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Progress of Mercury Pollution Research and Implementation of Minamata Convention in China

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Abstract

Mercury (Hg) is one of the most toxic heavy metal and a global pollutant. The Minamata Convention on mercury entered into force in August 2017, which aims to control and reduce global anthropogenic Hg emissions and use, and highlights that Hg pollution has become an important global environmental issue. At present, China is one of the larger countries on Hg production, use, and emission, which faced with great pressure of Hg pollution control and implementation of the Convention. Based on this background, this paper systematically describes the production, use, and emission of Hg in China, the migration, transformation, and health effects of Hg, the Minamata Convention on mercury, and the progress of Hg pollution control and implementation of Minamata Convention in China, and also points out five aspects on Hg research in China, which hopes to contribute to the environmental Hg pollution control and the implementation of the international convention in China.

Keywords

mercury pollution; Minamata Convention; research progress; China

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Abstract: Mercury (Hg) is one of the most toxic heavy metal and a global pollutant. The Minamata Convention on Mercury entered into force in August 2017, which aims to control and reduce global anthropogenic Hg emissions and use, and highlights that Hg pollution has become an important global environmental issue. At present, China is one of the large countries on Hg production, use, and emission, which is faced with great pressure of Hg pollution control and implementation of the Minamata Convention. In this context, this paper systematically describes the production, use, and emission of Hg in China, the migration, transformation, and health effects of Hg, the Minamata Convention, and the progress of Hg pollution control and implementation of Minamata Convention in China, and also points out five aspects on Hg research in China, which hopes to contribute to the environmental Hg pollution control and the implementation of the international convention in China. **DOI:** 10.16418/j.issn.1000-3045.20201015002-en

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Mercury (Hg) is one of the highly toxic heavy metals and a global pollutant. Hg emitted to the atmosphere can be transported over long distances around the world through atmospheric circulation and deposited into terrestrial and aquatic ecosystems, posing threats to the ecological environment and human health. Ever since the First Industrial Revolution, human activities have brought on a remarkable increase in the Hg content of the global atmosphere, water, and soil and caused a significant detrimental effect on the global environment [1]. The Minamata Convention on Mercury (hereinafter referred to as the Minamata Convention) was approved in January 2013 and formally entered into force in August 2017, which aims to control and reduce global anthropogenic Hg emission and use. This highlights that Hg pollution has become an important global environmental issue.

As the first batch of signatory countries, China is currently the country with the largest amount of Hg production, use, and emission. Every year, 500–600 tons of Hg were emitted into the atmosphere through human activities, accounting for about 30% of global anthropogenic emission [2,3]. Therefore, in-depth research on the source, distribution, health risk, and pollution control of Hg in the environment of China is a major demand for national environmental protection and implementation of the Minamata Convention.

1 Hg production, use, and emission in China

Hg has a wide scope of applications. China has a long history of using Hg and its compounds. Cinnabar (HgS), as a Hg-containing compound that was widely used in ancient times, is an important ingredient for the ancient “alchemy” of pursuing long life and also a widely used ore as Chinese medicinal material. Besides, the ancients used the chemical property of Hg generating amalgam with gold in gold-bearing ores to extract the gold. Nowadays, with the continuous development of science and technology, the applications of Hg and its compounds become more extensive, including fields such as chemistry and chemical engineering, pharmaceutical industry, metallurgical industry, electrical equipment, transportation, and military production [4].

China is the country with the largest Hg production, use, and emission in the world [5], as well as rich Hg mines, and the exploitation quantity of Hg leads the world. In 2017, the global annual Hg production was about 3 790 tons, of which China accounted for 89% [4]. The Hg consumption of China increased from 803 ± 95 tons in 2005 to a peak of 1 272 ± 110 tons in 2011 and then reduced to 903 ± 115 tons in 2014 [6]. Polyvinyl chloride (PVC) production is the largest Hg-consuming industry, the Hg demand of which accounts for above 60% of the total in the globe. In 2011, the Hg consumption in the production of PVC, clinical thermometers,

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and sphygmomanometers in China was 878 ± 61 tons, 152 ± 83 tons, and 97 ± 10 tons, respectively [6]. In the context of the Minamata Convention, the global restrictions on Hg-containing products got increasingly strict. Therefore, it is an urgent need to develop low-level Hg catalysts or Hg-free alternatives.

Hg can be discharged into the atmosphere, soil, and water bodies through natural and anthropogenic activities. Its natural sources mainly include volcanoes, geotherm, and other geological activities, along with water evaporation and soil emission [7]. Its anthropogenic sources mainly consist of coal-fired power plants, industrial boilers, nonferrous metal smelting, and cement production [2,8]. In 2018, the global Hg release into the atmosphere was 8 000 tons, of which natural courses released 5 500 tons and anthropogenic activities occupied 2 500 tons [9]. Different from anthropogenic sources, the vast majority (> 95%) of Hg released by natural sources is gaseous elemental Hg. The natural sources of atmospheric Hg are complex and diverse, which are distinctly affected by environmental factors. Therefore, research on the natural sources of atmospheric Hg has always been difficult for the international academic community. It is worth noting that Hg from some natural sources is caused by the re-release of Hg from anthropogenic emissions after deposition to the surface. On the basis of the research on Hg exchange flux between the atmosphere/soil, the atmosphere/water, and the atmosphere/plant leaves, as well as the data update of Hg from the soil in China, our group systematically builds a Hg emission model of natural sources in China and obtains a high-precision inventory of Hg emission from natural sources in China through model optimization with field monitoring data [10]. The research results indicate that the annual Hg emission from natural sources in China is 465.1 tons, which is basically equivalent to anthropogenic emissions. To be specific, 556.5 tons of Hg comes from the soil, 9.0 tons of Hg derives from terrestrial water bodies, and 100.4 tons of atmospheric Hg is absorbed by vegetation each year. A total of 80% of Hg emission from natural sources is from grassland and farmland ecosystems, which also bears significant seasonal variation, and the Hg emission in summer accounts for 51% of the total annual emission [10].

Since 1949, especially after the reform and opening up, China's Hg emission from anthropogenic sources has grown rapidly. In the initial period, it was 13 tons per year, then increased to 150 tons in 1978 and 500–800 tons in 2010, and decreased from 571 tons to 444 tons in 2013–2017 [11]. China's Hg emitted to the atmosphere from anthropogenic sources added up to 13 294 tons from 1978 to 2014, of which gaseous elemental Hg (Hg^0), gaseous divalent Hg (Hg^{II}), and particulate Hg (Hg^p) accounted for 58.2%, 37.1%, and 4.7% respectively [2]. At the same time, the sources and morphological distribution of atmospheric Hg from anthropogenic sources have also undergone significant changes. The largest emission source was industrial boilers before 1998, zinc metallurgy from 1999 to 2004, coal-fired power plants from 2005 to 2008, and cement industry since 2009 [2]. Currently, coal-fired industrial boilers and the cement industry have become key industries for atmospheric Hg emission control. The ratio for the chemical form of atmospheric Hg changed from 65%:28%:7% (Hg^0:Hg^{II}:Hg^p) in 1978 to 51%:46%:3% (Hg^0:Hg^{II}:Hg^p) in 2014. The increased proportion of Hg^{II} will pose an important impact on the local environment, and the Hg^{II} emission from the cement industry accounts for 45% of national Hg^{II} emission [2].

2 Migration, transformation, and health effects of Hg

Hg is a global pollutant. It is the only metal that is liquid and easy to flow under normal temperature and pressure, which can widely exist in various environments and biological media in different chemical forms, but the content of Hg in the crust is quite low. In the natural environment, Hg can migrate through volatilization, precipitation, sedimentation, and dissolution, and the mutual transformation between different forms can also be realized through processes such as oxidation, reduction, methylation, and demethylation [12]. Since gaseous elemental Hg stays a long residence time in the atmosphere, it can persist in the environment. Once released into the environment, it can be transported over long distances along with the atmospheric circulation, reaching the aquatic ecosystems in remote or even polar regions through dry and wet deposition, and causing global Hg pollution [13–15].

The toxic effect of Hg is closely related to its form. According to its chemical form, Hg can be classified into inorganic Hg (such as elemental Hg and divalent Hg) and organic Hg (such as methylmercury and ethylmercury). Elemental Hg is volatile and can enter the organisms via breathing, skin, or digestive tract, etc., due to its high diffusion and liposolubility, and cause damage to the immune, endocrine, and central nervous systems [16]. Divalent Hg can also have a certain toxic effect on organisms. However, its toxicity is relatively low due to its low bioavailability and the incapacity to penetrate the blood-brain barrier [16]. The toxicity of organic Hg is prominently higher than that of inorganic Hg. Methylmercury can enter the organisms through intestinal absorption and reach the organs and tissues following the blood, which will induce neurotoxicity and developmental neurotoxicity by acting on the central nervous system and cause irreversible damage to the cerebrum and cerebellum [16]. Besides, methylmercury has high bioaccumulation and biomagnification. The methylmercury content in fish at the top of the aquatic food chain is 10^6–10^7 times higher than that in water. As a result, the consumption of fish and other aquatic products is one of the main exposure pathways of humans to methylmercury [17]. However, the Hg content in fish and aquatic products in China is generally low [18–20], most of which is below the safety threshold for China's aquatic products (carnivorous: 1.0 μg/g; others: 0.5 μg/g). This is because most fish in China are artificially farmed with a simple food chain and a fast growth rate [21].

In recent years, some studies have indicated that rice is a kind of methylmercury-enriched crop and one of the main pathways for methylmercury exposure of specific residents. The average bioconcentration factor of methylmercury in rice is 800 times that of inorganic Hg [22]. The methylmercury content of rice in Guizhou Hg mining areas varies from 1.9–174 ng/g [22–24], and 94%–98% of the methylmercury exposure among residents in the related Hg mining areas comes from rice consumption, which indicated that rice consumption is the main way of methylmercury exposure in the mining areas [25]. The results of research in the Guizhou Hg mining area, historical artisanal zinc smelting area, coal-fired power plant area, and control area have shown that consumption of rice, vegetables, and meat all contributes to the total Hg exposure of residents and, however, rice consumption is the main way of methylmercury exposure (> 90%) [26].

The overall risk of methylmercury exposure for general residents in China is relatively low. The Hg content in fish and other aquatic products in China is generally low, and the risk of methylmercury exposure for the general population eating aquatic products is quite low [27]. The average content of total Hg and methylmercury in rice in seven provinces in south China is 10.1 ng/g and 2.47 ng/g, respectively, which is low [27]. The daily methylmercury intake of fish and rice for urban and rural residents in south China is 0.020 μg/kg and 0.028 μg/kg, respectively, which is far below the international limit (0.23 μg/kg) [28]. However, some people in coastal areas also have health risks of methylmercury exposure due to large amounts of aquatic product consumption. For example, methylmercury content in the hair of local fishermen in eastern coastal area is as high as 9.5 mg/kg [29]. In addition, residents in some Hg-contaminated areas still suffer certain risks. For example, the average methylmercury content in the hair of residents in a Hg mining area is 2.07 μg/g [30].

3 Minamata Convention

Minamata disease in Japan has caused widespread concern about Hg pollution from the world. A large amount of production, use, and emission of Hg and its compounds have caused Hg pollution in the global range. The most representative Hg pollution incident occurred in Minamata Bay, Japan in the mid-20th century. As Japan's manufacturing company Chisso discharged wastewater containing Hg into Minamata Bay, residents living in the surrounding area were inflicted with serious Hg poisoning after eating aquatic products with high methylmercury content. In mild cases, patients had slurred speech and hand-foot deformity, while in severe cases, people had mental disorders and even died. At least 50 000 people in Japan have been affected to various degrees and more than 2 000 cases of Minamata disease have been confirmed. This event has caused serious hazards to the environment and human health, which has drawn widespread concern about Hg pollution over the world.

The Minamata Convention aims to control and reduce Hg emission on a global scale. To control and reduce Hg emission worldwide, minimize the damage caused by Hg to the environment and human health, the United Nations Environment Programme carried out five sessions of intergovernmental negotiations and approved a global legally binding instrument on Hg on January 19, 2013, namely the Minamata Convention, which officially entered into force on August 16, 2017. It consisted of 35 articles and 5 annexes, and put forward management requirements in the entire life cycle of Hg, covering the supply and trade of Hg, Hg-added products, production processes using Hg or Hg compounds, historical artisanal gold smelting, point source emission, non-point source emission, environmentally sound temporary storage of Hg other than Hg waste, Hg waste, contaminated sites, financial resources and financial mechanisms, capacity building, technical assistance and technology transfer, health, public information, awareness and education, etc.

The Minamata Convention sets strict regulations on the production, emission, use, and trade of Hg. It restricts the use and emission of Hg, establishes a timetable for emission reduction to urge all signatory countries to reduce Hg emission, especially the Hg emission from coal-fired power plants, coal-fired industrial boilers, nonferrous metal smelting, waste incineration, cement manufacturing, etc. For example, the signatory countries are required to withdraw many products including Hg-containing batteries, switches, relays, cosmetics, fluorescent lamps, pesticides, barometers, clinical thermometers, sphygmomanometers, thermometers from the market before 2020, or make them meet the safety standards stipulated by the Minamata Convention. It is required to gradually decrease the use of dental amalgam and decommission the production of acetaldehyde that uses Hg and its compounds as a catalyst before 2018, as well as the production of chlor-alkali before 2025. In 2020, the use of Hg in PVC production shall reduce to 50% of that in 2010. It is also required to eliminate extraction of gold by amalgamation, burning of amalgam in the open air and residential areas. Besides, the Minamata Convention also makes specific provisions for the protection of people who are sensitive to Hg exposure, namely strengthening education and training of health care professionals and promoting health-care services to better diagnose and treat diseases related to Hg hazards.

4 Implementation of the Minamata Convention in China

As a major country of production, use, and emission of Hg, China has actively responded to the efforts of the United

Nations Environment Programme to cope with the global Hg pollution problem. On October 10, 2013, China signed the Minamata Convention as a member of the first batch of signatory countries. On April 28, 2016, the Standing Committee of the National People's Congress formally reviewed and approved the convention. On August 31, 2016, the Chinese government formally deposited the ratification of the convention with the United Nations, and became the 30th ratified country.

At present, the Hg mines currently being mined in China are mainly concentrated in Shaanxi Province. According to the requirements of the Minamata Convention, China will close all Hg mines within the borders 15 years after the convention takes effect (namely 2032). However, China will face the problem of the economic and social transformation after the closure of Hg mines.

The PVC industry is the largest consumer of Hg in China, which uses Hg as a catalyst and coal as the main raw material for production. In the past 10 years, China's PVC industry has developed rapidly and the consumption of Hg is huge. Therefore, it is urgent to research and develop new Hg-free or low-level Hg catalysts, and strictly control various aspects such as the quality of raw materials, low-level Hg catalysts, process control, and equipment quality and use so as to reduce the unit consumption of Hg catalysts [31]. The second-largest industry of Hg consumption in China is the manufacturing of measuring instruments. Specifically, Hg is mainly used for the production of clinical thermometers and sphygmomanometers. The third-largest industry of Hg consumption in China is battery production. In recent years, the Hg consumption in the production of clinical thermometers, sphygmomanometers, and batteries in China has begun to drop significantly.

The prevention and control of atmospheric Hg pollution is the top priority of China to implement the Minamata Convention, because China's anthropogenic Hg emission to the atmosphere ranks first in the world. Under the pressures of environmental Hg pollution and the implementation of the Minamata Convention, Hg emission control has become the next goal following desulfurization and denitration in atmospheric governance of China. In 2019, Wu et al. [32] suggested that the total control target for coal-fired power plants should be clarified, and the Hg emission to the atmosphere should be controlled on the basis of the alternative measures and the applications of control technologies. Besides, they also suggested the speeding up of revising the limit of Hg emission to the atmosphere by coal-fired power plants, and strengthening of the synergistic Hg removal effect of multi-pollutant control technology and its stability, as well as the research and development of special technology for Hg removal with high efficiency and low cost. Since 2009, the cement industry has become the largest emission source of anthropogenic Hg in China. In 2014, Hg emission has reached as high as 145 tons, indicating the rising pressure of Hg emission control in China's cement industry [2]. Therefore, it is urgent to establish and improve standard systems for Hg control and Hg emission reduction. A best available technology (BAT) and a best environment practice (BEP) should be developed, applied, summarized, and put into operation in new cement plants [33].

China has been taking active measures to conduct environmental Hg pollution research and Hg pollution control. The Ministry of Science and Technology of China has launched the Project "The Characteristics of China's Hg Pollution, Environmental Processes, and Technical Principles of Emission Reduction" in National Basic Research Program of China in 2013. The project was explored by the Institute of Geochemistry, Chinese Academy of Sciences in cooperation with six domestic excellent units. Aiming at the current situation of Hg pollution caused by a large amount of Hg production, use, and emission along with the implementation requirements of the Minamata Convention, China has carried out in-depth research on the source, sink, and migration rules of atmospheric Hg in China, the environmental processes and effects of Hg pollution, and the principles of flue gas Hg control and emission reduction technologies in typical industries. Besides, a process-based atmospheric Hg emission factor model has been built, and a high-resolution atmospheric Hg emission inventory by different forms from anthropogenic sources has been established. Further, field observations of atmospheric Hg migration between different surface systems (such as oceans, forests, and farmlands) have been comprehensively carried out, and the internationally advanced Hg emission model from natural sources has been built and China's natural Hg emission inventory has been made. The monitoring network of atmospheric Hg has been built up for long-term simultaneous continuous monitoring of atmospheric Hg form and wet deposition flux in typical regions of China. The research discovered that the Hg reactivity is not obvious in the Three Gorges Reservoir, and the risk of Hg pollution in the Bohai Sea is relatively small. However, the Hg mining areas in Guizhou face certain risks of Hg pollution. The project has developed high-efficiency adsorption materials for flue-gas Hg and zero-valent Hg catalytic materials containing mainly carbon-based and manganese-based oxides, built a multi-effect catalytic system to realize coordinated control of multiple pollutants, and achieved an internationally advanced integrated absorption and recycle technology for composite flue gas containing sulfur and Hg. The research results of this project provide important theoretical and technical support for China's Hg pollution control and the implementation of the Minamata Convention.

China has initiated a capacity-building project to implement the Minamata Convention. Before the Minamata Convention came into effect, the Ministry of Environmental Protection of China (now the Ministry of Ecology and Environment of China) and relevant ministries jointly announced that the Minamata Convention entered into force on August 15, 2017. Following the implementation requirements, a series of management measures related to Hg production, use, and emission have been issued. In order to promote comprehensive implementation and improve China's Hg control capability, the Foreign Economic Cooperation Office of Ministry of Environmental Protection (now the Foreign Environmental Cooperation Center of Ministry of Ecology and Environment) and the World Bank jointly launched a capacity-building project for China to implement the Minamata Convention. The project intends to complete the compilation of China's national strategy for implementation through investigations, monitoring, and strategy formulation. Moreover, pilot activities such as Hg flow reporting system, risk assessment of Hg-contaminated land plots, technical feasibility studies of Hg-containing waste recycling and disposal, improvement of atmospheric Hg monitoring capabilities, and publicity of achievements will be carried out to improve the implementation capabilities in pilot provinces, pilot cities, and the whole country.

5 Conclusions

The foundation of Hg pollution research in China is weak and not yet able to provide comprehensive scientific and technological support for China's Hg emission reduction, pollution prevention, and risk control. China is currently the largest country of Hg production, use, and emission, and faces more severe challenges from prevention and control of Hg pollution and implementation pressure than other countries. Therefore, it is necessary to carry out in-depth research in five aspects: (1) The natural sources of environmental Hg in China and the re-emission of the previous sedimentation of Hg; (2) Research on the long-range transport of atmospheric Hg and atmospheric Hg mass balance in China; (3) Hg exposure risks of residents in coastal areas and Hg-contaminated areas in China; (4) Research and development of low-level Hg catalysts in the PVC industry or alternative products; (5) Research and development of emission reduction technologies of typical anthropogenic Hg emission. The major technological needs of China's Hg pollution control and the implementation of Minamata Convention can be met through scientific research and technology development.

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