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Environmental Impact Statement

Biogeochemical Transformations of Mercury in Solid Waste Landfills and Pathways for Release

Sung-Woo Lee[1], Greg V. Lowry[2], and Heileen Hsu-Kim[1,*]

Numerous types of mercury-bearing commercial products and industrial solid wastes are frequently disposed to municipal waste landfills. While landfills are recognized to be a potential source of Hg to the atmosphere and groundwater, the processes that control Hg emissions are not well studied. This review article provides an analysis of the scientific literature documenting the flux of mercury from municipal solid waste landfills. Recent advances in mercury biogeochemistry, including processes related to microbial mercury methylation, mercury reduction, and colloidal transport of nanoscale phases, are relevant for the release of mercury in landfills setting. Future research is needed to determine the relative importance of these processes in the unique conditions of landfills and the potential release of mercury over the long term.

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Biogeochemical Transformations of Mercury in Solid Waste Landfills and Pathways for Release

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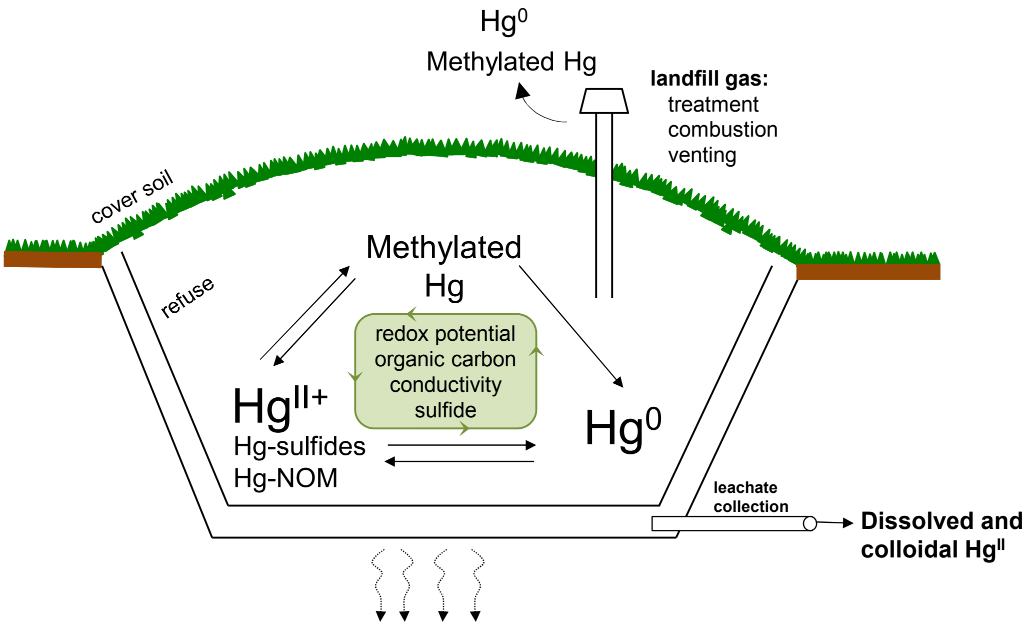
Graphical Abstract



This review summarizes pathways of mercury release from conventional landfills and describes biogeochemical conditions that can volatilize or mobilize this toxic metal from landfills.

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Abstract

Mercury (Hg) is present in a variety of solid wastes including industrial wastes, household products, consumer electronics, and medical wastes, some of which can be disposed in conventional landfills. The presence of this neurotoxic metal in landfills is a concern due to the potential for it to leach or volatilize from the landfill and impact local ecosystems. The objective of this review is to describe general practices for the disposal of mercury-bearing solid wastes, summarize previous studies on the release of mercury from landfills, and delineate the expected transformations of Hg within landfill environments that would influence transport of Hg via landfill gas and leachate. A few studies have documented the emissions of Hg as landfill gas, primarily as gaseous elemental Hg(0) and smaller amounts as methylated Hg species. Much less is known regarding the release of Hg in leachate. Landfill conditions are unique from other subsurface environments in that they can contain water with very high conductivity and organic carbon concentration. Landfills also experience large changes in redox potential (and the associated microbial community) that greatly influence Hg speciation, transformations, and mobilization potential. Generally, Hg is not likely to persist in large quantities as dissolved species, since Hg(0) tends to evolve in the gas phase and divalent Hg(II) sorbs strongly to particulate phases including organic carbon and sulfides. However, Hg(II) has the potential to associate with or form colloidal particles that can be mobilized in porous media under high organic carbon conditions. Moreover, the anaerobic conditions within landfills can foster the growth of microorganisms that produced monomethyl- and dimethyl-Hg species, the forms of mercury with high potential for bioaccumulation. Much advancement has recently been made in the mercury biogeochemistry research field, and this study seeks to incorporate these findings for landfill settings.

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1. Introduction

Mercury is a toxic element that is capable of wide dispersal in the environment due to its ability to navigate through all compartments of the biosphere including air, water and soil [1-3]. The metal, particularly in the form of monomethylmercury, is capable of biomagnifying in the food web, resulting in risks for human health via dietary exposure to mercury-contaminated food such as fish [4]. Mercury-containing products have been widely used for numerous purposes including fluorescent lamps, computer monitors, ignition switches, and batteries, among others [5, 6]. In addition to these household products, mercury can also be found at levels of parts per million or more in solid wastes of geological origin such as dredge spoil of mercury-contaminated sediments, coal combustion residuals, and solid wastes produced at oil refineries [7-10].

Mercury-containing solid wastes are generally disposed in landfills or by incineration, depending on costs and regulations for disposal. The release of mercury from conventional landfills contributes approximately 5% of anthropogenic Hg emissions to the atmosphere[11, 12] and a relative small portion of the overall global atmospheric Hg pool [12]. Unintended releases could also have local and regional implications if the mercury is deposited or mobilized to nearby ecosystems. Redeveloped land over closed landfills could be specific locations of concern, as these types of landfills may have been closed long before requirements for leachate and gas collection systems were implemented. Therefore, landfill operators and other stakeholders will need to be aware of potential issues related to disposal of mercury-containing solid wastes.

The objectives of this paper are to review management practices for mercury-bearing solid wastes (as they pertain to disposal in conventional landfills), summarize previous work documenting the routes and flux of mercury released from solid waste landfills, discuss major

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transformation pathways within landfills that would influence its release, and identify major gaps in knowledge. Several studies have quantified the release or flux of mercury via landfill leachate or gas [13-17], but few have examined the speciation of the released mercury or investigated the transformations of mercury species *in situ*. To the best of our knowledge, no longitudinal studies on mercury release from landfills have been reported in the scientific literature. Therefore, a full understanding of transformations and release of mercury during all stages of landfill maturation is lacking. This study attempts to utilize recent discoveries pertaining to mercury biogeochemistry and discuss the relevance of these findings for the fate of mercury in solid waste landfills.

2. Management of Solid Wastes and Conventional Landfills

2.1 Regulatory Framework Guiding the Disposal of Mercury-Bearing Solid Wastes

Insight to the types of mercury-bearing wastes in landfills can be gained by an examination of regulatory policies for solid waste disposal. In the United States, disposal practices are typically guided by the Resource Conservation Recovery Act (RCRA) Subtitles C and D[18], as well as applicable state and local rules that sometimes add more stringent requirements. The classification of the waste as hazardous (Subtitle C) and non-hazardous (Subtitle D) is generally determined by the toxicity characteristic leaching protocol (TCLP)[19], a weak acid leaching test (typically pH 5) that is meant to represent landfill conditions. If the concentrations of potentially toxic elements in the leachate (i.e., mercury, among others) are above thresholds, then RCRA stipulates that the waste should be disposed in a Subtitle C landfill that is designed to contain hazardous waste. The Universal Waste Rule [20] is another federal

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regulation that aims to divert electronics (e.g. batteries, lamps) and other mercury-containing equipment to hazardous waste landfills.

Even with the regulations, however, mercury-bearing wastes can be disposed in non-hazardous waste landfills due to poor compliance or due to exemptions of these rules. Exempted waste streams include household hazardous solid waste, fossil fuel combustion residuals, waste generated from the exploration and production of oil, gas, and geothermal energy, and waste from the extraction and processing of ores and minerals[18]. (We note that in 2014 the U.S. EPA revisited and reaffirmed the non-hazardous waste classification for coal combustion residuals.[21]) All of these wastes are allowed to be disposed in non-hazardous waste landfills, including municipal solid waste landfills, and can potentially be an input of Hg. For example, the recycling rate of fluorescent lamps in 2001-2003 in the U.S. has been estimated to be approximately 25% [22], while a large portion of the remaining 75% was presumed to enter the solid waste stream and discarded.

The disposal of Hg-bearing solid wastes in municipal landfills is also a growing concern in China[23], one of the largest consumers of mercury in the world.[24] Most household waste in Chinese cities are disposed in municipal landfills, and this waste include mercury-containing products.[23, 25] While there are efforts to reduce the use of mercury in products such as batteries, fluorescent lamps and thermometers, the recycling rates at the end-of-life for these products are low in China, perhaps due to the lack of centralized collection programs for these types of wastes.[23]

In the European Union (EU) solid waste management practices follow Directive 2008/98/EC and 1999/31/EC (subsequently amended by Directive 2011/97/EU) that provide the framework in regulating waste and landfills, respectively. Mercury-containing wastes under

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these regulations are all considered hazardous waste and are subjected to leaching and percolation tests, similar to the TCLP testing in the U.S., to determine requirements for landfill disposal. Different types of landfills have different "limit values" under the EU regulations.

TCLP-type leaching tests for risk assessment are generally appropriate for most metals, as their mobilization is often greatest under acidic conditions. However, this approach may not be applicable for mercury. The adjustment of pH (i.e., acidic or basic) is a poor predictor of Hg mobilization potential because this metal is emitted through the gas phase as well as leachates, and these processes are controlled by a variety of chemical and biological transformations within the landfill (to be discussed in later sections of this review).

In summary, the regulations attempt to divert most mercury-bearing wastes to hazardous waste landfills. However with the exceptions and exclusions noted above, mercury-containing solid wastes will continue to be disposed in conventional landfills for the foreseeable future, and the legacy of this disposal practice needs to be understood.

2.2 Generation and Management of Landfill Leachates and Gases

As refuse in a landfill decomposes over time, leachates and gases are continuously generated in the landfill and provide pathways for the release of mercury. The composition of leachates and landfill gases (LFG), including the mercury concentration and speciation, depends on the conditions within the landfill and the age of the landfill. A landfill undergoes at least four stages of maturation during its lifetime (Figure 1): (I) an initial aerobic phase, (II) an anaerobic acid phase, (III) an initial methanogenic phase, and (IV) a stable methanogenic phase [26]. During the initial aerobic phase (Phase I), organic wastes are degraded by aerobic microorganisms, which results in the consumption of oxygen and an increase in CO_2. Meanwhile, leachate at this stage is derived from moisture extracted from the refuse during the compaction process and also

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from atmospheric precipitation (in the case of open landfills or closed landfills without surface liners). Once oxygen is depleted inside the landfills, anaerobic microorganisms become active during this second stage (Phase II). These microbes include hydrolytic, fermentative, and acetogenic bacteria that decompose organics and form acetate, hydrogen, and CO_2. Carboxylic acids and alcohols can also build-up as intermediates of these processes. Therefore during Phase II, LFG primarily consists of CO_2 and the leachate is generally acidic with pH values of 4.5-7.5 (average 6.1) [27]. The leachate will also contain acid-soluble constituents such as metal cations and high biological and chemical oxygen demand (BOD and COD, respectively). As Phase II transitions to Phase III, the pH is neutralized by the consumption of organic acids and the buffering capacity of the solid wastes. Methanogenic microorganisms become more active during this stage. Therefore Phase III is characterized by an increase in pH in the leachate and methane concentration in LFG [26, 27]. This stage is followed by a stable methanogenic phase (Phase IV) where the conditions are stabilized for methanogens to continuously produce methane. Leachates typically exhibit low BOD and COD in Phase IV.

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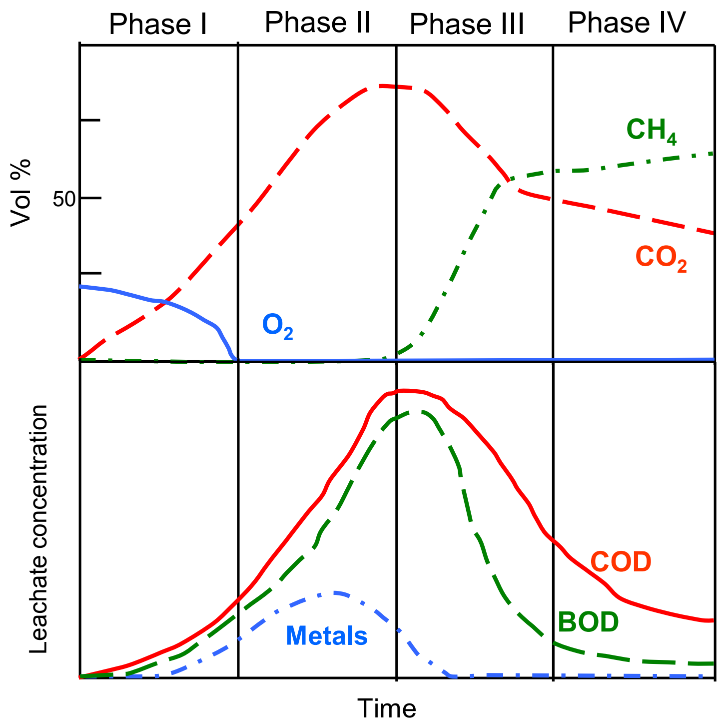

Figure 1. Trends in the composition of landfill gas and leachate during the major phases of maturation for landfills (modified from Kjeldsen et al 2002)[26]. The phases are distinguished by microbial decomposition of the refuse that alter the major gas composition in the landfill and leachate characteristics such as organic carbon (typically quantified as chemical and biological oxygen demand – COD and BOD, respectively) and dissolved metals concentrations. (Note: figures are not to scale with respect to the length of time for each phase).

Leachate can contain soluble toxic substances (organic and inorganic) that originated from the waste material. Likewise, LFG can contain NH_3 and non-methane organic compounds that could contribute to poor air quality or pose health risks to local communities [26]. For this reason solid waste landfills in the U.S. and other developed nations are generally required to monitor and control the release of toxic constituents in leachates and gases. For conventional landfills in the U.S. (i.e., nonhazardous Subtitle D landfills), these requirements include a double layer of materials with low permeability at the base of the landfill with leachate collection systems and double surface layers on top to minimize extra moisture from entering the landfills. LFG vents are often installed to aid the treatment of gas that would otherwise accumulate in the

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landfill and escape in an uncontrolled manner. We note that the implementation of many of these requirements in the U.S. was in 1991 and coincided with a large decrease in the number of open landfills. (The U.S. Environmental Protection Agency reported 7924 municipal solid waste (MSW) landfills in 1988 and 1767 MSW landfills in 2002 [28]). This suggests the existence of thousands of closed landfills in the U.S. that do not have impermeable liners. Therefore, the subsurface and atmosphere near closed landfills may be susceptible to unrestricted release of leachates and LFG.

LFG vents are installed primarily to prevent accumulation of pressure inside the landfill. Pressure buildups can be problematic and an explosion hazard, especially if the LFG contains sufficient concentrations of CH_4 (typically 5-15% v/v) [29]. LFG can be vented directly to the surrounding atmosphere or collected for specific purposes such as energy recovery or flaring. In landfills that collect LFG for gas utilization, certain cleanup procedures are employed to remove moisture and trace constituents (e.g., non-methane organic carbon and H_2S) and to minimize health hazards, odors, and deterioration of pipelines and other infrastructure [30].

3. Environmental chemistry of mercury

Mercury is emitted to atmospheric and aquatic environments from a variety of natural and anthropogenic sources and is capable of traveling between all compartments of the biosphere (atmosphere, water, and soil), as summarized in reviews by others [3, 31-33]. Mercury can occur as one of three oxidation states (0, +I, and +II) and as different compounds based on the conditions and constituents of the environmental medium (Table 1). Gaseous forms of mercury include elemental mercury Hg(0), methylated mercury species, and volatile ligand complexes of inorganic Hg(II), including $HgCl_{2(g)}$. Oxidized gaseous Hg species generally have smaller

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Henry's Law constants than Hg^0, indicating that the oxidized species tend to readily partition into water droplets and aerosol particles [34].

In natural waters, dissolved Hg species primarily include oxidized Hg(II) such as Hg^{2+}-ligand complexes and organo-mercury species such as monomethylmercury (MMHg) and dimethylmercury (DMHg). Because Hg^{2+} tends to form strong bonds with ligands such as chloride, sulfide and organic matter, the fully hydrated Hg^{2+} ion is not expected to exist in appreciable quantities for the range of pH values relevant to landfills. Dissolved gaseous mercury could also persist in certain cases, and this form of mercury is generally perceived as $Hg^0_{(aq)}$ (which has a solubility of $10^{-6.5}$ M at 25°C [35])

Monovalent Hg(+I) occurs as the Hg_2^{2+} dimer in the aqueous phase. This species is generally not considered to be thermodynamically stable at environmentally relevant mercury concentrations and tends to disproportionate to Hg(0) and Hg(+II) species [2, 36]. However, low levels of Hg(+I) are possible in water since this species is the likely intermediate of discrete 1 e^- transfer steps during redox cycling between Hg(0) and Hg(+II) [37]. Solid phase species of mercury include minerals phases of Hg(II) (e.g., HgS, HgO) and Hg(II) sorbed to particles of organic carbon, mineral oxides and sulfides. Liquid phases of Hg(0) are also possible in porous media, such as mine tailings of gold and mercury mines [38].

Table 1. Major species of mercury in the gas phase, aqueous phase, and solid phase compartments of the biosphere. Mercury-containing compounds can be broadly classified into inorganic Hg (with 0, +I, +II oxidation states) and organic Hg such as monomethylmercury (MMHg) and dimethylmercury (DMHg) species.

Mercury oxidation state	Gas Phase	Aqueous Phase	Soil/Particulate Phase
Hg(0)	$Hg^0_{(g)}$	$Hg^0_{(aq)}$	$Hg^0_{(l)}$

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Hg(I)		Hg_2^{2+} (not common)	$Hg_2Cl_{2(s)}$
Inorganic Hg(II)	$HgCl_{2(g)}$, $Hg(OH)_{2(g)}$, $HgO_{(g)}$	Hg^{2+}-ligand complexes (where ligands = Cl^-, OH^-, HS^-, sulfhydryls)	$HgS_{(s)}$, $HgO_{(s)}$, Hg^{2+} adsorbed to mineral phases and particulate organic matter
Organic Hg(II) (MMHg and DMHg)	$(CH_3)_2Hg_{(g)}$, $CH_3HgCl_{(g)}$	CH_3Hg^+-ligand complexes $(CH_3)_2Hg_{(aq)}$	CH_3Hg^+ adsorbed to minerals and particulate organic matter

The transformations of mercury-based compounds from one species to another generally involve chemical, photochemical, or microbial processes. Important pathways include redox transformations, which can govern the distribution and mobilization of mercury in atmospheric and aquatic compartments. Redox reactions of mercury are known to be induced by photochemical and microbial processes[37, 39], which are relevant at various stages in the lifetime of a landfill (open and closed). The formation and degradation of methylated mercury species is also of great interest due to the high bioaccumulation potential of MMHg and known health risks for humans and wildlife [40]. The production of MMHg in the environment is mediated primarily by anaerobic microorganisms that reside in anaerobic settings such as the bottom waters of stratified aquatic systems, saturated soils, benthic sediments, and biofilms of periphyton. The degradation of MMHg can occur by microbial or photochemical processes. The formation of dimethylmercury (DMHg), another form of methylated mercury, has not been studied as closely as the process of MMHg production. However, we note that measurement methods for methylated mercury typically include both MMHg and DMHg, and MMHg is often presumed to be the dominant form of total methylated mercury in terrestrial and freshwater environments [41]. The production of DMHg in surface waters is thought to be mediated by microorganisms and is a pathway for mercury evasion to the atmosphere [33, 42].

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4. Documented releases of mercury from landfills

Because mercury can exist in all three phases (gas, liquid, and solid), the release of this metal from landfills occurs through both LFG and leachate. Several studies have monitored total mercury contents in landfill leachates[43, 44] and in landfill gases[45-49]. Only a few studies have attempted to determine the Hg speciation and these studies are mainly for the gas phase[13, 14, 50, 51].

4.1 Emission and speciation of gaseous mercury from landfills

LFG emissions have gained much interest in recent years, as landfills have been identified as one of the major anthropogenic sources of CH_4, a potent greenhouse gas.[52] However, other gaseous compounds (e.g., gaseous mercury) can also be present in LFG. In landfills, gaseous mercury can potentially be emitted through three different pathways: (i) the working face of open landfills, (ii) LFG vents, and (iii) landfill cover soils [15].

The working face of a landfill is the area where solid wastes are actively added and compacted [30]. Several studies have found that emissions at the working face of the landfill were greater than emissions at LFG vents or cover soils.[15, 51, 53] As summarized in Figure 2, Hg emissions quantified at the working face of landfills ranged from 75 to 3200 g yr^{-1} and were always higher than any other pathway monitored at the same landfill.[15, 51] The large variability among different sites probably reflects the variety of mercury contents and species in the refuse and the processing of the waste material. For example, among the landfill working faces examined by Lindberg *et al.* (Figure 2), the highest Hg emissions were observed at the Brevard County landfill. The refuse at this landfill was shredded, which may have increased Hg emissions relative to other landfills where the waste was not shredded [15]. Similarly, another study

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demonstrated the heterogeneous nature of landfill wastes[54] by reporting mercury concentrations ranging from <0.1 to 17 mg kg^{-1} in more than 100 samples from the same landfill.

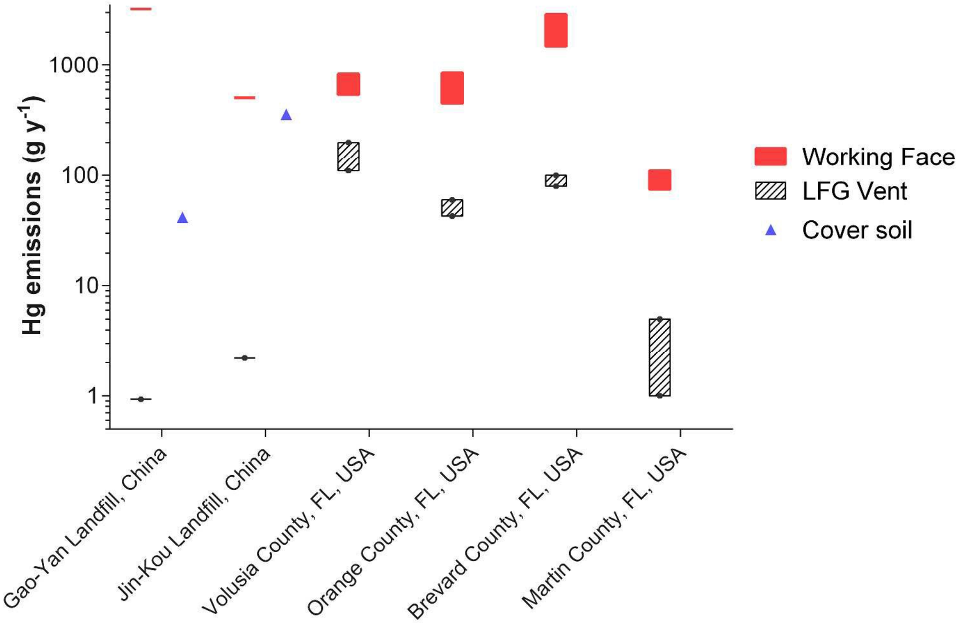

Figure 2. Measurements of gaseous Hg emissions at the working face, landfill gas (LFG) vent, and cover soil of solid waste landfills in China (Li et al., 2010)[51] and the United States (Lindberg et al., 2005)[15].

The relatively large rates of Hg release at the working face compared to other emission pathways at landfills are likely due to the lack of a barrier (e.g., cover soil or liners) for volatile Hg compounds. Elevated mercury emissions at the working face can also be attributed to the active process of waste compaction as the solid wastes with encapsulated Hg(0) (e.g., fluorescent lamps) are mechanically degraded. We note that not all gaseous mercury compounds encapsulated in the refuse may be released at the working face. Studies have shown that broken fluorescent lamps can partially release mercury vapor in 4 days (~ 30 % of total mercury in the product) and can take 43 days to release all of the mercury in the product [55, 56].

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Unlike emissions in the working face where the mercury is likely to be directly released from refuse materials, the pathway towards the production of gaseous mercury in the covered portions of the landfill can be more complex. Gaseous mercury emitted via LFG vents and landfill cover soils can be due to (i) direct release of gaseous mercury contained in the waste that was not emitted at the working face, and (ii) release of gaseous mercury that was produced in the landfill through biogeochemical processes. The latter would occur if aqueous or solid-phase Hg(II) in the refuse was converted to volatile mercury species within the landfill (mostly likely by a microbial process) .

Based on a selection of measurements of Hg concentrations at LFG vents, total mercury emissions in the U.S. has been projected to be 70-80 kg yr^{-1} [57]. We note that this value does not consider emissions by cover soils and other pathways. Moreover, no long-term studies are available to document mercury emissions from a single landfill. However, it should be noted that LFG of newer landfills tended to have higher concentrations of mercury relative to older landfills, as described by Lindberg and Price [58]. Specifically, this study reported gaseous mercury concentrations of 55.1-156 ng m^{-3} and 166-1464 ng m^{-3} in LFG of older and newer landfill, respectively. Perhaps the decrease in concentrations of gaseous mercury in LFG of older landfills can be explained by the decrease in readily volatile mercury species in landfills.

Landfill cover soils, the final cover that sits on top of the wastes[59], can also emit gases that are produced within this layer, depending on the presence of liners and transformations of gases emitted from the buried waste materials. The surface liners of landfills are designed for low permeability and generally divert the gas generated in landfills to the LFG vents. In the absence of surface liners or in cases of failures, LFG can move upwards with relatively fewer restrictions, and gaseous mercury then be emitted simultaneously through LFG vents and landfill

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cover soils. Interestingly, however, emissions of mercury via cover soils were higher than via LFG at two landfills in China (Figure 2). It is unknown whether these landfills had surface liners. It is also possible that the cover soil itself was contaminated with mercury and therefore served as a source of gaseous Hg that contributed to emissions over the landfill.

The importance of emissions via landfill cover soils relative to the working face and LFG vents is not clear. Gaseous mercury concentrations at the LFG vents have been observed at levels of 15-900 times greater than background atmosphere[15], while the contribution of Hg emissions from cover soils is sometimes at background levels and sometimes above. In two separate studies, the Hg emission fluxes from cover soils had relatively high mean values of 39.0 and 253 ng m^{-2} h^{-1} [46, 60]. For reference, Hg emissions of ~1-10 ng m^{-2} h^{-1} have been observed from soils with other types of land cover (deciduous forest and agricultural fields).[61] Other landfill studies demonstrated much lower mercury emissions from cover soils, with fluxes of 2-11 ng m^{-2} h^{-1} and similar to background reference soil.[15, 58] The magnitude of Hg emissions from cover soils is likely to depend on the presence or absence of surface liners, as stated above. However, failures of liners are known to occur, as indicated by enhanced methane emissions and dead vegetation caused by LFG [58]. At such locations with defective underlying liners, gaseous mercury fluxes were 18-22 ng m^{-2} h^{-1} and approximately 4-fold higher than the background levels (5 ng m^{-2} h^{-1}). [58] Moreover, soil samples at areas with dead vegetation exhibited slightly elevated levels of mercury (31.2 to 369 ng g^{-1}) compared to the control soil sites (30 to 60 ng g^{-1}) [58]. This study also indicated that methane and mercury emissions from the cover soils were not correlated, likely due to sorption of gaseous mercury to the cover soil. Further efforts to assess the long-term fate of mercury emitted from landfills should investigate the sorption capacity of the cover soils and possible transformations of sorbed mercury.

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In addition to gaseous Hg release at the landfill site (e.g., the working site, LFG vents and cover soil), gaseous Hg can potentially be released off-site as a result of horizontal migration of landfill gas in the subsurface unsaturated zone.[62] This emission pathway would be relevant in arid regions where low soil moisture allows for broader mobilization of gaseous Hg.

The speciation of gaseous Hg in LFG is predominantly in the form of Hg(0).[13, 51] Methylated mercury species, MMHg and DMHg, have also been detected in LFG vents (Table 3). [13, 14, 51] The concentrations of DMHg in LFG were generally higher than that of MMHg[13, 14, 51], likely due to the greater volatility of DMHg relative to MMHg. The Henry's constant ($HgX_{(g)}/HgX_{(aq)}$ (v/v)) for DMHg is approximately 0.31 at 25°C and similar to the Henry's constant for Hg(0) (0.29 at 20-25°C) [63-65]. In contrast, the Henry's constant for MMHg (in the form of CH_3HgCl) and $HgCl_2$ are approximately 10^{-5}-10^{-8} at 25°C [35, 66]. Therefore, if DMHg and Hg(0) are formed within the landfill, one can reasonably expect these compounds to partition into the gaseous phase. However, there appears to be no correlation between the sum of MMHg + DMHg and total gaseous mercury, as shown in Table 3. For example, concentration of total mercury emitted from a landfill in Palm Beach County was below 150 ng m^{-3} at one time point while it was above 10000 ng m^{-3} at another time. At these time points, the concentration of DMeHg was 8.7 and 6.5 ng m^{-3}, respectively.[13]

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Table 3. Concentrations of total gaseous Hg, monomethylmercury (MMHg), and dimethylmercury (DMHg) measured in landfill gas. Values are reported either as a range of concentrations or average ± standard deviation.

Site	Sampling dates	Total gaseous Hg (ng m^{-3}) [b]	MMHg (ng m^{-3})	DMHg (ng m^{-3})	Reference
Asia					
Gao-Yan landfill, Guiyang, China	2003-2006	2.0-1406.0	0.14-6.37	1.64-19.05	51 50
Jin-Kou landfill, Wuhan, China	2004	5.0-74.0	nd	nd	51
Nanjido landfill, Seoul, Korea	2000	4.59-2646	nd	nd	45
Laogang landfill, Shanghai, China	2011-2012	3 - 1130 [a]			53
North America					
Mexico City, Mexico	2003	52.4±15.6	nd	nd	48
Marin County, California, USA	2001	4700±3700	nd	<0.03	13
Kent County, Delaware, USA	2003	380-440	1.3±0.05	38±0.74	13
Brevard County, Florida, USA	1998-1999	7190-11500	6-39	30-77	14
Orange County, Florida, USA	1999	1400±230	1.7±0.7	66±24	13
Volusia County, Florida, USA	2001	6900±2000	25±3	63±3	13
Palm Beach County, Florida, USA	2002	66-12000	nd	6.5-8.7	13
Martin County, Florida, USA	2002	10-760	nd	4.5±2.4	13
St. Lucie County, Florida, USA	2002	31-340	nd	15-39	13
Anoka County, Minnesota, USA	2000	8600±1400	nd	42±4	13
Eight unidentified landfills, Washington, USA	2003	16.5-8012	nd	7.1-46.1	67
Europe					
Unidentified landfills, Germany	Not specified	0.1-11	nd	nd	47
Central Germany	Not specified	49-130	nd	Qualitatively observed	49
Göteborg landfill, Sweden	late 1990s	8.7±2.9	nd	Below detection	68

[a] Gaseous elemental mercury

nd: not determined

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In addition to observations in LFG vents, one study in Volusia County (USA) observed gaseous DMHg at the working face of a landfill at concentrations of 10 and 56 pg m^{-3} [13]. While the small sample number from this study (n = 2) does not allow for generalizations, the observations do suggest that DMHg was present in the waste or was formed during the waste collection, transport, or storage in the landfill. The potential for DMHg emissions from landfills require more attention as part of the need to understand the fate of mercury in solid waste landfills.

We note that the quality of gaseous Hg measurements remains an active area of debate, even though sampling methods for gaseous Hg (such as the methods used in studies reported in Table 3) have been available for many years.[69, 70] The difficulties include the variable range of precision that has been reported in the literature, challenges in calibration for specific Hg species, and uncertainty of the species captured by the measurements, whether they include only gaseous elemental Hg or also a portion of gaseous oxidized Hg and particulate Hg. Nevertheless, the values shown in Table 3 appear to be a good basis of comparison to ambient air concentrations that would typically be less than 10 ng m^{-3}.

Exposure to Hg(0) and methylated mercury species can impart severe adverse neurological effects[71]. However, the fate of mercury originating from LFG, and in particular the pathways for human and wildlife exposure, is not well known. Most Hg concentration values in LFG were below exposure limits as delineated by occupational safety regulations in the U.S. (50 and 10 µg m^{-3} 8-hour time average for Hg(0) and methylated Hg, respectively)[72]. At some landfills, average Hg concentrations exceeded the recommended action level for indoor residential settings (1 µg m^{-3})[73], a threshold that considers exposure to vulnerable individuals (e.g. children) but perhaps would not be applicable to LFG where exposures would be intermittent.

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Overall, the direct risks of Hg emissions from landfills depend not only on concentration or flux of Hg from LFG, but also are also governed by local factors including atmospheric conditions and the proximity of communities.

4.2 Transport of mercury via landfill leachates

The release of mercury via land fill leachates is widely variable, as a considerable range of total Hg concentrations have been reported in the literature (0.05 – 160 µg L^{-1}).[17, 74] The lower end of this range is likely due to constraints on method detection limits. For example, one study[17] examined leachates from 12 different landfills and only 5 leachate samples contained quantifiable total mercury concentrations (0.04-1.9 µg L^{-1}). The remaining samples were below the method detection limit of 0.04 µg L^{-1}. For reference, the U.S. EPA's National Water Quality Criterion for surface waters is 0.77 µg L^{-1} for mercury.

Mercury is likely to exist primarily as inorganic forms in landfill leachates (i.e., the non-alkylated forms). Few studies are available in the scientific literature that report MMHg and DMHg concentration data in landfill leachates.[16, 17, 75] The low number of samples likely stem from the use of analytical methods that are not sensitive enough to detect the low concentration of organo-Hg species (detection limits were typically in the ng L^{-1} range). For those studies that report measurable concentrations, the relative proportions of the total Hg as MMHg and DMHg varied widely, with several samples containing less than 5% as methylated Hg[17, 75] and one or two samples with 20-30% as an organic-Hg species[16, 17]. The conditions leading to a large percentage at one site compared to another site were not described.

We are not aware of studies that quantified dissolved Hg(0) in landfill leachates. Since Hg(0) is actively released in LFG emissions, the presence of dissolved Hg(0) could be

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reasonably expected in leachates. Likewise, data on the partitioning of Hg between dissolved and particulate phases are not available, to the best of our knowledge, in the peer-reviewed scientific literature. Measurements for other metals such as Pb, Ni, and Cu have demonstrated that a substantial proportion of these metals in landfill leachates (e.g., 80% or greater) was associated with colloidal particles.[43] Trends for Hg associations in the particulate phase could be similar.

In summary, the speciation of Hg in landfill leachates, and the relative partitioning of dissolved and colloidal species, will have great implications for subsurface migration of Hg downgradient of the landfill. Clearly more data are needed to identify the types and typical concentrations of Hg species in leachates and particularly to understand how Hg speciation and solid-water partitioning vary with conditions at the landfill site.

5. Potential biogeochemical transformations of mercury in landfills

Mercury that enters landfills can originate in a variety of forms. For example, mercury in fluorescent lamps will initially be present as Hg(0), while Hg(II) may be the dominant form of mercury in other types of refuse.[7, 9, 10, 76] Industrial wastes of geological origin and dredged sediments contain mostly particulate-bound Hg(II) and much smaller amounts of soluble Hg(II), Hg(0), and methylated mercury.[76]

While landfills receive refuse containing a large variety of Hg species, transformations of mercury have not been directly studied for landfill conditions. Processes that involve the production or degradation of volatile compounds (e.g., Hg(0) and DMHg) and the production of soluble and colloidal-bound Hg can greatly influence total Hg release from the landfill. Here, we discuss the current understanding of mercury biogeochemistry in the soil/water environment as a

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means to provide clues to the relevant transformation pathways for mercury in the landfill setting.

5.1 Production and emissions of Hg(0)

The major species of mercury in LFG emitted from landfills is Hg(0) [13, 51]. Likewise, the presence of dissolved Hg(0) might enhance the mobility of Hg in the subsurface, a process that has been hypothesized and observed in the groundwater of coastal areas[77-79]. The formation of Hg(0) from Hg(II) species can occur under aerobic conditions (e.g., Phase I in the landfill) and anaerobic conditions (Phases II, III, and IV). Under aerobic conditions, formation of Hg(0) is likely to be associated with microbial processes. Bacteria and Archaea microorganisms are known to possess the mercuric reductase enzyme (MerA) that catalyzes the reduction of Hg(II) and MMHg to Hg(0)[80]. This process is thought to provide a detoxification pathway for microorganisms exposed to mercury. The *merA* gene has been found in 1-10% of cultured heterotrophic aerobes.[81] Therefore, microbes that are capable of mercury reduction are relatively abundant in the environment and could be reasonably expected to persist in landfill settings. Also, microbial reduction of mercury is a relatively rapid process as whole cells containing the *merA* gene were reported to reduce about 0.1 µmole of Hg(II) (added as $HgCl_2$) to Hg(0) in less than 1 hour [82]. Thus, aerobic microbial reduction of Hg during Phase I of a landfill may occur even though the time frame of the Phase I stage is short relative to the entire lifetime of the landfill. One limiting factor would be the bioavailability of mercury for these microbes. If most of the Hg(II) is strongly complexed or associated with particulate materials, then speciation and bioaccessibility of Hg(II) for microorganisms may be a major factor controlling rates of aerobic Hg reduction processes during the Phase I stage of a landfill.

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Under anaerobic conditions, pathways other than the *merA*-mediated process may play prominent roles in formation of Hg(0). Anaerobic bacteria that do not have *merA* have been implicated in the reduction of mercury. Specifically, several bacteria that use oxidized forms of iron or manganese as terminal electron acceptors for energy generation were reported to reduce Hg(II).[83] The mechanism for this particular pathway for mercury reduction is not yet known. However, it should be noted that mercury reduction rates by metal-reducing bacteria were approximately an order of magnitude lower than that by microorganisms with *merA* [83].

Abiotic Hg reduction pathways are also relevant in anaerobic conditions, such as the pathway involving Fe(II) as the electron donor [84]. Sorbed Fe(II) and Fe(II)-bearing minerals have been shown to convert Hg(II) to Hg(0).[84-87] In contrast, freely dissolved Fe(II) ions do not reduce Hg(II) [83]. A recent study reported that mercury reduction can also be catalyzed by FeS, a form of Fe(II) that would be prominent under sulfate-reducing conditions [88].

Mercury reduction assisted by dissolved organic matter is another abiotic transformation pathway that generates dissolved gaseous Hg compounds[89-91]. This process could be particularly relevant for landfills, since leachates contain large amounts of total organic carbon (from 30 to 29000 mg L^{-1})[26] relative to most natural aquatic ecosystems. Humic and fulvic acids contain a variety of electron-donating functional groups such as phenols and catechols that have reduction-oxidation potentials suitable for Hg reduction [89, 90]. Humic substances are also capable of chelating Hg^{2+} ions[92-97], which might inhibit Hg reduction[91]. Thus, abiotic reduction of Hg by organic matter in landfills will depend on the prevalence of electron donating moieties as well as the ratio of organic-C relative to Hg[91].

While these anaerobic Hg reduction pathways are expected to occur in Phase II-IV stages of the landfill, they may be slowed if the conditions are reducing enough for sulfate reduction as

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the major terminal accepting process. At low reduction potentials where oxidized iron and manganese are depleted, sulfate reducing microorganisms and methanogens can dominate the microbial community in the landfill and the activity of metal-reducing bacteria (e.g., Fe and Mn reducers) would be diminished. Furthermore, the formation of sparingly soluble HgS particles or strongly complexed dissolved Hg-sulfide species, which could be expected in the presence of sulfate-reducing (i.e., sulfide-generating) microorganisms, can limit the reactivity of Hg for microbial and abiotic metal reduction reactions. Therefore, in landfills the anaerobic Hg reduction processes would be important immediately after all the oxygen has been consumed (Phases II-III) but perhaps not when methanogenic conditions are firmly established (Phase IV).[98]

5.2 Chelation and mineral precipitation/dissolution

Hg(II) compounds are likely to exist in landfills as sulfide phases (e.g., $HgS_{(s)}$,) and Hg(II) species associated with dissolved and particulate organic matter.[54] The relative proportions of these forms of Hg(II) depends on the concentrations of sulfide and organic matter. Organic matter in landfills is derived from the decomposition of a variety of refuse materials that includes paper (approximately 36% of total refuse mass) and other organic-based wastes (discarded food and yard trimmings that comprise approximately 30%).[99] Previous studies have reported that humic acids, fulvic acids, and hydrophilic fractions are the dominant portions of organic matter in landfill leachates.[100-102] The chelation of Hg^{2+} ions by humic substances primarily involve reduced sulfur moieties on the humic molecules[103-107] and the thermodynamic stability of these complexes have been studied extensively.[40, 108]

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In addition to mercury associated with organic matter, sulfide plays an important role in controlling Hg(II) speciation through the formation of $HgS_{(s)}$ particles or through sorption of Hg(II) to other metal sulfide particles.[40] As stated earlier, the relative amounts of sulfide generated in the landfill would depend on the anaerobic stage of the landfill.

The competition between sulfide and organic matter for Hg(II) involves a variety of reactions that can result in a mixture of products with a range in size (i.e., particle diameter) and reactivity for microbial processes. For instance, humic substances are known to increase dissolution rates and decrease precipitation rates of HgS mineral phases, even in scenarios of HgS supersaturation.[109, 110] Likewise, humic substances can stabilize HgS nanoparticles (<30 nm in diameter) as they precipitate from solution[111-113], and these nanoparticles are more reactive than well-crystalline phases of HgS for releasing Hg to methylating microorganisms.[114-117] Nanoparticulate HgS could also form during the aging of Hg-thiolate complexes, an abiotic reaction that occurs within external addition of inorganic sulfide and in the presence and absence of dissolved oxygen.[107]

While nanoparticulate HgS has not been directly observed in landfills, nanoscale particles of other metals such as cadmium have been observed in landfill leachates.[118, 119] Thus, the migration of Hg with leachates could occur via colloidal transport, a process that has been surmised in other types of porous media.[120] HgS nanoparticles have been shown to persist in aerobic soils.[107, 120, 121] Therefore, if leachates migrate to oxygenated zones, the HgS nanoparticles would likely resist oxidation. In summary, it is reasonable to expect the formation of mercury bound to small particles (as HgS or Hg adsorbed to humus and metal-sulfide nanoparticles) as a means of enhanced transport in landfill leachates.

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5.3 Methylation and demethylation of mercury

Another important transformation process for Hg in landfills is methylation of inorganic Hg(II), a process that is primarily mediated by microorganisms.[122, 123] All known microorganisms that can methylate mercury are obligate anaerobes and include a diverse group such as sulfate reducers, iron reducers, methanogens, syntrophs, acetogens, and fermentative Firmicutes.[124-128] These organisms share two a gene cluster, *hgcA* and *hgcB,* that encodes for proteins essential for the transfer of a methyl group to a Hg(II) substrate, yielding MMHg as the product. It is unknown if this process is involved in DMHg production.

Methylating microbes are expected to thrive during Phases II-IV of the landfill maturation (Figure 1). For example, Phase II of a landfill is distinguished by active fermentation and acetate production by microorganisms while microbial methane production is prominent at late Phase III [26]. It should be noted that only a subset of anaerobic microorganisms are capable of mercury methylation. The conditions for which methylating sulfate reducing bacteria, for example, will thrive over non-methylating sulfate reducing bacteria are not well established.

Abiotic methylation of mercury can occur via reaction between methylcobalamin and inorganic Hg(II).[129, 130] However, methylcobalamin in the environment has not been well-studied and information on environmental concentrations in any environmental system is scarce. A previous study reported the presence of 0.91 $\mu g\ g^{-1}$ (dry weight) of methylcobalamin in a sediment site. However, no correlations were observed between the concentration of methylcobalamin and MMHg partitioning [131].

While substantial breakthroughs have been made in recent years to understand the process of microbial MMHg production, much less is known concerning the formation of DMHg g. DMHg production has been shown to occur in cultures of Hg methylating bacteria.[132] The

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mechanism of this process, particularly in the context of the *hgcAB* system, is unknown, as stated earlier. Abiotic formation of DMHg can occur from a reaction between MMHg (as CH_3HgCl) with H_2S, yielding volatile products such as Hg^0 and DMHg.[133] However, this pathway has yet to be verified under conditions and concentrations relevant for landfills and other environmental systems.

The decomposition of methylated mercury species is also not well characterized. Degradation of MMHg can occur through abiotic photochemical reactions[134-137] and microbial pathways[138-141]. Microbial MMHg degradation, which is most relevant for landfills, can occur through the *mer*-operon system. This pathway is a reductive demethylation process that yields Hg(0) and CH_4 as products[122]. MMHg decomposition can also occur through an oxidative pathway, resulting in Hg(II) and CO_2 as products[138]. These processes may be important for controlling release of inorganic and methylated Hg species from landfills; however, environmental factors that control the relative rates of demethylation and methylation are not well understood.

6. Conclusions and Future Research Needs

In summary, several studies have demonstrated that mercury can escape from landfills via emissions in the gas phase and through landfill leachates. A portion of the emitted mercury is likely a result of direct release from mercury-containing refuse, while the rest is a result of biogeochemical processes within the landfill that convert mercury in the waste material into a volatile or mobile form. The potential for biogeochemical transformations of mercury in landfills can be assessed through the general scientific knowledge of mercury transport and transformations in the environment. However, the relative importance of these processes is

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unknown for the unique conditions within landfills. This information should be of interest to landfill operators as well as solid waste producers who may retain some long-term liability for their wastes disposed in landfills.

The predominant composition of the refuse material will greatly influence the chemical and microbiological conditions within the landfill, and these factors will then control the major transformation pathways for mercury. For example, the presence of waste material with high leachable sulfate concentrations (e.g., coal combustion residuals) likely results in significant production of sulfide in the landfill that can sequester Hg via $HgS_{(s)}$ formation. Likewise, conductivity and organic matter concentration are important for colloidal transport processes. We note that protocols to classify solid wastes for disposal (e.g., TCLP) do not capture these transformation processes relevant to the mobilization of mercury in landfill leachates. Moreover, landfills that are exclusively for industrial wastes may have conditions that are very different from municipal waste landfills, and these differences need to be understood with respect to mercury emissions.

Over the long term after methane production ceases in the landfill (i.e., beyond Phase IV), oxygen intrusion will eventually occur. This will increase the redox potential in the landfill and can promote oxidative dissolution of the mercury-associated solid phases (e.g., FeS and to a limited extent HgS).[121] The dissolved forms of mercury then may be susceptible to microbial reduction (mediated by MerA) and emitted into the atmosphere. The significance of this long term process is unknown and is worth consideration, particularly in relation to timeframes that may exceed the monitoring requirements for a closed landfill (typically 30 years in the U.S.).

In addition to the need to better understand Hg transport and transformations in landfill conditions, there is a need to address other knowledge gaps related to mercury in solid waste,

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including the speciation of Hg in refuse materials. Some have suggested that most of Hg(0) encapsulated in waste is lost to the atmosphere during transport to landfills [142]. If this is the case, then one cannot presume that Hg(0) emissions at the landfill are from direct release from the refuse.

New engineering designs for landfills could also influence Hg emissions. For example, the recirculation of leachate can accelerate the stabilization of waste and enhance gas production relative to more conventional landfills that do not recirculate leachate.[143] This acceleration in waste stabilization could also accelerate 'aging' processes for mercury (e.g., HgS formation) that sequester the metal to (presumably) chemically inert forms. In contrast, active gas collection systems have been reported to have higher fluxes of emitted mercury than passive gas collection systems [58]. The reason for this observation is unknown.

Finally, the release of mercury from the landfill, alone, does not necessarily confer hazard or exposure. Mercury that originates from landfills would be a concern only if there was a path between the landfill release point and subsequent bioaccumulation in the food web or exposure to humans in nearby communities. Risk assessments of mercury released from landfills should consider relevant receptors for exposure and balance this risk with other possible sources of mercury to these receptors.

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