

Review

Emission Characteristics, Speciation, and Potential Environmental Risks of Heavy Metals from Coal-Fired Boilers: A Review

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Abstract: Coal-fired boilers, including coal-fired power plants (CFPPs) and coal-fired industrial boilers (CFIBs), are an important area for achieving sustainability globally as they are one of the globally important sources of anthropogenic emissions of heavy metals (HMs) due to huge amount of coal consumption. To date, the investigation of atmospheric emission characteristics, speciation, and potential environmental risks of HMs from coal-fired boilers has received widespread attention and achieved significant progress. To characterise the emissions of HMs from coal-fired boilers, research is currently being carried out in the areas of (1) studying the release of HMs from coal combustion processes, (2) developing emission factors and emission inventories, and (3) revealing the cross-media partitioning of HMs between different output streams. Research on the chemical forms of HMs in waste from coal-fired boiler is currently focused on chemical valence and speciation components. The sequential chemical extraction method is currently the most widely used method for investigating the chemical fractionations of HMs in wastes from coal-fired boilers. Studies indicate that different HM elements display differentiated characteristics of speciation in waste from coal-fired boilers. Early studies on potential environmental risk and ecological risk caused by HMs are usually based on actual monitoring values of HMs in the target environmental media. The risk assessment code method and the leaching toxicity method are the most widely used method to study the potential environmental risk of HMs in waste from coal-fired boilers. With the implementation of global carbon emission reduction strategies, the scale of coal-fired boilers and air pollution control technologies are bound to change in the future. Therefore, as an important component of global efforts to achieve sustainable development, more research is needed in the future to improve the accuracy of emission inventories, reveal the mechanisms of HM chemical transformation, and establish methods for potential environmental risk assessment at regional scales.

Keywords: coal-fired boiler; heavy metals (HMs); emission characteristics; speciation; potential environmental risks



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1. Introduction

Coal-fired boilers, including coal-fired power plants (CFPPs) and coal-fired industrial boilers (CFIBs), are one of the important anthropogenic sources of heavy metal (HM) emissions globally due to their huge coal consumption [1,2]. Therefore, emissions of HMs from coal-fired boilers are an important aspect that affects the achievement of sustainable development globally. HMs are generally defined as those with a density greater than 4.5 g/cm³ [3,4]. HMs such as mercury (Hg), chromium (Cr), cadmium (Cd), lead (Pb), and arsenic (As) are of wide concern worldwide due to their volatility, bioaccumulation, and

long-range transport, which can have significant adverse effects on the environment and human health [5,6]. Hg and inorganic Hg compounds, As and inorganic As compounds, Cd and Cd compounds, Cr (VI) compounds, and inorganic Pb compounds are included in the list of carcinogens published by the International Agency for Research on Cancer of the World Health Organization [7]. The Draft Convention on Long-Range Transboundary Air Pollution on HMs issued by the United Nations Economic Commission for Europe entered into force in 2003 with the aim of adopting measures to reduce emissions of Cd, Pb, and Hg into the atmosphere [8]. The international community agreed on the global legally binding Minamata Convention on Mercury (hereinafter referred to “the Convention”) in October 2013, and China committed to take a variety of measures to control Hg and its compound pollution. In addition, Hg, Cr, Cd, As, and Pb are also the priority HMs identified in the Opinions on Further Strengthening Prevention and Control of Heavy Metal Pollution (issued on 16 March 2022) executed by the Ministry of Ecology and Environment (MEE) of China for the implementation of total pollutant emission control [9]. With global urbanisation and industrialisation, the increasing intensity of human activities will lead to more HMs entering the ecosystem through various means, posing a huge threat to human health and the ecosystem, and hindering the path of sustainability worldwide. Therefore, the study of the environmental problems of HMs from anthropogenic sources has gradually become one of the major hotspots in the field of air pollution control research in the study of global sustainable development pathways.

Coal combustion is an important anthropogenic source of HM emissions. In 2015, approximately 21% of global anthropogenic Hg emissions by sources came from coal combustion, and it was the primary source of stationary combustion, with the contribution of coal combustion Hg emissions in Asia exceeding 30% [10]. The share of Cd, Pb, and Hg emissions from industrial energy consumption and industrial processes in the European Union was 57.4%, 57.1%, and 40.9% in 2020, respectively [11]. CFPPs contributed to 50% of all major Hg emissions in the United States, and emissions of Hg from CFPPs in the United States have been reduced by about 90% since the implementation of the Mercury and Air Toxics Standards [12]. From 1949 to 2012, the average annual growth rate of anthropogenic emissions of Hg and other HMs in China was about 5.1–8.0%, of which 33–90% came from coal combustion [13,14]. Coal-fired boilers are a type of energy conversion equipment apparatus that uses the thermal energy released from the combustion of coal to heat water or other fluid media to certain parameters [15,16]. According to the application industry, there are two main categories including CFPPs used for power generation and CFIBs used for heating supply and various industrial production [17,18]. China is the leading producer of coal-fired power generation worldwide, with its total power generation accounting for 52.2% of the global coal-fired power generation in 2020 [19]. Due to the influence of energy resources and economic level, China has the largest number of CFIBs in the world, which are widely used in various industrial production processes and domestic heating, mainly in densely populated cities and suburban areas [16]. The coal consumption of CFIBs comprised approximately 10.3% of total industrial coal consumption in China in 2020 [20,21]. The Convention entered into force for China on 16 August 2017, and CFPPs and CFIBs are included in the top five atmospheric emissions sources of Hg and its compounds [22]. Until now, the control of HM emissions from the stack flue gas of coal-fired boilers has mainly been achieved through the coordinated removal of conventional air pollutant control devices (APCDs) including dust removal (de-PM), desulphurisation (de-SO₂), and denitrification (de-NO_x). The MEE of China issued and implemented the Emission Standard of Air Pollutants for Thermal Power Plants (GB 13223-2011) [23] and the Emission Standard of Air Pollutants for Boiler (GB 13271-2014) [24], which introduced new Hg emission requirements and proposed emission limits of 0.03 mg/m³ and 0.05 mg/m³ for Hg and its compounds for CFPPs and CFIBs, respectively.

In addition, HMs are enriched to varying degrees in various types of waste from the operation of coal-fired boilers. The third Conference of the Parties to the Convention has also included wastes from APCDs in the Indicative List C of wastes contaminated with Hg

and its compounds [19]. During the combustion of coal in the boiler chamber, some of the HMs are released into the flue gas in gaseous form, leaving the remaining in the slag; when the flue gas passes through various conventional APCDs downstream, some of the HMs in the flue gas enter the APCD system along with particulate matter (PM), SO₂, and NO_x, migrating into various wastes (e.g., fly ash and gypsum) generated from coal-fired boiler operation. Statistics from MEE indicated that in 2019 the electricity and heat production and supply industry and various industrial processes produced about 540 Mt of fly ash, 320 Mt of slag, and 130 Mt of gypsum, of which 86%, 53%, and 83% of fly ash, slag, and FGD gypsum were produced in the electricity and heat production and supply industry, respectively [25]. The HMs contained in fly ash, slag, and gypsum can be released into the environment again under certain conditions during stockpiling and disposal, posing a threat to the environment and human health [26,27]. As can be seen, the environmental problems associated with HMs in wastes such as fly ash, slag, and gypsum from coal-fired boilers cannot be ignored.

Driven by the basic need for environmental improvement, there has been a sustained global effort to combat air pollution from coal-fired sources. With the upgrading of de-PM, de-SO₂, and de-NO_x technologies in CFPPs and CFIBs, HM emissions have become a priority air pollutant of concern after PM, SO₂, and NO_x. Currently, coal is still an important type of energy consumption globally. Although the proportion of coal in global energy consumption structure has been decreasing in recent years, the coal-based energy consumption structure will continue to be maintained for a long period time in the future with huge amounts of HMs entering the environment as a result of coal combustion. Therefore, reducing emissions of HMs from coal-fired boilers will remain a huge challenge in the long term, and the environmental problems caused by the release of HMs from the various types of waste generated by the operation of coal-fired boilers cannot be ignored. To date, abundant research has been conducted on HMs from coal-fired boilers worldwide; however, there is a lack of systematic analysis of their emission characteristics, speciation, and potential environmental risks. In particular, the common characteristics of HM emissions and speciation from coal-fired boilers have not been revealed. Therefore, this study intended to conduct an overview of the research progress on the emission characteristics, speciation, and potential environmental risks of coal-fired boilers, which is an important anthropogenic source of HMs on a global scale, based on the published literature. It aims to provide important support for scientific research on HM-related issues, including global long-range transport modelling, human health effects assessment, and the development of global sustainable development strategies.

2. Methodology

In this study, the systematic literature review (SLR) method was used to search for Chinese and English literature on HM emission characteristics, speciation, and potential environmental risks from coal-fired boilers in the Web of Science database, Elsevier ScienceDirect database, Springer e-journal database, and China Knowledge Network database. The keywords were “coal-fired boilers”, “heavy metals”, “emissions/emission inventories”, “fate/partitioning”, “leaching”, and “environmental risks”. The criteria for literature included were that (1) the article type was a published journal, (2) the study was about coal-fired boilers globally, and (3) the article was published between 1979 and 2023. After setting the keywords and included criteria, the literature was searched based on topic relevance. Subsequently, non-compliant literature was further excluded based on abstract, keywords, and completeness of the literature.

3. Emission Characteristics of HMs from Coal-Fired Boilers

Coal is a fossil fuel with an extremely complex composition, and its combustion process can emit conventional air pollutants (particulate matter, SO₂, and NO_x) and HMs. During the combustion of coal in the furnace of a coal-fired boiler, HMs in coal in the form of monomers, minerals, and compounds undergo a series of complex physico-chemical

reactions under high temperature combustion conditions and are emitted into flue gas. When the flue gas passes through various APCDs including de-PM, de-SO₂, and de-NO_x, HMs are partially trapped, and the remaining HMs are eventually discharged into the atmosphere with the flue gas through the chimney [28]. To date, studies on the emission characteristics of HMs in coal-fired boilers can be summarised in the following three aspects: (1) to investigate the release of HMs from coal combustion, (2) to develop the emission factor and emission inventory, and (3) to reveal the cross-media partitioning of HMs between different output streams.

3.1. Release of HMs from Coal Combustion

Most HMs are partially or completely vaporised during coal combustion in the furnace of coal-fired boilers, condensing and enriching on flue gas particles with a large specific surface area as the temperature of the flue gas downstream of the boiler decreases [17]. Konieczynski and Zajusz-zubek [29] studied the dynamic release of HMs during coal pyrolysis and showed that at a combustion temperature of 400 °C, Cd and Pb had already started to be released in large quantities. However, when the combustion temperature increased to 1000 °C, about 90% of Cd, 85% of Hg, and 80% of Pb, respectively, were released from the coal into the flue gas [29]. The volatility of HMs in lignite was found to be in the order of Hg > As > Cd > Pb, with Hg having a very high volatility at 300 °C and being largely volatile when the combustion temperature rose to 500 °C [30]. The volatilisation of HMs during coal combustion is also related to the type of HMs binding components. HMs in coal with stronger affinities to organic matter and sulphides are more volatile than elements with stronger affinities to silicate minerals [31].

HMs volatilised from the coal into the flue gas are condensed on the particulate matter in the flue gas during the cooling of the flue gas downstream of the furnace [27,28], thereby reducing the eventual atmospheric emissions. The HMs enriched on the particulate matter in the flue gas are firstly trapped by the de-PM device into the fly ash. The field data demonstrated that the average Hg removal efficiency of CFPPs installed with the electrostatic precipitator (ESP), ESP+ wet flue gas desulphurisation (WFGD), and fabric filter (FF) was 29%, 62%, and 67%, respectively [32]. ESP is the most widely used de-PM device, with nearly 99% of particulate Hg removed [33]. Due to the fact that HMs are more enriched in smaller particle sizes, the electrostatic FF (EFF) can increase the relative enrichment factor of Hg and As in fly ash [34,35]. In addition, the selective catalytic reduction (SCR) system can improve the synergistic removal efficiency of Hg by oxidising Hg⁰ in the flue gas, with up to 40% of Hg⁰ being oxidised to Hg²⁺ in some cases, as found in a study by Zheng et al. [36]. In WFGD systems, desulphurisation slurry circulation could facilitate the adsorption of SO₂ and enrich HMs such as Hg, Pb, As, and Cd into the de-SO₂ by-products [37,38]. With the tightening of air pollutant emission controls on coal-fired boilers, ultra-low emission retrofitting of CFPPs has now been largely implemented in China. A comprehensive assessment of the effectiveness of ultra-low emission technologies for HMs control in CFPPs by Wen et al. [34], using field measurements, model calculations, and literature review, found that ultra-low emission technologies applied to CFPPs significantly improved the HM removal efficiency from 75% to 87%, with this improvement mainly coming from de-PM technologies. Zheng et al. [36] investigated the effect of de-PM technology on the control of Hg and As in an ultra-low emission CFPP and revealed that the lower inlet temperature of a low-temperature ESP contributed significantly to the simultaneous removal of Hg and As. HM emissions from different coal-fired boilers vary depending on factors such as coal properties, combustion temperature, APCDs, and other factors. The differences in Hg removal efficiencies between coal-fired boilers with ESP installation can be 2–3 times [39]. The correlation between Hg emissions and coal consumption is less than for Pb and As due to the higher synergistic removal capability of Hg by de-PM, de-SO₂, and de-NO_x technologies than for Pb and As [40]. However, field data from some studies have also identified that EFF can achieve removal efficiencies of over 94% for Cd and Pb in particulate form [41].

3.2. Emission Factor and Inventory of HMs

The establishment of localised emission factors and refined emission inventories for pollution sources is the basis for quantifying HM emissions, identifying key emission areas, and analysing major emission sources, as well as supporting the development of environmental management regulations and standard policies. Researchers have earlier established global inventories of anthropogenic HM emissions from sources at different time scales, using emission factors obtained through literature research [5,6,42,43]. The above emission inventories have been established to initially quantify HM emissions including coal-fired sources, and these studies are important for understanding the atmospheric spatial and temporal emissions of HMs from coal-fired boilers. To date, researchers focus on atmospheric emissions of HMs from stationary coal-fired sources in China due to their huge coal consumption, with particular attention paid to atmospheric Hg emissions from CFPPs [13,19,20]. As there are significant differences in the generation and emission control levels of HMs from coal-fired boilers in different regions, how to obtain localised emission factors and high-precision emission inventories is the key to improving the characterisation of HM emissions. Table 1 presents the studies of emission inventory of five typical HMs from coal-fired boilers. Recently, researchers have established an inventory of atmospheric emissions of 12 HMs in China from 1949 to 2012 [13,44,45] and an anthropogenic source emission inventory of atmospheric Hg from 1978 to 2014 [19,46], by combining field measurement data. However, the emission factors for HMs from CFIBs are not available and are treated to be surface sources. In addition, there are differences in HM emissions from different coal-fired boilers due to factors such as coal characteristics, combustion temperature, and APCDs [17].

Table 1. Comparison of HM emission inventories of coal-fired boilers.

Type	Country or Region	Hg (t)	As (t)	Cd (t)	Cr (t)	Pb (t)	Year	Reference
CFPPs & CFIBs	World	2081	2037	673	12,683	11,690	1995	Pacyna (1988) [1]
	Europe	186	143	109	1999	2683	1995	Pacyna and Pacyna, 2001 [6]
	Africa	197	41	40	746	1116	1995	
	Asia	860	342	237	4282	4845	1995	
CFPP	World	292	—	—	—	—	2015	UN Environment (2018) [10]
	China	73	—	—	—	—	2015	Liu et al., 2018 [19]
	Japan	0.638	0.251	0.00702	0.243	0.518	2000	Ito et al., 2006 [2]
CFIB	China	171	821.3	104.0	5317.6	5449.5	2012	Tian et al., 2015 [4]
		25.46	115.33	7.04	371.40	589.76	2017	Gao et al., 2021 [20]

Note: CFPP is coal-fired power plant; CFIB is coal-fired industrial boiler; “—” represents no data.

3.3. Cross-Media Partitioning of HMs among Output Streams

Establishing the mass balance of HMs in coal-fired boilers based on the mass balance theory and the content levels of HMs in different output streams of coal-fired boilers (including combustion products, waste from the operation of APCDs and stack flue gas) is the main approach for carrying out research on the cross-media partitioning behaviour of HMs in coal-fired boilers. The cross-media partitioning of HMs between different output streams of coal-fired boilers is related to the nature of the elements themselves, coal properties, combustion conditions, APCDs, and other factors and involves a variety of physico-chemical processes such as gasification, adsorption, and morphological transformation [28]. Due to the extremely high volatility of Hg, its content in the slag is mostly no more than 5% [47–49], while the content of Hg in fly ash and WFGD systems usually varies widely, from about 5.0 to 96.9% [50,51] and from 1.1% to 78.5% [52], respectively. Agarwalla et al. [50] investigated four pulverised-fired (PC) furnaces and a circulating fluidised bed (CFB) furnace in CFPPs all equipped with ESP to reveal that about 80–90% of Hg in PC furnaces was emitted to the atmosphere, with the remaining Hg enriched in fly ash, whereas the proportion of Hg enriched in fly ash in the CFB furnace was about 64.8%, much higher than that of PC furnaces, and only 32.4% of Hg was emitted into the atmosphere by stack flue gas. For four PC CFPPs installed with SCR + ESP + WFGD, it was similarly found that Hg was mainly partitioned into fly ash and gypsum with a

combined percentage of 93.3–98.0%. As, Pb, and Cr were mainly partitioned into fly ash with a percentage of 95.8–96.9%, 94.0–96.7%, and 84.9–89.8% and 1.45%, 1.98%, and 2.93% for As, Pb, and Cr in gypsum, respectively. The percentage of typical HMs in the slag increased with decreasing volatility, with volatile Hg (0.06–0.23%) < semi-volatile As and Pb (1.51–3.40%) < non-volatile Cr (6.62–12.6%) [47]. In a study by Zhao et al. [49], it was also identified that As, Cr, and Pb in a CFPP equipped with LNB + SCR + ESP-FF + WFGD were mainly distributed in the slag and fly ash (97.8–99.9% in total), with the proportion of Cr in the slag being higher than that of As and Pb, and 0.04–2.18% of As, Cr, and Pb were distributed in the WFGD system (including gypsum and wastewater). As a volatile element undergoes volatilisation in the furnace, it is mainly captured by fly ash as the flue gas temperature decreases [53]. Gaseous As can also react with Ca to form thermodynamically stable calcium arsenate compounds [54]. Cr is mainly associated with illite in coal, which determines that Cr is not volatile during combustion [55].

4. Speciation of HMs in Waste from Coal-Fired Boilers

The release of HMs from waste exposed to the natural environment poses a significant threat to the environment and human health. The environmental stability, mitigation, and bioavailability of HMs contained in waste from coal-fired boilers, such as fly ash, slag, and gypsum, is closely related to their chemical fractionation [56]. Chemical fractionation analysis of HMs in fly ash, slag, and gypsum can provide basic data for their environmental risk research.

4.1. Sequential Chemical Extraction Method for Speciation Analysis of HMs

Research on the chemical forms of HMs in waste from coal-fired boiler is currently focused on chemical valence [54] and speciation components [57]. Given the applicability and availability of the results, the sequential chemical extraction (SCE) method is currently the most widely used method for investigating speciation characteristics of HMs in solid samples including the binding strength of HMs and information on their major binding sites [58,59]. The principle of the SCE method is to use a combination of chemical extractants to continuously separate HMs bound by different components in a solid sample according to the chemical binding capacity of the chemical components [49]. The SCE method is currently being used in a wide range of samples such as soil [60], sediment [61], sludge [26], fly ash [62], and gypsum [63]. Tessier et al. [64] were the first to propose a four-step SCE method for the analysis of HMs bound in soil. Five chemical extractions, including exchangeable fraction (F1), carbonate-bound (acid-soluble) fraction (F2), Fe-Mn oxide-bound fraction (F3), organic matter-bound (oxidisable) fraction (F4), and residue fraction (F5), were obtained. The Tessier method has been studied and applied for a long time but still has certain drawbacks. Firstly, the compounds formed by Cd and Cl during the extraction step of the exchangeable fraction are quite stable in a high concentration chloride medium (lgk values between 1.98 and 2.4), which could lead to high determination results; secondly, there is resorption and redistribution during the extraction of the different fractions of the form, resulting in poor comparability of the analytical results. Subsequently, the former European Community Bureau of Reference (BCR) improved on the Tessier three-step SCE method and further proposed the BCR method [61]. The BCR method divides the HMs in solid samples into four chemical fractionations including exchangeable fraction (F1), reducible fraction (F2), oxidisable fraction (F3), and residual fraction (F4). The BCR method is an experimentally based method for the analysis of speciation for HMs, which is widely used and reproducible, and is most used for the study of the chemical fractionation of HMs in wastes of coal-fired boilers including gypsum [57] and fly ash [65]. The Tessier method has a high detection limit (>100 mg/kg) for Hg, while Hg content in gypsum from CFPPs can be as low as 0.01 mg/kg [49]. Therefore, the Tessier method and BCR method are generally not suitable for the study of the chemical fractionation of Hg in solid samples. Subsequently, Bloom et al. [66] proposed a modified five-step SCE method for Hg by improving the existing SCE method, which classified the chemical fractionations

of Hg into water-soluble fraction (F1), acid-soluble fraction (F2), organic-chelated fraction (F3), strong complex fraction (F4), and residual fraction (F5).

4.2. Chemical Fractionations of HMs in Wastes

The SCE method has been well applied to the analysis of chemical fractionations of HMs in wastes from coal-fired boilers [47,65,67] (see Table 2). Different HM elements display differentiated characteristics of speciation in waste from coal-fired boilers [57,58,65]. The residual fraction was considered to be the main chemical fractionation of Hg and Cr in fly ash, while As has a high proportion of acid-soluble and exchangeable fractions in fly ash [65]. Hg was predominantly in the strong complex fraction in most of the seven gypsum samples in Hebei Province in China, with a range of 15.3–76.8%; the lowest Hg content was in the acid-soluble and organic-chelated fraction [68]. In addition, the residual fractions of Hg, As, Se, and Pb in the wastewater sludge and gypsum could account for up to 49.7–73.3% and 62.0–72.3%, respectively, while the exchangeable fraction of Cd had the highest contribution, with the exchangeable Cd content in the wastewater sludge accounting for 21.1% more than that in the gypsum [59]. The speciation characteristics of HMs in coal-fired boiler waste are closely related to coal properties, combustion conditions, and APCDs. Sun et al. [69] found that Hg was mainly distributed in the strong complex fraction in the gypsum, with a range of 60–80%, where the high chlorine content in the coal led to a higher percentage (30%) of Hg in the water-soluble fraction in the gypsum samples. Similarly, Chang et al. [26] identified that the proportion of water-soluble and acid-soluble Hg in gypsum samples from three CFPPs (SCR + ESP + WFGD) was 30–39%, which was slightly higher than the results of Hao et al. [70]. This is mainly due to (1) the higher generation of HgO and (2) the higher HgS in the 400-mesh gypsum sample, which had a higher proportion of oxidised Hg in the extraction fraction in the study by Chang et al. [26]. However, Zhao et al. [49] revealed that Hg in three gypsums was mainly present in the residual fraction with a range of 73.11–86.69%, which is similar to the results of Zhang et al. [59]. It has been found that the percentage of oxidisable Cr, As, Cd, and Pb in the fly ash of CFB furnace was higher than that of the fly ash of PC furnace, which could be related to the lower combustion temperature of CFB furnace [57]. In addition, it was also discovered that the chemical fractionation of HMs differed even in different ash hoppers of the same de-PM device. More than 90% of the Pb in the fly ash samples from different ash hoppers was present in the residual fraction, while the percentage of As, Cr, and Cd in the exchangeable, reducible, and oxidisable fractions increased significantly, with unburned carbon and particle size being the main factors controlling fly ash formation [71]. The chemical fractionation of HMs in fly ash was found to be very different from that in gypsum. Zhang et al. [59] revealed that Hg, As, and Pb were mainly present in the fly ash as residual fractions (60–90%), while the residual Cr and Cd fractions in both fly ash and gypsum were lower than the remaining fractions. Fu et al. [57], on the other hand, found that the effective fractions (all fractions except the residual state) of Cr (43.1–53.2%), Cu (79–87.8%), Zn (66.8–89.6%), and As (64.5–75.6%) were significantly higher in gypsum than in fly ash. However, different chemical fractionations of As were found in a CFB furnace, with exchangeable and reducible As in slag and fly ash accounting for more than 60% while oxidised and residual As accounted for approximately 20% [72]. The exchangeable and reducible As are dominated by components bound to Ca, while the oxidised and residual As are dominated by components bound to Fe/Al [52]. Therefore, Huang et al. [72] concluded that gaseous As mainly reacted with calcium-based minerals in fly ash and slag during the combustion of CFB furnace. Additionally, it was found that SO₂ can inhibit the interaction between gaseous As and minerals [73]. Also, certain research explored the chemical transformation behaviour of HMs in the waste during the whole operation processes of coal-fired boilers by conducting studies on the chemical fractionation changes of HM fractions in coal, slag, and fly ash. Wang et al. [33] revealed that the content of As, Pb, and Cr fraction with high mobility (sum of exchangeable fraction, reducible fraction, and oxidisable fraction) in slag and fly ash was significantly lower compared to that in

feed coal; however, the content of exchangeable As in fly ash and slag was significantly higher than that in feed coal. Gaseous As in flue gas reacts with minerals to form arsenate (As^{5+}), so that As in fly ash exists mainly in As^{5+} fraction, whereas the content of arsenite (As^{3+}) fraction in slag is relatively high due to the formation of As^{3+} in the combustion zone of the chamber [72]. This is mainly attributed that the intense combustion reaction in the coal-burning area in the chamber creates a local reduced atmosphere, which is not conducive to the oxidation of As^{3+} to As^{5+} .

Table 2. Comparison of chemical fractionations of HMs in wastes from coal-fired boilers.

Type	Waste	Boiler Type	APCDs	HM	Chemical Fractionations	Reference
CFPP	Gypsum	Pulverised coal furnace	SCR + EFF + WFGD	Hg As Cr Cd Pb	F4 > F3 > F2 > F1 F3 > F4 > F2 > F1 F4 > F2 > F3 > F1 F4 > F1 > F2 > F3 F4 > F2 > F1 > F3	Zhao et al. [49]
	Gypsum	—	ESP + WFGD	Hg	F4 > F5 > F1 > F2 > F3	Al-Abed et al. [58]
	Fly ash	Pulverised coal furnace	SCR + ESP + WFGD + WESP	Hg As Cr Cd Pb	F4 > F2 = F3 > F1 F2 > F1 > F4 > F3 F4 > F1 > F2 > F3 F2 > F3 = F1 > F4 F2 > F4 > F3 > F1	Zhao et al. [65]
CFIB	Fly ash	Circulating fluidised bed furnace	LNB – SCR + ESP + WFGD + WESP	Hg As Cr Cd Pb	F4 > F5 > F3 > F2 > F1 F3 > F1 > F2 > F4 F4 > F3 > F1 > F2 F4 > F3 > F1 > F2 F4 > F3 > F2 > F1	Tong et al. [15]
	Slag	Pulverised coal furnace	LNB – SCR + EFF + WFGD	Hg As Cr Cd Pb	F4 > F5 > F3 > F1 > F2 F3 > F2 > F4 > F1 F4 > F3 > F2 > F1 F4 > F1 > F3 > F2 F4 > F3 > F2 > F1	
	Gypsum	Circulating fluidised bed furnace	SNCR + FF + WFGD	Hg As Cr Cd Pb	F4 > F5 > F3 > F2 > F1 F4 > F1 > F3 > F2 F4 > F1 > F3 > F2 F4 > F1 > F3 > F2 F4 > F1 > F3 > F2	

Note: CFPP is coal-fired power plant; CFIB is coal-fired industrial boiler; LNB is low NO_x burner; SCR is selective catalytic reduction; SNCR is selective non-catalytic reduction; FF is fabric filter; ESP is electrostatic precipitation; EFF is electrostatic FF; WFGD is wet flue gas desulphurisation; WESP is wet electrostatic precipitator; “—” represents no data.

5. Potential Environmental Risks of HMs from Coal-Fired Boilers

Pollution control of HMs from coal-fired boilers is an issue of great concern in recent years. Wastes (e.g., fly ash, slag, and gypsum) containing HMs are subject to significant environmental risks due to the re-release/leaching of HMs under certain conditions during the process of stockpiling, reuse, and disposal [74,75]. It has been confirmed that once Hg is leached from gypsum, it is converted to Hg^0 by reaction with reducing substances such as sulphites in the environment and then released into the atmosphere [69]. Therefore, the accurate assessment of the potential environmental risk of HMs in various types of waste is currently the focus of HM control in coal-fired boilers.

5.1. Methodology for Potential Environmental Risk of HMs

Early studies on the potential environmental risk and ecological risk caused by HMs are usually based on actual monitoring values of HMs in the target environmental media. The most widely used methods for investigating the potential environmental risks of HMs includes the Potential Ecological Risk Index method [76], the Geo-accumulation Index method [77], and the Nemerow Index method [78,79] (see Table 3). The Geo-accumulation Index method and Nemerow Index method use real level of HM content to quantitatively assess the potential environmental risk of HMs by comparison with background value

of HMs. The Potential Ecological Risk Index method introduces toxicity response factors for HMs based on the background value of HMs, integrating the biological toxicity and environmental effect of HMs for quantitative investigation. In addition, the above three methods differ in terms of assessment criteria and grading of results. The Potential Ecological Risk Index method, the Geo-accumulation Index method, and the Nemerow Index method are mainly used to assess the level of contamination and ecological risk of HMs in media such as atmospheric particulate matter, soil, and lake/river sediments. All three methods require background values for HMs and have limited application for potential environmental risk assessment of HMs in waste as there are currently no environmental limits of HMs in wastes from coal-fired boilers [80]. Wang et al. [80] studied the contamination levels of 12 HMs in de-SO₂ products from two CFPPs using the Nemerow Index method, and the results showed that the overall contamination level reached a light to moderate level, with the contamination level of Cd reaching above the alert level.

Table 3. Comparison of common environmental risk assessment methods for HMs [49,55,56,76–79,79–86].

Method Name	Feature	Calculation Formula	Classification	Application Field
Geo-accumulation Index method	Consider HM content level	$I_{geo} = \log_2 \left(\frac{c_i}{1.5 \times S_i} \right)$ Where I_{geo} is the Geo-accumulation Index; c is the HM content level; S is the standard value of HM content; i is HM.	Seven level	Soil, agricultural land, municipal sludge, sediment, and atmospheric particulate matter
Nemerow Index method	Introduce average and maximum values	$P_i = \sqrt{\frac{p_i \times \frac{w_i}{S_i}}{\frac{(p_{i,max})^2 + (p_{i,ave})^2}{2}}}$ Where P is the Nemerow Index; w is the HM content level; S is the standard value of HM content; i is HM.	Five level	Soil, agricultural land, municipal sludge, sediment, and gypsum
Potential Ecological Risk Index method	Introduce toxicity response factors	$RI = \sum_{i=1}^n E_r^i = \sum_{i=1}^n (T_r^i \times c_f^i) = \sum_{i=1}^n \left(T_r^i \times \frac{c_i}{c_d} \right)$ Where E_r is the Potential Ecological Risk Index; T_r is the toxicity response factor; c_f is the pollution index; c_i the HM content level; c_d is the standard value of HM content; i is HM.	Five level	Soil, agricultural land, municipal sludge, and sediment
Risk Assessment Code method	Consider HM chemical fractionation	$RAC_i = \frac{F_x}{\sum_{n=1}^n F_n}$ Where RAC is the Risk Assessment Code; F is the amount of chemical fractionation; x is the potentially releasable HM; n is the total number of chemical fractionation.	Five level	Soil, sediment, and solid waste
Leaching toxicity method	Consider cross-media migration capability	Concentration of HM in the leaching solution or leaching rate of HM	/	Solid waste

There are two types of methods most widely used to study the potential environmental risk of HMs in waste from coal-fired boilers, the risk assessment code (RAC) method and the leaching toxicity method. The RAC method explores the potential environmental risk of waste containing HMs by quantifying the proportion of potentially releasable HMs based on their chemical fractionations obtained by the SCE method [81]. The RAC method classifies the potential environmental risk of wastes containing HMs into the following five risk classes: no-risk class for less than 1%, low-risk class for 1–10%, medium-risk class for 11–30%, high-risk class for 31–50%, and very high-risk class for more than 50%. The RAC method has been widely applied to the potential environmental risks of HMs in waste from coal-fired boilers [49,55,59]. The leaching toxicity method has also been used to simulate the potential environmental risks associated with the cross-media transport of toxic and hazardous substances in waste in contact with water, which was originally proposed to control the contamination of groundwater by pollutants [82–84]. The leaching of hazardous substances from waste is influenced by a variety of factors, and therefore different leaching approaches differ in terms of parameters such as leaching agent, leaching temperature, liquid to solid ratio (L/S), and leaching time [85–88]. To date, numerous researchers have conducted extensive studies on the leaching toxicity of HMs from various types of wastes and have established and proposed a variety of standardised methods, and the most commonly used of which are Method 1312 Integrated Precipitation Leaching (SPLP) [89], Method 1311 Toxicity Characteristic Leaching (TCLP) [90], Method 1320 Con-

tinuous Leaching (MEP) [91], and the Leaching Environmental Assessment Framework (LEAF) series of standard methods [92]. However, as the TCLP, MEP, and SPLP methods are standard methods specifically developed to assess the leaching toxicity of municipal waste and can only reveal the leaching behaviour under fixed leaching conditions, they can lead to an overestimation of the leaching of HMs from the waste of coal-fired boiler. Therefore, the TCLP, MEP, and SPLP methods are not suitable for exploring the potential environmental risks of HMs in coal-fired boiler wastes by conducting leaching toxicity studies. Therefore, studies have been carried out on the basis of standard leaching methods by adjusting leaching parameters [93,94] and designing leaching experiments [88,95–97] to conduct leaching characterisation of HMs in wastes from coal-fired boilers.

5.2. Potential Environmental Risks of HMs

Environmental risk studies based on various research methods have identified the potential environmental risk of HM-containing waste from coal-fired boilers. The results of the RAC studies revealed that all types of waste from coal-fired boilers (e.g., fly ash, slag, and gypsum) pose some degree of environmental risk and that there are differences in HMs in different types of solid waste. Zhao et al. [65] studied the potential environmental risk levels of HMs in feed coal of four CFPPs based on the RAC method, where Hg, As, and Pb showed no or low risk levels, Cd showed medium risk levels, and the risk levels of Cr in different feed coal varied widely. This study also revealed that the highest risk levels for Hg, Cr, Cd, and Pb in fly ash from four CFPPs were medium-risk, while As exhibited high or very high risk levels. A study by Fu et al. [57] found that the RAC results for Cr, Pb, Cd, and As in fly ash showed no or low risk levels, while the RAC results for Cr, Pb, Cd, and As in gypsum showed medium or high risk levels. The study by Zhang et al. [59] similarly identified that Hg, Cr, Cd, Pb, and As in gypsum exhibited higher environmental risks due to their weaker environmental stability than fly ash. The potential environmental risk of different HM elements varies among types of waste, which is closely related to the HM properties [59], combustion type [98], and APCDs [71,99]. In addition, as waste containing HMs from coal-fired boilers has gradually attracted the attention of researchers and environmental administrators, abundant studies have been conducted on the leaching behaviour of HMs from fly ash [82–85,88], slag [100,101], and de-SO₂ by-products [49,95] from coal-fired boiler. Jones et al. [101] used a standard leaching method to investigate the leaching characteristics of HMs such as As, Cr, and Pb from slag and fly ash and found that the leaching of HMs from fly ash was higher than that from slag. Gong et al. [102] studied the leaching behaviour of HMs in a typical ash heap plant in Guizhou Province, China, using a column leaching test and showed that the leaching concentration of Cd remained stable after 16 days. The leaching of HMs from fly ash was considered to be sensitive to changes in pH [84]. Although the elemental composition and mineral composition of the same type of waste from different coal-fired boilers varies, most HMs in the same type of waste exhibit similar leaching characteristics [84].

6. Conclusions and Future Perspectives

To date, the study of the atmospheric emission characteristics, speciation, and potential environmental risks of HMs from coal-fired boilers has received widespread attention and achieved significant progress. However, the following systematic and in-depth research into the emissions, speciation, and potential environmental risks of HMs from coal-fired boilers is still urgently needed.

In terms of research on the emission characteristics of HMs, studies have been carried out mainly for CFPPs, focusing on the establishment of emission factors, the development of emission inventories, and the distribution of HMs in different materials (flue gas, fly ash, slag, and de-SO₂ byproducts), basically revealing the spatial and temporal distribution characteristics of HM emissions. However, there is a remarkable lack of research on the above aspects for CFIBs. The reasons for this are primarily explained by the fact that there is a serious limitation of field data for CFIBs to support the study of emission characteristics

of HMs from CFIBs. Most studies have adopted HM emission factors from CFPPs, resulting in a large uncertainty in the inventory of HM emissions from CFIBs, and the spatial and temporal characteristics of their HM emissions have not been fully revealed. Therefore, there is an urgent need to establish localised emission factors for HMs from CFIBs based on field measurement data from CFIBs and to reduce uncertainty in the emission inventories of HMs from CFIBs. In addition, in the context of the global carbon emission reduction strategy, it is important to conduct research on HM emission pathways from coal-fired boilers under the global sustainable development goals for global HM emission control.

With regard to the study of HMs in various types of waste from coal-fired boiler, abundant research has been carried out on the speciation of HMs in waste from CFPPs including fly ash, slag, and gypsum, and mature and widely used methods have been established to study the chemical fractionation of HMs in waste from coal-fired boiler. However, as previously mentioned, studies of the speciation of HMs in waste from CFIBs are very limited due to the lack of in situ samples of emission sources. The relationship between the chemical fractionation of HMs in waste from coal-fired boilers and factors such as APCDs, combustion type, and coal properties has not been fully revealed. The mechanisms for the transformation of HMs in different types of waste from coal-fired boilers are not comprehensively defined. Therefore, research on the speciation of HMs in coal-fired boilers needs to be enriched with in situ sample analysis data in the future to reveal the transformation mechanism of HMs in the whole system of coal-fired boilers including furnaces, de-NO_x systems, de-PM systems, and de-SO₂ systems, based on the chemical fractionation of HMs in the whole waste type.

In terms of research on the potential environmental risks of HMs in coal-fired boilers, studies have been carried out on potential environmental risk assessment methods and applications. Studies on the potential environmental risks of HMs in coal-fired boilers are primarily based on two categories: chemical fractionations and leaching toxicity, and the identification of potential environmental risks of HMs in waste is achieved by quantifying unstable fraction and leaching levels, respectively. However, there are differences in the results of applying the above two types of methods to investigate the potential environmental risks of HMs from coal-fired boilers. Therefore, there are limitations in the methodology to consider only the chemical fractionation or leaching levels for potential environmental risk studies. In addition, the existing methodology for studying the potential environmental risk of HMs from coal-fired boilers is only applicable to specific coal-fired boiler emission sources, and the study of the potential environmental risk of HMs from coal-fired boilers on a regional scale is limited. Therefore, it is necessary to enrich the systematic research on the emission characteristics and speciation of HMs from coal-fired boilers based on the field measurement data of emission sources and to establish a method for determining the potential environmental risks of HMs from coal-fired boilers suitable at the regional scale. On this basis, the spatial distribution characteristics of the potential environmental risks of HMs from coal-fired boilers needs to be revealed.

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