

ENVIRONMENTAL CHEMISTRY AND TOXICOLOGY OF MERCURY

Edited by
GUANGLIANG LIU
YONG CAI
NELSON O'DRISCOLL

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PREFACE

Mercury is a global contaminant posing severe risks to the health of ecosystems and humans worldwide. The biogeochemical cycling of mercury is rather complicated, involving various transformations and transport processes of mercury species in the environment. A comprehensive review of all the various aspects of mercury transformation and transport is essential for better understanding the mercury cycle and assessing the risks of mercury contamination. Substantial progress has been made in the area of mercury biogeochemistry over the past years; however, there are currently few places where researchers and students can obtain a complete review of the state of the science in this field. This book brings together many of the foremost experts in the field of environmental chemistry and toxicology of mercury and provides a comprehensive overview of the current mercury science. We believe that this book will serve as an excellent resource for researchers, graduate students, environmental regulators, and others.

This book is organized as follows. The first chapter of the book provides a brief overview of mercury in the environment, followed by two chapters discussing environmental analytical chemistry of mercury species and measurement of industrial gas phase mercury emissions. The main part of the book is then devoted to addressing the important transformation and transport processes of mercury in the environment. The following topics are covered under mercury transformation: atmospheric chemical processes, microbial transformations, and aquatic photochemical reactions of mercury species, mercury speciation in soils/sediments, interaction of mercury with organic matter, and isotopic fractionation. For mercury transport, the following topics are examined: atmospheric transport, partition

between water and solids, and exchange between the atmosphere and the earth surface (including oceans and terrestrial systems) of mercury. The last part of the book covers bioaccumulation, toxicity, metallomics, and human health risks of mercury. Author's name in boldface on the chapter opening pages indicates the lead author of that chapter.

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YONG CAI
NELSON O'DRISCOLL

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CHAPTER 1

OVERVIEW OF MERCURY IN THE ENVIRONMENT

**GUANGLIANG LIU, YONG CAI, NELSON O'DRISCOLL, XINBIN FENG,
and GUIBIN JIANG**

1.1 INTRODUCTION

Mercury (Hg) is a naturally occurring element that is present throughout the environment. Mercury is recognized as a global contaminant because it can undergo long-range transport in the atmosphere, be persistent in the environment, be accumulated in the food web, and pose severe adverse effects on the human and ecosystem health (Nriagu, 1979; Fitzgerald et al., 2007b). The environmental contamination of land, air, water, and wildlife in various ecosystems with mercury around the world due to the natural release and extensive anthropogenic use of Hg has been a global concern for decades (Lindberg and Turner, 1977; Ebinghaus et al., 1999; Fitzgerald et al., 2005; Mason et al., 2009). This being the first chapter of the book, it will briefly discuss the health risks associated with mercury exposure and the natural and anthropogenic sources of mercury emissions, and then provide a very brief overview of the biogeochemical cycling of mercury.

In the environment and in biological systems, mercury can exist in three oxidation states, namely, Hg(0) (metallic), Hg(II) (mercuric), and Hg(I) (mercurous), with the monovalent form being rare owing to its instability (Ullrich et al., 2001; Fitzgerald et al., 2007a,b). In general, the dominant form of mercury in water, soil, and sediment is the inorganic Hg(II) form while methylmercury (MeHg) is dominant in biota, and in the atmosphere Hg(0) is the primary species (USEPA, 1997; Ullrich et al., 2001).

1.2 TOXICITY AND HEALTH RISKS OF MERCURY EXPOSURE

All forms of mercury are toxic, but particularly problematic are the organic forms such as MeHg, which is a neurotoxin (Committee on the Toxicological Effects of Methylmercury, 2000; Clarkson and Magos, 2006). Acute mercury exposure can produce permanent damage to the nervous system, resulting in a variety of symptoms such as paresthesia, ataxia, sensory disturbances, tremors, blurred vision, slurred speech, hearing difficulties, blindness, deafness, and death (USEPA, 1997; Committee on the Toxicological Effects of Methylmercury, 2000; Clarkson and Magos, 2006). In addition to neurotoxicity, mercury, in inorganic and/or organic forms, can affect other systems and sequentially cause adverse effects including renal toxicity, myocardial infarction, immune malfunction, and irregular blood pressure (USEPA, 1997; Committee on the Toxicological Effects of Methylmercury, 2000).

Human exposure to Hg can pose a variety of health risks, with the severity depending largely on the magnitude of the dose. Historically, there were two notorious poisoning episodes associated with the extremely high MeHg exposures, that is, in Minamata where individuals were poisoned by MeHg through consumption of contaminated fish and in Iraq where the consumption of MeHg-treated (as a fungicide) grain led to poisoning (Committee on the Toxicological Effects of Methylmercury, 2000). Nowadays, acute poisoning incidents from high Hg exposure are rare and the health risks mercury poses to human population are mainly from chronic MeHg exposure through consumption of contaminated fish and other aquatic organisms, particularly large predatory fish species (USEPA, 1997). A major concern related to the health risks of chronic MeHg exposure is the possibility of developmental toxicity in the fetal brain, since MeHg can readily cross the placenta and the blood–brain barrier (Clarkson and Magos, 2006). Prenatal Hg exposure interferes with the growth and migration of neurons and has the potential to cause irreversible damage to the developing central nervous system (Committee on the Toxicological Effects of Methylmercury, 2000). For instance, because of prenatal MeHg exposure from maternal fish consumption, infants might display deficits in subtle neurological endpoints such as IQ deficits, abnormal muscle tone, and decrements in motor function (Committee on the Toxicological Effects of Methylmercury, 2000).

1.3 SOURCES OF MERCURY

Both naturally occurring and anthropogenic processes can release mercury into air, water, and soil, and emission into the atmosphere is usually the primary pathway for mercury entering the environment (Camargo, 1993; Berg et al., 2006; Jiang et al., 2006; Bone et al., 2007; Bookman et al., 2008; Streets et al., 2009; Cheng and Hu, 2010). It is estimated that the total annual global input to the atmosphere from all sources (i.e., from natural and anthropogenic emissions) is around 5000–6000 t (Mason et al., 1994; Lamborg et al., 2002; Gray and Hines,

2006). The relative importance of natural versus anthropogenic sources of mercury has not been accurately determined, with the ratio of natural to anthropogenic mercury emissions being reported to be within a wide range (e.g., from 0.8 to 1.8) (Nriagu and Pacyna, 1988; Nriagu, 1989, 1994; Bergan et al., 1999; Gustin et al., 2000; Lin and Tao, 2003; Nriagu and Becker, 2003; Seigneur et al., 2003, 2004; Gbor et al., 2007; Shetty et al., 2008).

1.3.1 Natural Sources of Mercury

There are a number of natural processes that can emit Hg into the atmosphere. These processes may include geologic activities (in particular volcanic and geothermal emissions), volatilization of Hg in marine environments, and emission of Hg from terrestrial environments (including substrates with elevated Hg concentrations and background soils) (Nriagu, 1989, 1993, 1994; Gustin et al., 2000, 2008; Gustin, 2003; Nriagu and Becker, 2003; Gray and Hines, 2006). Owing to the lack of data and the complexity of geological processes (e.g., vast variability spatially and temporally) (Gustin et al., 2000, 2008), it is rather difficult to accurately estimate natural Hg emissions, resulting in high degrees of uncertainties being associated with the reported Hg emissions from natural sources. The annual global Hg emissions from natural sources are estimated to range from 800 to 5800 t, with a middle range from 1800 to 3000 t (Lindberg and Turner, 1977; Nriagu, 1989; Lindberg et al., 1998; Bergan et al., 1999; Pirrone et al., 2001; Seigneur et al., 2001, 2004; Lamborg et al., 2002; Mason and Sheu, 2002; Pacyna and Pacyna, 2002; Pirrone and Mahaffey, 2005; Pacyna et al., 2006; Shetty et al., 2008). Among different natural processes, the global volcanic, geothermal, oceanic, and terrestrial Hg emissions are estimated to be 1–700, ~60, 800–2600, and 1000–3200 t per year, respectively (Nriagu, 1989; Lindberg et al., 1998, 1999; Bergan et al., 1999; Ferrara et al., 2000; Lamborg et al., 2002; Mason and Sheu, 2002; Nriagu and Becker, 2003; Pyle and Mather, 2003; Seigneur et al., 2004; Fitzgerald et al., 2007b). Gaseous elemental mercury (GEM) is the predominant form (>99%) of Hg from natural emissions, which is different than anthropogenic emissions that may also contain reactive gaseous mercury (RGM) and particulate Hg (PHg) (Stein et al., 1996; Streets et al., 2005; Pacyna et al., 2006). It should be noted that some processes of natural Hg emissions include reemission of Hg previously deposited from the atmosphere by wet and dry processes derived from both anthropogenic and natural sources. For instance, emission from low Hg-containing substrates and background soils is assumed to be predominantly reemission of Hg previously deposited (Gustin et al., 2000; Seigneur et al., 2004; Gustin et al., 2008; Shetty et al., 2008).

1.3.2 Anthropogenic Sources of Mercury

Extensive anthropogenic emission and use of Hg have caused worldwide mercury contamination in many aquatic and terrestrial ecosystems (Lee et al., 2001; Streets

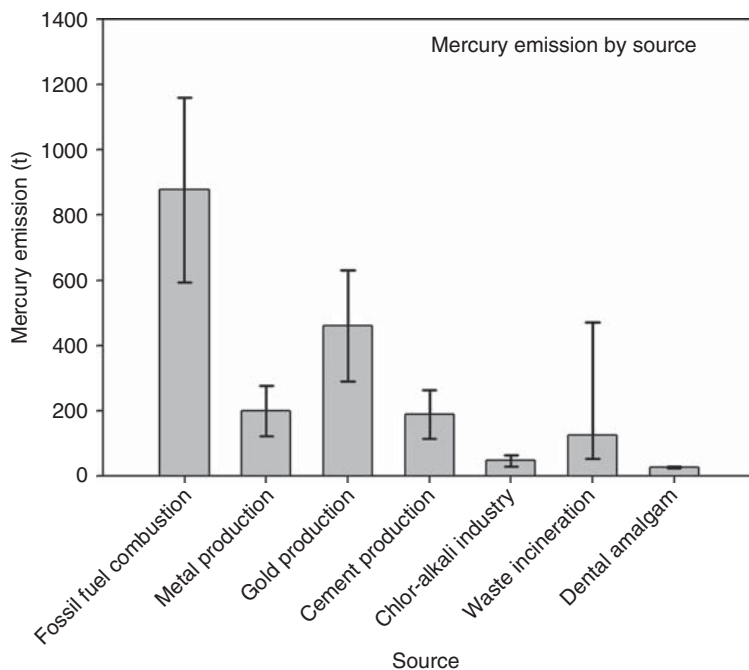


Figure 1.1 Annual global mercury emission (tons) from major anthropogenic sources. *Source:* Data are extracted from the UNEP reports (AMAP/UNEP, 2008; UNEP Chemicals Branch, 2008). Fossil fuel combustion refers to burning of coal and other fossil fuels in power plants and commercial and residential heating units. Metal production includes mercury production, but does not include gold mining and production, which is listed separately.

et al., 2005, 2009; Hope, 2006; Wu et al., 2006; Zhang and Wong, 2007; Sunderland et al., 2009). Comparisons of contemporary (within the past 20–30 years) measurements and historical records indicate that the total global atmospheric mercury burden has increased by a factor of between 2 and 5 since the beginning of the industrialized period (USEPA, 1997). Although anthropogenic emission of Hg has been reduced in the past three decades, anthropogenic processes are still responsible for a significant proportion of global Hg input to the environment. It has been suggested that, among the 5000–6000 t of Hg that is estimated to be released into the atmosphere each year, about 50% may be from anthropogenic sources (Mason et al., 1994; Lamborg et al., 2002; Gray and Hines, 2006), which agrees with some other studies where the annual global anthropogenic emissions of mercury are estimated to be in the range of 2000–2600 t (Pacyna et al., 2001, 2006; Pirrone et al., 2001; Pacyna and Pacyna, 2002; Pirrone and Mahaffey, 2005). Unlike natural sources, anthropogenic sources can emit different species of Hg including GEM, RGM, and PHg with a distribution of about 50–60% GEM, 30% RGM, and 10% PHg (Streets et al., 2005; Pacyna et al., 2006).

Anthropogenic emissions of mercury can be from point (e.g., incinerators and coal-fired power plants) as well as diffuse (e.g., landfills, sewage sludge amended fields, and mine waste) sources (Nriagu, 1989; Sigel and Sigel, 2005; Malm, 1998; Schroeder and Munthe, 1998; Quemerais et al., 1999; Lee et al., 2001; Horvat, 2002; Gustin, 2003; Nelson, 2007; Feng et al., 2010; Pacyna et al., 2010). Point sources, including combustion, manufacturing, and miscellaneous sources (e.g., dental amalgam), are thought to be the main anthropogenic sources of mercury, accounting for approximately more than 95% of anthropogenic mercury emissions (USEPA, 1997). Combustion sources include burning of fossil fuels (e.g., coal and oil), medical waste incinerators, municipal waste combustors, and sewage sludge incinerators. Fossil fuel combustion can be associated with power generation, industrial and residential heating, and various industrial processes. Combustion processes emit divalent mercury and elemental mercury, in gaseous as well as particulate form, depending on the fuels and materials burned (e.g., coal, oil, municipal waste) and fuel gas cleaning and operating temperature, into the atmosphere (USEPA, 1997; UNEP Chemicals Branch, 2008). Manufacturing sources refer to extensive use (especially in the past and in some undeveloped areas) of mercury compounds in many industrial processes such as gold mining, chlor-alkali production, and paper and pulp manufacturing. Unlike combustion sources, manufacturing processes can release mercurial compounds directly into aquatic and terrestrial environments, in addition to the atmosphere (Lindberg and Turner, 1977; Nriagu et al., 1992; Nriagu, 1994; USEPA, 1997; AMAP/UNEP, 2008; UNEP Chemicals Branch, 2008).

Of the three anthropogenic point sources, combustion generally contributes more than 80% of anthropogenic mercury emissions, although varying from region to region (USEPA, 1997; UNEP Chemicals Branch, 2008). Figure 1.1 illustrates the global inventory of mercury emissions from major anthropogenic sources, as estimated by the United Nations Environmental Programme (UNEP) (AMAP/UNEP, 2008; UNEP Chemicals Branch, 2008). Fossil fuel combustion for power generation and industrial and residential heating contributes about 45% of total global emission (880 t out of 1930 t) (Fig. 1.1). Owing to the enormous amount of coal that is burned, coal burning is the largest single source of anthropogenic emissions of Hg to the atmosphere (AMAP/UNEP, 2008). Waste incineration contributes another significant proportion (about 120 t) of mercury emission, but with a wide range between 50 and 470 t due to lack of reliable estimation data, in particular in countries outside Europe and North America. In addition, fuel combustion in industrial processes, including cement and metal production, can release mercury into the atmosphere. Meanwhile, these industrial processes, in particular, the production of iron and nonferrous metals, can release mercury as it can be present as impurity in ores (AMAP/UNEP, 2008). The data illustrated in Fig. 1.1 for these industrial processes include mercury from fuel combustion and from impurities in ores.

Manufacturing sources mainly include gold mining and chlor-alkali industry. Globally, gold mining and production, primarily artisanal and small-scale

gold mining using mercury to extract gold, contribute about 20% of anthropogenic mercury emission, while the fraction for chlor-alkali production is about 3% (Fig. 1.1) (AMAP/UNEP, 2008; UNEP Chemicals Branch, 2008). Although industrial use of mercury has been largely reduced in developed countries, it may still contribute to a significant portion of Hg emission in developing countries (e.g., in Asia and South America). As seen from Fig. 1.2, there are significant geological disparities in anthropogenic mercury emissions, with Asia alone accounting for about 65% of total global emission (1280 t out of 1930 t). It should be borne in mind that the data in Fig. 1.2 refer merely to the current emission inventory by region estimated by UNEP, with historical contributions being unaccounted for. Moreover, the relative contributions of different sources to total anthropogenic mercury emission vary with geological region (Fig. 1.3). The most striking characteristic in geological variability of anthropogenic mercury emissions is the dominant contribution of gold mining to overall anthropogenic mercury emission in South America. On the global scale, fossil fuel combustion for power and heating is the primary source of mercury emission, but in South America, gold mining contributes over 60% of total anthropogenic mercury emission (Fig. 1.3).

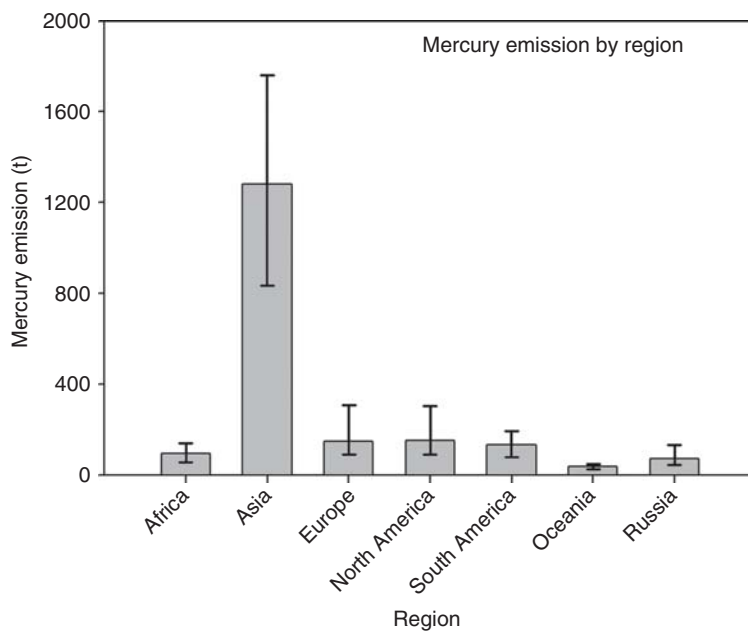


Figure 1.2 Annual global anthropogenic mercury emission (tons) in different regions of the world. *Source:* Data are extracted from the UNEP reports (AMAP/UNEP, 2008; UNEP Chemicals Branch, 2008). Fossil fuel combustion refers to burning of coal and other fossil fuels in power plants and commercial and residential heating units. Metal production includes mercury production, but does not include gold mining and production, which is listed separately.

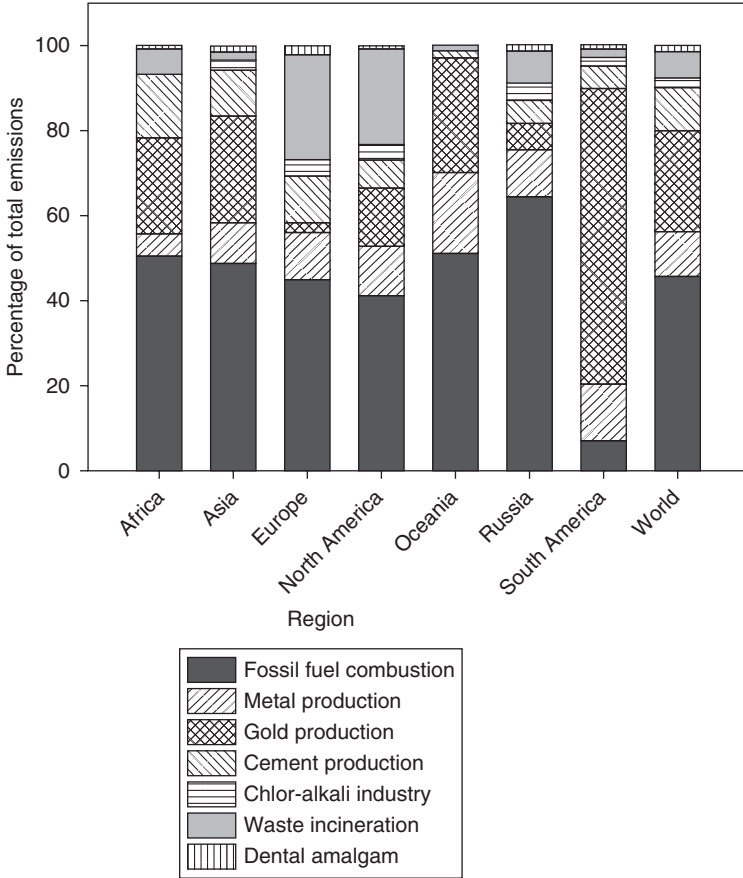


Figure 1.3 Relative percentages (%) of anthropogenic mercury emissions from different sources worldwide and in different regions of the world. *Source:* Data are extracted from the UNEP reports (AMAP/UNEP, 2008; UNEP Chemicals Branch, 2008). Fossil fuel combustion refers to burning of coal and other fossil fuels in power plants and commercial and residential heating units. Metal production includes mercury production, but does not include gold mining and production, which is listed separately.

1.4 OVERVIEW OF MERCURY BIOGEOCHEMICAL CYCLING

After entering the environment, mercury undergoes a series of complicated transport and transformation processes during its biogeochemical cycling. The biogeochemical cycling of mercury is closely associated with the chemical forms of mercury present in different phases of the environment.

In the atmosphere, elemental mercury ($Hg(0)$) constitutes the majority of Hg (>90%) and is the predominant form in the gaseous phase, which facilitates the long-range transport of Hg at a global scale (USEPA, 1997; Ebinghaus et al.,

1999; Pirrone and Mahaffey, 2005). On the other hand, Hg(II) species present in atmospheric waters, either dissolved or adsorbed onto particles in droplets, has a tendency to readily deposit on the earth's surface through wet and dry deposition, which is important to the local and regional cycle of Hg (Nriagu, 1979; Schroeder and Munthe, 1998).

In water, sediment, and soil environments, mercury is present primarily as various Hg(II) compounds, including inorganic (e.g., mercuric hydroxide) and organic (e.g., MeHg) mercuric compounds, and secondarily as Hg(0), which plays an important role in the exchange of mercury between the atmosphere and aquatic and terrestrial surfaces (Stein et al., 1996; Ullrich et al., 2001; Fitzgerald et al., 2007a,b). These Hg(II) compounds (including inorganic and organic) are present in a variety of physical and chemical forms through complexing with various inorganic (e.g., chloride and sulfide) and organic (e.g., organic matter) ligands (Ullrich et al., 2001). Although in aquatic and soil environments MeHg may constitute a minor fraction of total mercury present (typically less than 10% and 3% in water and soil/sediment, respectively), the formation of MeHg is an important step in mercury cycling (USEPA, 1997; Ullrich et al., 2001). This is because MeHg can be bioaccumulated along the food web and reach high concentrations in organisms, in particular, in aquatic environments. In fishes and wildlife that prey on fish, MeHg can be the dominant form of mercury species owing to bioaccumulation and biomagnification (Stein et al., 1996; Fitzgerald et al., 2007a).

Associated with transformation between different mercury species and transport of mercury between different environmental phases, there are a number of processes that are important in the biogeochemical cycling of mercury. These processes include oxidation of Hg(0) and reduction of Hg(II) (including photochemical and microbial processes), methylation of inorganic mercury (primarily mediated by microbes), distribution of mercury between water and sediment, deposition of mercury from the atmosphere, long-range transport of mercury in the atmosphere, exchange of mercury between the earth surface (oceans and terrestrial ecosystems) and the atmosphere, and bioaccumulation of mercury through food webs (Nriagu, 1979; Ebinghaus et al., 1999; Pirrone and Mahaffey, 2005; Fitzgerald et al., 2007b).

1.5 STRUCTURE OF THE BOOK

The biogeochemical cycling of mercury is rather complicated, involving various transport and transformation processes that determine the fate of mercury and the health risks on ecosystem and humans. A comprehensive summary of the various aspects regarding transformation and transport of mercury is essential for better assessing the risks of mercury contamination. In the past years, a great deal of research has been done to advance the understanding of important aspects of mercury biogeochemical cycling and has produced a wealth of material. This book is aimed to develop a comprehensive review of the state of environmental mercury research by summarizing all the key aspects of the mercury cycle.