droplets of Hg\(^0\) are often found at roasting and amalgamation sites [26,38,100,111]. As stated earlier (Figure 4), Hg\(^0\)-contaminated terrestrial landscapes would then become sources of Hg to both the atmosphere and aquatic systems. In fact, mining sites impacted by the use of Hg in amalgamation techniques during historic gold rushes continue to experience Hg contamination (e.g., California, Nevada) and Hg\(^0\) concentrated in tailings mobilized through leaching, infiltration, surface run-offs, and particle transport into aquatic systems [26,35,69,144]. Hg leaching from soils is also accelerated by shifts in soil land use [112]. Overall, the above transport mechanisms lead to the contamination of both surface and ground waters, and they are more pronounced in regions with high annual precipitation [84].

In aquatic systems, metallic Hg can be found as liquid droplets accumulated at the water–sediment interfaces and as dissolved gaseous mercury (DGM) or Hg(0)\(_{aq}\). The solubility of the latter decreases with increasing water temperatures due to volatilization,
reducing the concentrations of DGM. However, recent reports on the redox chemistry of Hg at the water–atmosphere interface show that the solar-radiation-driven oxidation of Hg(0)_{aq} occurs at rates greater than those of the reduction of Hg(II) to Hg(0)_{aq} \[14–16,159\]. Therefore, the balance tends to favor the accumulation of Hg(II), which remains in the aquatic system. Next, because of its high particle-reactive nature, Hg(II) partitions between liquid and solid phases and predominantly accumulates in bottom sediments following the settling of Hg-contaminated particles. Over time, the contaminated sediments could behave as a source of Hg as a result of physical (e.g., bioturbation, diffusion), microbial, and/or chemical processes \[25,160\].

For a long time, metallic mercury has been assumed as being not very reactive and having little to no toxicity \[3,161–163\]. Besides the different transport pathways discussed above, Hg(0) introduced into soils or sediments can be oxidized to Hg(II). Several laboratory studies have shown that, once introduced into the environment, the poorly reactive Hg(0) could undergo oxidation. For instance, in oxygenated waters (e.g., exposed to air), metallic mercury can be easily oxidized by molecular oxygen at ambient temperature and in the presence of halides such as chloride and organic compounds such as fulvic and humic acids \[3,161–163\]. Further studies have shown that liquid metallic Hg, which accumulates at the water–sediment interface in AGM-impacted aquatic systems, could undergo oxidation under dark (i.e., absence of light) and oxygenated conditions, excluding photo-oxidation as a potential mechanism, and with oxidation rates correlating with chloride concentrations and droplets’ surface areas \[164\]. Dark oxidation of DGM has also been reported under extreme conditions, mimicking polar ice and in the presence of a variety of materials, including hydrogen peroxide, nitrous acid, and the sulfuric acid/O\(_2\) couple \[165\]. In addition, under anoxic conditions, which tend to prevail in most sediments, the oxidation of metallic Hg has been demonstrated experimentally, with significant Hg(0)_{aq} oxidation observed with organic compounds containing thiol groups, while the rate and extent of Hg(0)_{aq} oxidation varied greatly with the chemical and structural properties of thiol compounds, thiol/Hg ratios, and the presence or absence of electron acceptors \[166\]. Laboratory studies have also shown that certain soil bacteria (e.g., Bacillus and Streptomyces) could oxidize Hg(0) \[108\]. Later studies confirmed that certain soil and sediment anaerobic microorganisms (e.g., sulfate- and iron-reducing bacteria) could oxidize Hg(0) as well \[167, 168\]. These observations strongly suggest that Hg(0) would undergo oxidation under a wide variety of environmental conditions. The results reported in the literature on this aspect of the cycling of Hg suggest that reactivity toward Hg(0) is widespread among diverse anaerobic bacteria, and that even the passive microbial oxidation of Hg(0) could play an important role in the redox transformation of Hg in subsurface environments. Therefore, although Hg released from AGM is in the metallic form, it undergoes oxidation to produce Hg(II) species. Hg(II) is susceptible to microbial transformation, explaining why Hg found in the tissues of aquatic organisms inhabiting most Hg-contaminated systems primarily exists as MeHg \[169–171\]. These observations point out the importance of Hg(0) oxidation as a key step in the methylation, bioaccumulation, and biomagnification of Hg. It should be emphasized that the potential exists for both non-biological and biotic processes to mediate the methylation of Hg(II) under environmental conditions \[172\].

Hence, MeHg that accumulates in soils and sediments as a net product of the above-described processes finds its way into living organisms and food chains via a combination of (1) direct absorption by diffusion through the lipid bilayer of cell membranes and (2) intake through diet. This aspect of the biogeochemistry of Hg is discussed herein in relation to the impact of Hg on human health.

3.5. Mercury and Human Health Impacts

The forms of Hg of greatest health concern in gold mining by amalgamation are Hg\(^0\) and the resulting MeHg \[16,29,76,128,173–176\]. Exposure by inhalation includes Hg\(^0\) vapor during the processing of the gold ore and the refining of Au-Hg amalgams as well as releases from untreated wastewater directly discharged into water bodies \[3,10,123,177\]. At
both historic and present AGM sites, miners wear very limited to no protective equipment, such as face masks, respiratory protectors, or gloves, during the amalgamation process and refining. Therefore, miners frequently exhibit Hg intoxication (sleep disturbance, irritability, fatigue, and excessive salivation). A few studies from North America, Australia, and South Africa on the Hg intoxication of miners in both recent and past years confirmed the incidents in historic mining centers [14–16,29,99,128,178–180] by unveiling what might have been the most disastrous and worst health impacts of Hg. The health impacts of Hg on current AGM miners in the tropics, non-miners, and the environment have also been studied in Africa, Asia, and Latin America, and evidence of human contamination has been found at several of the studied sites [9,21,50,124,181,182]. Health assessment of artisanal gold miners in Tanzania, Indonesia, and the Philippines in recent times showed that Hg-exposed workers exhibited symptoms of Hg intoxication, with high Hg levels in urine and symptoms of brain damage, like ataxia, tremor, and movement disorders [15,16,149,182–185]. The same studies identified the Au-Hg amalgam burners as the most impacted.

The accumulation of MeHg in fish and other aquatic organisms is the result of coupled biogeochemical and ecological processes [17]. As mentioned earlier, and when not already present as Hg(II), the process begins with the oxidation of metallic Hg to Hg(II), followed by the methylation of produced Hg(II) by microorganisms, usually in anoxic sediments. Subsequent accumulation in biota occurs via bioconcentration and biomagnification through different trophic levels in the aquatic food chain. Bioconcentration results from the uptake of MeHg via diffusion across cell membranes [37,186] and its rapid accumulation in tissues [187]. Once inside cells, MeHg binds strongly to sulphydryl groups of proteins, hence allowing for its accumulation in living tissues [188]. Finally, because of its relative stability in biological systems, MeHg is eliminated more slowly than the inorganic forms of Hg. Biomagnification, however, results from food intake across successive trophic levels [189–191]. Accordingly, the higher the trophic level of a given species of fish, the greater the likelihood of it being contaminated with MeHg via combined processes of bioconcentration and biomagnification [17,18]. Thus, high-trophic organisms such as the predatory fish are particularly prone to MeHg contamination. Due to biomagnification, fish MeHg levels will be several orders of magnitude above levels in the surrounding waters [171,189,190].

Humans contract Hg contamination upon ingestion of Hg-contaminated dietary items such as fish, beef, chicken, goat, vegetables, etc. MeHg is rapidly absorbed from the gastrointestinal tract of humans due to its fast transport through biological membranes, which, in association with tissue, is very stable and is neither degraded nor excreted from the body at any significant rate. Consequently, MeHg is accumulated by organisms through their lifetime [175,176]. MeHg neurotoxicity is of concern, particularly to the developing fetus [52,192–194], and exposure to Hg by consumption of Hg-contaminated fish has been linked to neurological damage and myocardial infarction [8,9,195–197]. Many studies have documented Hg levels in fish collected from Hg-contaminated and non-impacted sites in the developed world, resulting in several posted fish consumption advisories [10,20,198,199]. By contrast, the levels of Hg in fish inhabiting water bodies impacted by AGM in developing nations are moderately documented [48,50,133,174,200,201], and no fish consumption advisories exist in most of these regions where subsistence fishing is the main source of proteins.

Most studies examining the correlation between artisanal gold mining activities and environmental pollution have primarily relied on mercury (Hg) concentration data. However, a growing number of recent studies have shifted their focus to measuring stable Hg isotope ratios. These studies, primarily conducted at local scales, aim to understand the sources, processes, and fate of mercury in both AGM-impacted and non-impacted environmental compartments (e.g., [202–208]). This approach is driven by the understanding that Hg introduced into the environment by mining activities exhibits isotopic differences from background mercury, aiding in the tracing of anthropogenic mercury’s fate.
Tracing studies utilizing stable Hg isotopes to investigate the fate of Hg(0) volatilization have shown considerable success, while, in matrices such as fish tissues, the fate of Hg(0) associated with AGM has been difficult to trace because these samples represent mixtures of multiple Hg sources and are influenced by complex processes leading to Hg isotope fractionation [207].

In French Guiana, a study on a comparison of Hg isotopic signatures in fish collected from AGM-impacted and non-impacted study sites revealed challenges due to differences in biotic and abiotic processes between the areas. One of the sites, affected by AGM activities, did not allow for the resolution of the contribution of gold-mining-related liquid mercury in fish tissues [208]. Another study utilized a mercury isotope binary mixing model combined with multiple linear regression based on physicochemical parameters measured in sediment samples. This study found that active mined creek sediments were contaminated by AGM activities, with up to 78% of the total mercury (THg) being anthropogenic. Of this anthropogenic mercury, more than half (66%–74%) originated from liquid mercury released during AGM, while the remaining anthropogenic Hg came from the AGM-driven erosion of Hg-rich soils into the river [206]. In the Brazilian Amazon, a study conducted downstream of AGM sites found that the elevated Hg levels originated predominantly from the increased erosion of soils rather than from Hg(0) used during gold extraction [203].

Regarding human exposure, a study by Sherman et al. [202] found that THg concentrations in hair and urine among small-scale gold mining populations in Ghana exhibited similar $\Delta \text{Hg}^{199}$ values to Hg derived from ore deposits. This suggests that urine THg concentrations reflected exposure to inorganic Hg among this population. Hair samples displayed low positive $\Delta \text{Hg}^{199}$ values and low percentages of THg occurring as MeHg, indicating that the majority of Hg in these miners’ hair samples was exogenously adsorbed inorganic Hg and not fish-derived MeHg. In contrast, hair samples from Indonesian gold miners who consumed fish daily showed a wider range of positive $\Delta \text{Hg}^{199}$ values and percentages of THg as MeHg, suggesting that THg in the hair samples from Indonesian gold miners was likely a mixture of ingested fish MeHg and exogenously adsorbed inorganic mercury.

Overall, the review of the literature shows that the resolution power of the Hg stable isotopes needs improvement for samples with complex mixtures and in which Hg accumulates after undergoing fractionation. Therefore, more research is needed. Additionally, AGM activities contribute to both land-cover and land-use change and local contamination of soils by Hg(0). Accordingly, effective Hg mitigation strategies should address land-use practices in addition to Hg(0) pollution from AGM.

3.6. Ongoing Efforts to Curve Hg Contamination of Natural Systems by AGM

Previous reviews of the literature on the global sources and pathways of Hg in the context of human health [15,16,209] concluded that research is still needed on the improvement of Hg release inventory data, the chemical and physical behavior of Hg in the atmosphere, the improvement of monitoring network data, and predictions of future releases and speciation, as well as on the subsequent effects on the environment, human health, and economy. As one of the civilization’s oldest technologies, gold extraction by Hg amalgamation holds the dubious distinction of having escaped the waves of innovation that swept comparably ancient practices such as those used in historic agriculture or medicine [49], and has the potential to significantly impact the environment, human health, and economy. Accordingly, the Global Mercury Project (GMP), the most significant endeavor in a series of efforts aimed at mitigating Hg pollution from artisanal and small-scale gold mining (ASGM), concluded in 2008. Since then, a plethora of publications and critical reflections on its mixed results have emerged. Notably, the GMP slowed the pace of international endeavors to address Hg contamination, and, along with the drafting of the Convention, they provided an opportune moment to evaluate the efficacy of approaches to combating mercury pollution in ASGM.
It is also a timely opportunity to contemplate the nature of future interventions and to possibly reorient the approaches used to address this pollution issue [210].

The Minamata Convention, an international treaty aimed at addressing global mercury emissions, was ratified in October 2013, with considerable attention given to the substantial mercury emissions associated with ASGM. The Convention adopted a life-cycle approach to the production, use, emissions, releases, handling, and disposal of Hg [211]. In 2017, the Minamata Convention on Hg control came into effect. However, its effectiveness and its impact on reshaping the global Hg flow remain uncertain [212]. Article 7 of the Convention mandates that governments establish National Action Plans (NAPs) to reduce and, where feasible, eliminate Hg use in ASGM, a rapidly expanding informal economic sector in gold-rich nations in Africa, South America, and Asia. These strategies are to be monitored by the Convention Secretariat [213]. Recent data from submitted Minamata NAPs confirm the ongoing widespread use of mercury in ASGM, but addressing this usage of Hg necessitates effective strategies that not only promote Hg-free technologies but also tailor them to the geological, technical, social, and economic conditions under which ASGM operates [214].

While the Minamata Convention on mercury control represents a positive step forward, the firsthand experiences of the authors in most countries in Africa reveal that miners frequently find ways to circumvent or disregard regulations. Law enforcement in these countries is often hindered by corruption, with compliance dependent on bribery rather than adherence to the law.

4. Conclusions and Recommendations

We found that the use of Hg(0) in AGM remains the method of choice in most developing countries. This process is generally performed outdoors, thus resulting in Hg discharges to soils, aquatic systems, and into the atmosphere. The environmental fate and the impacts of the released metallic Hg have been extensively investigated in historic gold mining sites found in North America and in a good number of European countries. Meanwhile, for sites of ongoing gold mining by Hg amalgamation, the Amazon River basin has been the focus of most recent studies on the environmental and health impacts of AGM. However, the situation in Asia and Africa remains poorly studied and the extent and gravity of the problem remain quasi-unknown. Additionally, and due to the lack of alternative employment in most gold-rich developing nations, AGM is seen by thousands of people as the only route to prosperity. Therefore, we conclude that this growing economic sector is here to stay. However, the lack of safe and environmentally sound gold production methods is leading to severe contamination of the environment, with potential adverse effects on human health. Since AGM in developing nations cannot be simply stopped, the growth of this economic sector should be accompanied with a set of measures that help to protect both the environment and human health. We suggest the following approach: first, necessary financial resources should be allocated to research that seeks the development of efficient, affordable, and easy-to-use technologies aimed at either eliminating or reducing the amount of Hg released into the environment during AGM. Pending the development of a Hg-free gold extraction technology that can be easily used by artisanal gold miners, the focus should be on the improvement of the current Hg amalgamation technique. This can be carried out in a way that includes incentives to miners, such as an efficient recovery of Hg used in the amalgamation and the possibility of recycling the recovered Hg. International organizations such as the World Bank Global Environment Facility (GEF) and the United Nations Industrial Development Organization (UNIDO) could support research initiatives with such objectives. For any tested and proven technology that becomes available, the second step would be to get it used on a regular basis by gold miners. To meet such an objective, advocacy groups, academic institutions, and local government agencies should work in concert toward the implementation of the developed technology. In contrast to the common traditional approaches for the dissemination of scientific and engineering findings and the resultant formulation of public policy that are primarily “top-down” in nature, the suggested approach here would be to use the
incentives provided by the developed technology (e.g., Hg recovery and recycling). These incentives, in combination with the education of miners on the impact of Hg on human health, would help to drive the implementation of the developed technology. The premise of the proposed approach is to ensure that technical solutions to Hg issues are in sync with the miners’ perceptions and acceptance of the recommended solutions. The process should be consultative in nature and effectively planned, and the implementation should involve the identification and involvement of all key players. The education component would help the miners to understand the implications of Hg contamination and hopefully become knowledgeable and motivated to actively support and even help in the design and monitoring of prevention/remediation procedures. The information/education of the miners could be developed following the approach that has been used quite successfully in sexual education to prevent the spread of HIV/AIDS in Uganda. However, unlike HIV/AIDS, AGM is a source of income for those involved in this activity. Therefore, it will not be reasonable to push for a complete cessation of such activities since local governments cannot provide the miners with alternative income-earning sources. However, the Ugandan example could be used partly, in that local leaders could help to communicate a credible message of alarm and advice based on current knowledge of the effects of Hg on human health. Powerful teaching tools such as video tapes, films, pictures, etc., could be employed in the dissemination process. Meanwhile, some of the alternative Hg-free mineral processing technologies that have been successfully utilized to alleviate environmental impacts in AGM, currently in parts of South America, could be adopted in many of the gold-rich developing nations. Methods including gravity separation, which isolates minerals based on differences in densities, and the Knelson concentrator [174,215–217] could be used as alternatives in Hg mitigation.

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