

Review

Emissions of Toxic Substances from Biomass Burning: A Review of Methods and Technical Influencing Factors

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Abstract: In the perspective of energy sustainability, biomass is the widely used renewable domestic energy with low cost and easy availability. Increasing studies have reported the health impacts of toxic substances from biomass burning emissions. To make proper use of biomass as residential solid energy, the evaluation of its health risks and environmental impacts is of necessity. Empirical studies on the characteristics of toxic emissions from biomass burning would provide scientific data and drive the development of advanced technologies. This review focuses on the emission of four toxic substances, including heavy metals, polycyclic aromatic hydrocarbons (PAHs), elemental carbon (EC), and volatile organic compounds (VOCs) emitted from biomass burning, which have received increasing attention in recent studies worldwide. We focus on the developments in empirical studies, methods of measurements, and technical factors. The influences of key technical factors on biomass burning emissions are combustion technology and the type of biomass. The methods of sampling and testing are summarized and associated with various corresponding parameters, as there are no standard sampling methods for the biomass burning sector. Integration of the findings from previous studies indicated that modern combustion technologies result in a 2–4 times reduction, compared with traditional stoves. Types of biomass burning are dominant contributors to certain toxic substances, which may help with the invention or implementation of targeted control technologies. The implications of previous studies would provide scientific evidence to push the improvements of control technologies and establish appropriate strategies to improve the prevention of health hazards.

Keywords: biomass burning; toxic substances; methods of measurement; stoves; technical factors



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1. Introduction

Biomass is an important renewable residential solid fuel, contributing to 7.5% of total global energy consumption [1]. However, biomass burning is also an important source of air pollutants [2–4], including particulate matter (PM), volatile organic compounds (VOCs), elemental carbon (EC), polycyclic aromatic hydrocarbons (PAHs), and carbon monoxide (CO). These pollutants not only induce bad air quality in local, regional, and global scales but also cause severe indoor air pollution and the premature death of rural residents. In addition to utilization, there are still huge amounts of biomass burned for domestic cooking/heating or burned in the field for compensating for soil fertility [5].

This paper has systematically reviewed the emission characteristics, influencing factors, and partial mechanisms of four toxic substances, focusing on heavy metals, polycyclic aromatic hydrocarbons, elemental carbon, and volatile organic carbons, which may have hazardous effects on human health. Most heavy metal elements have significant biological toxicity, are very difficult to biodegrade, and accumulate hundreds of times over through biological amplification of the food chain, eventually entering the human body. Heavy metals can strongly interact with proteins and enzymes in the human body, rendering

them inactive, and can accumulate in some organs of the human body, causing chronic poisoning [6]. For instance, lead disrupts the intestinal flora of the body, not only leading to the onset of growth- and development-related diseases [7] but also affects the energy metabolism of the body by inhibiting the gluconeogenesis process [8]. (Cr (VI)) is a Class I carcinogen [9,10] that induces oxidative stress, DNA damage, genomic instability, and epigenetic disorders that result in induced lung cancer [11]. PAHs induce carcinogenicity, immunotoxicity, and reproductive development toxicity by entering the organism through metabolic activation with various enzymes in the organism, inducing cancer [12]. For instance, exposure to various O-PAHs and N-PAHs increase lung risks by promoting cellular inflammation and oxidative stress [13].

Biomass burning causes severe air pollution and smoke and promotes the formation of secondary inorganic/organic aerosols [14]. Emissions from biomass burning enhance the heterogeneous reaction of sulfur dioxide and promote the formation of sulphate [15], while causing atmospheric brown clouds [16], contributing to regional warming in the lower atmosphere. EC in biomass burning emissions is also a short-lived global warming agent that affects the visibility and radiative properties of the atmosphere [17]. The emission of VOCs from biomass burning are precursors of ozone formation and secondary organic aerosols (SOA) based on photochemical reactions [18–20].

Toxic emissions vary across regions, depending on the type of combustion technology (stove, boiler, or open fire) and the regional dominant biomass (crops, wood, etc.) [21]. Increasingly, studies focus on biomass burning emissions associated with different technologies. The empirical investigation associated with various parameters represented the characteristics of burning emissions [21–27]. Emissions from biomass burning are conducted in labs or real residential homes. So far, approximately 83% of the published indoor combustion emission measurements are in labs or simulated homes [28–32]. Emission factor is an important parameter and purpose of empirical studies, which represents the mass of pollutants emitted per the mass of unit biomass burned. The amount of emissions in regions are calculated by the combination of emission factors and biomass consumption. However, a few empirical investigations of emission factors are available, compared with the numbers of regions that utilize biomass as residential fuel. Additionally, the technologies of combustion, types of biomasses, environmental factors, etc., vary throughout regions. Moreover, the method of emission testing contains differences as well.

In the case of applications of renewable energy and sustainability, utilization of biomass as a solid fuel faces various challenges, such as improving combustion efficiency, investigating control technologies, and sustainability. Research on biomass burning emissions would provide technical support and scientific data and help with the evaluation of new technologies and strategies.

2. Applied Methods to Investigate the Biomass Burning Emissions

2.1. Methods of Sampling

Sampling methods for the biomass burning sector varied according to the target toxic substances [26]. The main concepts of the sampling system design were similar, with no standard method. The inlet design depends on the type of burning. A hood/smoke chamber above the stove was applied to collect the VOCs and PM samples [21,27]. The hood was also used to collect samples for open burning in the field. In some studies, the smoke gun inserted into or above the chimney was applied to conduct the biomass burning sampling for stoves. Due to the high density and concentrations of flue gases and smoke, the dilution system/channel is an important part of the emission sampling system (Figure 1). The selection of samplers and real-time monitors depends on the targeted toxic substances.

Combustion technologies impact emissions significantly, which relate to combustion efficiency, thermal efficiency, and transfer efficiency, etc. Fiber content, carbon content, water content, etc., of various biomasses are different, associated with the emission of toxic substances and air pollutants. The measurement facilities are fundamental devices for

biomass emission testing. The reliability of those facilities affected the accuracy of testing results, especially the values of emission factors. Combustion technologies, biomass, and measurement facilities of most current studies are illustrated in Table 1.

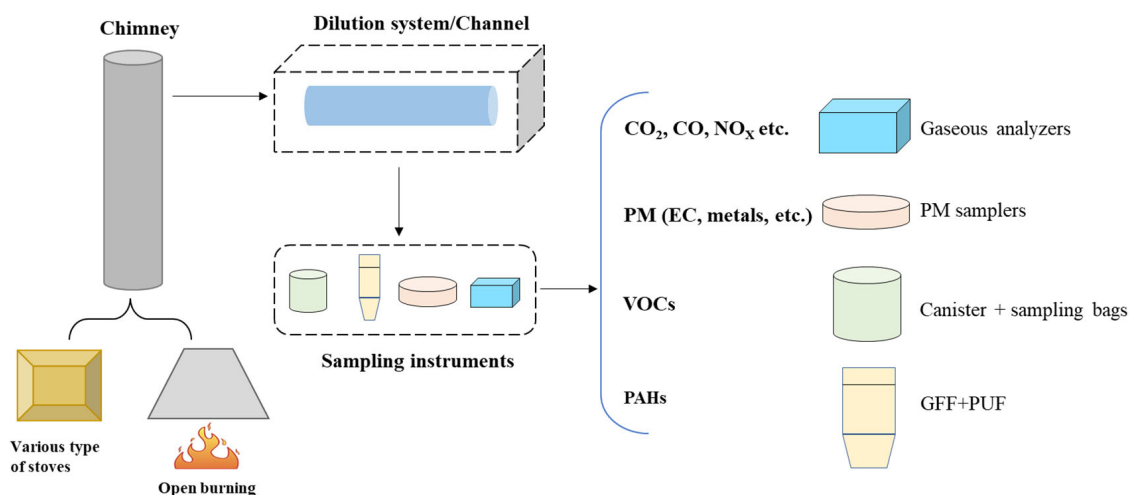


Figure 1. Sampling system of biomass burning (glass fiber filter, GFF; polyurethane foam, PUF).

Table 1. Combustion technologies, biomasses, and measurement facilities in studies.

Combustion Technologies	Types of Biomass	Measurement Facilities
Traditional stoves (Three stones) [28]	Rice straw [33,34]	Dilution and sampling Systems [1]
Brick wok stove [35]	Bean straw [33]	Water boiling test (WBT) protocol [28]
Modern cooking stoves [36]	Wheat straw [33,34]	Feasible experimental designs [37]
Stoves with chimney [38]	Cotton straw [34]	Lab-based full-capture dilution system [38]
Wood gasifier stoves [39]	Rape straw [33,34]	Simulated rural kitchen chamber [35]
Traditional clay stoves [40]	Maize straw [41,42]	Kitchen Performance Test (KPT) [39]
Open fire burning	Wood [33]	Burning chamber for open fire burning [33]
	Animal dung [40]	
	Biomass briquet [43]	

2.2. Detection Methods of Toxic Substances

2.2.1. Heavy Metals

Heavy metals from stove burning are divided into bottom ash (BA), fly ash (FA), and gas phase, according to the forms of existence [44]. The distribution of heavy metals in bottom ash is analyzed by the X-ray diffraction (XRD) technique [45]. The concentration of heavy metal is determined by an atomic absorption spectrophotometer [46,47]. Additionally, some chemical models, combined with elemental analysis software, are used to understand the emission inventory of heavy metals [21,48].

2.2.2. Polycyclic Aromatic Hydrocarbons

For the detection and analysis of PAHs, GC-MS and High-Performance Liquid Chromatography (HPLC) have been widely and frequently used in PAH research [25,49,50]. GC-MS is mainly used for the analysis of volatile and thermally stable organics, including dioxins, PCBs, etc. HPLC is complementary to GC-MS as a method for the analysis of high boiling point or thermally unstable organic compounds [51,52].

Prior to analysis, the complicated pretreatment procedures of PAH samples, which are associated with quality assurance and quality control, included extraction, clean-up, fractionation, and concentration [53].

2.2.3. Elemental Carbon

EC and OC are analyzed by the methods of thermal oxidative decomposition (TMO) [54–56], thermo-optical transmission (TOT) [57], element analyzer (EA) [42], ambient carbon particulate monitor (ACPM) [58], etc. The most popular method was introduced by Desert Research Institute, U.S. A thermal/optical carbon analyzer (Desert Research Institute, model 2001, Atmoslytic Inc., Calabasas, CA, USA) was applied to analyze the amount of organic carbon (OC) and elemental carbon (EC), following the Interagency Monitoring of Protected Visual Environments Advanced (IMPROVE_A) protocol [59,60].

2.2.4. Volatile Organic Compounds

The sampling and analysis of ambient VOCs were based on the development of high-resolution gas chromatography-mass spectrometry (HRGC-MS), which allowed for the identification and quantification of more than 300 components in a single sample [61]. The pretreatment methods of VOCs sample in the air were mainly solvent desorption, thermal analysis, three-stage cold trap preconcentration, etc. Among them, the micro-enrichment technology of three stage cold trap preconcentration was introduced successively in recent years, which is a new and effective sample preparation method that has been rapidly applied in recent years [62].

2.3. Source Apportionment

The source apportionment discriminant including positive matrix factorization (PMF) and chemical mass balance (CMB) has been widely implemented and described in detail in previous studies [63–65]. For some relatively complicated receptors, the combined model called PMF-CMB is applied to the source apportionment feasibly [66].

The indicators of source identification regarding biomass burning vary according to the targeted toxic substances. To identify the typical sources of VOCs, the biomass composition consisting of cellulose, hemicelluloses (typically 50–70% dry matter), lignin (15–35%), proteins, amino acids, metabolites, methane chloride substituted by HCN, and acetonitrile were significant parameters [67–69]. Studies show that biomass burning contributes most to aromatics, formaldehyde, and acetaldehyde [70]. CH_3CN was chosen as a tracer, and its enrichment ratio was used to estimate the contribution of biomass burning to ambient VOCs [71].

To apportion the source of carbonaceous aerosols, a simple isotopic mass balance equation, which is based on the $\Delta^{14}\text{C}$ data, was applied to estimate the contributions from biomass and fossil fuel [72]. The $^{14}\text{C}/^{12}\text{C}$ isotope ratio of an EC sample allowed for the determination of the biomass burning fraction [73]. Levoglucosan has been identified as a molecular marker for the long-range transport of biomass burning aerosols, due to its longer stability and high abundance in different environmental media [74,75].

For the source apportionment of PAHs, acenaphthene and acenaphthylene are typically synthesized by biomass burning, whereas cadalene and retene are typically found in plant-derived materials [76]. Among these, the more thermodynamically stable PAHs (e.g., pyrene, whose ring consists of six atoms) were selected as indicators of biomass burning [49,77].

2.4. Emission Inventory

Toxic substance emissions from the biomass burning sector can be calculated from the combination of activity data, technology distribution, unabated EFs, and penetration of emission control technologies [78–80]. The emission factor of the biomass burning sector represents the emissions from the unit mass of biomass burned, associated with the burning modes (domestic stove or open fire in the field), the type of stoves, control technologies, etc. The detailed calculation method depends on the research design and the parameters of the sampling system. Activity datasets should be constructed at different scales (local, regional, and global scales), according to the tasks of emission calculations. Key data of

the activity dataset include the type of biomass, the amount of biomass production, the fraction of other utilization, proportion of burning mode, etc.

$$E = \sum_i A_k \times EF_{k,m}$$

where E is the emissions in year; A is activity data; EF is the net emission factor; i represents the region; k represents biomass type; and m represents the technology distribution.

3. Emissions of Toxic Substances

The targeted toxic substances (heavy metals, PAHs, EC, and VOCs) emitted from biomass burning have been studied extensively and in sufficient detail. Heavy metals, PAHs, and EC are chemical compositions of particulate matter. Meanwhile, VOCs, as the major gaseous pollutant, have direct or indirect adverse effects on the climate, environment, and human health [18–20]. The targeted toxics can be removed as a co-benefit to PM and VOCs control by applying the proper abatement process. Hence, the characteristics of the emissions of heavy metals, PAHs, EC, and VOCs associated with technical factors are illustrated as follows.

3.1. Emissions of Heavy Metals

Various heavy metals emitted from biomass burning sources induced high biotoxicity and carcinogenic risk [45,81]. Compared with the pollutants generated owing to incomplete burning (PAHs, VOCs, BC, etc.), heavy metal emissions associated with the substances contained in the biomass itself and are related to its characteristics. The emission factors of Cr, Mn, Ni, As, Cd, and Pb in the particulate matter of firewood, bamboo, and oil crop straw (soybean straw and peanut straw) are significantly different, whereas the emission factors of heavy metal elements of oil crop straw are significantly higher than those of firewood [82]. The uncontrolled discharge of heavy metals, especially Cr, Pb, Cd, Zn, and Hg, will cause serious damage to the environment and human health [83,84].

Biomass burning is a series of complex physical and chemical reactions [85]. Heavy metals in biomass can be volatile (Hg), semi-volatile (Cd, Pb, Se), or finite volatile (Sb, As, Be, Cr, Co, Mn, Ni) during combustion. Metal condenses to the surface of the solid burning residue particles (fly ash) and are always present in the flue gas, while some limitedly volatile metals remain in the combustion chamber ash [85]. The amount of emissions is influenced by the burning process associated with the characteristics of the biomass and the combustion technology [22,83,84].

The chemical properties of the biomass affect its thermal efficiency, burning process, and flue gas purification technologies [85–87]. The proportion of metals in fly ash and residues varies, owing to the application of different biomass burning technologies. Cd and Zn are less dependent on the type of biomass, which is generated by forming gaseous compounds during burning. Hence, the increase concentration of Cd and Zn is associated with decreasing precipitation temperature and particle size [88]. As the smoke cools, they aggregate or condense on the fly ash particles. Hg escapes almost completely with the flue gas due to its high vapor pressure but is found in very low concentrations in untreated biomass [89].

Burning various types of biomass makes a difference in the emission factors of heavy metals (Table 2). Fe, Mn, Cd, Cu, Zn, and Pb are the dominant elements from biomass burning. EFs of Hg were significantly lower than that of other heavy metals. Differences of EFs from studies attribute to straw type, stove design, combustion temperature, and feeding control mode, etc.

Table 2. Emission factors of heavy metals [21,37,90].

EF	Wheat Straw		Corn Straw		Rice Straw		Wood
Pb (mg kg ⁻¹)	1.30 ± 0.50	0.5	2.72 ± 1.71	0.99 ± 0.35	2.66 ± 0.13	1.44 ± 0.51	1.69 ± 0.66
Cr (mg kg ⁻¹)	0.42 ± 0.17	7.5	0.24 ± 0.03	0.29 ± 0.09	0.33 ± 0.12	0.60 ± 0.21	0.19 ± 0.05
Cd (mg kg ⁻¹)	1.91 ± 1.33	0.04	-	0.75 ± 0.53	-	2.38 ± 2.27	-
As (mg kg ⁻¹)	0.01 ± 0.06	0.2	-	0.02 ± 0.04	-	0.99 ± 0.12	-
Mn (mg kg ⁻¹)	1.25 ± 0.61	2.4	0.50 ± 0.33	0.99 ± 0.31	0.83 ± 0.78	2.14 ± 1.10	0.24 ± 0.04
Fe (mg kg ⁻¹)	3.53 ± 1.20	113	2.13 ± 0.94	2.28 ± 0.44	2.42 ± 1.15	3.78 ± 1.51	1.32 ± 0.53
Cu (mg kg ⁻¹)	0.93 ± 0.28	2.2	1.62 ± 0.35	0.73 ± 0.26	0.81 ± 0.31	1.18 ± 0.38	0.43 ± 0.04
Zn (mg kg ⁻¹)	1.00 ± 0.37	4.5	4.19 ± 2.17	0.62 ± 0.18	0.81 ± 0.31	1.54 ± 0.77	3.12 ± 2.27
Hg (μg kg ⁻¹)	11.09 [91]	11 [35,92]		7.94 [91]		5.56 [91]	9 [92,93]

Wu et al., 2022;
Huang et al., 2022;
Sun et al., 2019

Heavy metal deposition associated with the risks of ecosystem and human health showed seasonal variations in different regions. Monthly fluxes of soluble/insoluble components of Cu, Pb, Cd, Cr, and Zn varied in the Pearl River Delta region and distinguished with the summer monsoon and winter monsoon, influenced by the Asian monsoon shift [91]. In 2019, Cd, Hg, Cr, As, and Pb were considered as hazardous air pollutants (HAPs) in China. The emissions of Cd, Hg, Cr, As, and Pb from biomass burning emitted PM_{2.5} were 399.5 Mg, 6.36 Mg, 203.7 Mg, 68.67 Mg, and 434.8 Mg, respectively, in 2014 [21].

Understanding the material fluxes during the combustion of different types of biomass will influence the design and control of future biomass stoves. Understanding the content of inorganic elements in different biofuels and their reactions and effects during combustion is very important for the rational design of combustion devices and control systems for the biofuels to be used or, conversely, for the selection of appropriate biofuels for existing installations [89].

The application of mixed combustion technologies might change the characteristics of heavy metal emissions. The addition of wheat straw during the co-combustion of sewage sludge and wheat straw reduced the volatility of Cd and As and increased the volatility of Pb and Cr [94]. Although coal and biomass co-burning has been applied in industrialization in some countries and regions, there are limited studies on the migration characteristics of heavy metals in the process of coal and biomass co-burning. Variation in biomass properties is evidently greater than that of coal, associated with types of biomass. Hence, the especial characteristics of biomass, including high water content, high chlorine content, and low calorific value, affect the thermal efficiency, requiring an advanced stove design of mixed firing systems [88].

3.2. Emissions of PAHs

Polycyclic aromatic hydrocarbons (PAHs) are a class of harmful air pollutants mainly generated from the incomplete combustion of fossil fuels, biomass, and other hydrocarbon containing organic matter [3]. PAHs are recognized as the most important organic pollutant affecting human health because of their carcinogenicity and other toxicities, which damage a wide range of human organs. A total of 16 species of PAHs have been recognized by the US Environmental Protection Agency (EPA) as priority components for control. In terms of global atmospheric emissions of the 16 PAHs, the sources, technologies, and characteristics of emissions from biomass burning vary considerably at regional and national levels. In most developing countries, residential solid fuel combustion is the major source of the emission of PAHs (polycyclic aromatic hydrocarbons) [39,95]. Biomass burning is the second largest solid fuel source, contributing to 32.1% of the emission of residential PAHs [96].

In the biomass burning sector, PAHs emitted from stove burning (e.g., household stoves, etc.) and open burning (e.g., open fires, straw burning, etc.). Increased studies reported on the emission of PAHs from stoves that burn crop residues for cooking or heating. Characteristics of the emission of PAHs varied by burning technologies. However,

data on polycyclic aromatic hydrocarbon emission factors (EFs) are scarce, resulting in a high uncertainty in emission inventories [23], as laboratory-derived EFs were significantly underestimated in the inventory (Figure 2) [24,34]. An empirical study of the factors of the emission of PAHs for 9 commonly used crop residues showed that emission factors of stove emissions were 1–2 orders of magnitude higher than those for open fires. The correlation between PAHs and fine particulate matter tended to be higher due to the influence of fuel properties and combustion conditions (such as moisture and combustion efficiency) [24,97].

Traditional domestic heating and cooking stoves (e.g., brick stoves, iron stoves) typically associated with lower burning efficiency emit higher PAHs than the improved stoves (Figure 2). Gasifiers are a sort of improved stove, reducing the incomplete combustion owing to the application of an advanced ventilation system and a furnace temperature control system. Moreover, the size of the stove and its airflow would affect the air/biomass ratio and the evenness of the furnace temperature [98,99]. Abundant oxygen supply accelerates burning, whereas surge induces incomplete combustion and results in higher emissions of PAHs. Control of oxygen supply and combustion rate is considered to reduce the emission of PAHs [34].

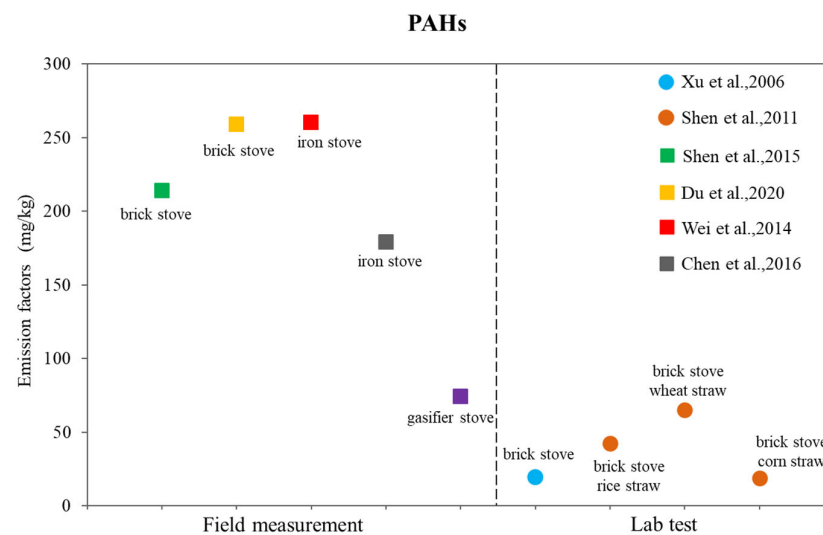


Figure 2. Emission factors of PAHs [23,34,100–103].

Large amounts of the emission of PAHs from biomass burning are associated with higher volatile content in biomass, cellulose, lignin, potassium salt, and water content [104]. Higher temperatures or an insufficient oxygen supply in stoves can result in an increase in the emission of PAHs. Therefore, the formation and emission of PAHs can be reduced by pelleting [105], pressing, or carbonizing biomass to improve its density and combustion efficiency [106].

Moreover, spatiotemporal distribution, associated with various meteorological conditions, results in the applications of different types of biomasses and their corresponding stove technologies. A comprehensive assessment of the emission of PAHs from biomasses showed that the toxic potential of PAHs emitted from crop straw burning in northern China is greater than that from wood burning in southern China [102]. Crop straws in the North China Plain and Sichuan Basin contain a large number of wheat straws, and their emission of PAHs factors are significantly higher than other crop straws. A large amount of rice straw has also been burned in the southern region, but the emission factor of rice straw is low, and the emission of PAHs is low. The emission of PAHs from biomass burning was higher in the cold season (November to March), due to the increased biomass consumption for heating, and lower in the warmer season [27].

3.3. Emissions of Elemental Carbon

Elemental carbon (EC) is mainly emitted from the incomplete combustion of the carbon content fuels. So far, incomplete combustion is difficult to avoid during the biomass burning process. Epidemiological literature has reported that EC is causally involved in lung cancer [107]. The World Health Organization (WHO) reported its adverse health effects in 2012. Increasing epidemiological evidence recognized EC as a better indicator of cardiovascular, all-cause mortality and lung cancer, to whom they exposed the ambient air pollution [107]. Biomass burning is a significant source of EC emissions [77]. Biomass burning also contributes approximately 42% of black carbon emissions on a global scale [108].

The level of EC emissions in the biomass combustion sector is influenced by combustion conditions and technologies, including stove design, operator behaviors, fuel properties, etc., which can result in emission factors differing by two orders of magnitude. Stove design is strongly influenced by the type of biomass. The application of improved stoves with chimneys reduced PM_{2.5} emissions by 57.56%, compared to the traditional stoves without chimneys [40]. The chimney enhances air ventilation and boosts combustion efficiency [38]. Emissions from old stoves are 2–4 times higher than those from new stoves (Figure 3) [34,36,40]. Thermal efficiency is crucial in the biomass combustion process, i.e., the heating capacity per unit of fuel, which determines the amount of biomass consumed in the process. Thermal efficiency is related to heat transfer efficiency and combustion efficiency, which is inversely related to emission factors. Therefore, the higher the thermal efficiency, the less biomass is used [36]. The thermal efficiency can be improved by increasing the heat transfer efficiency, but the combustion efficiency may be reduced due to poor ventilation conditions [109].

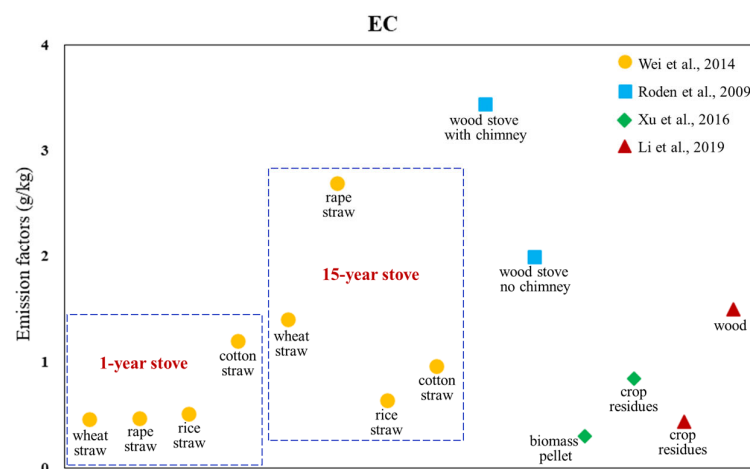


Figure 3. Emission factors of EC [34,40,109,110].

Emissions varied according to the type of biomass. Straw, firewood, and livestock excrement burning are used for domestic cooking or heating. For example, EC emissions from excrement burning were higher than those from wood [1,42]. EC emissions from wood logs and crop residues (rice straw, maize residues, wheat residues, etc.) were 0.43 ± 0.32 g/kg and 1.49 ± 0.69 g/kg, respectively (Figure 3) [38]. Crop residues have higher burning rates, thus the insufficient air supply leads to poor burning conditions. For wood seasonings, different proportions of hemicellulose, lignin, and cellulose result in different EFs [111].

Open burning includes straw burning in fields and forest and grassland fires. Burned area data can be derived from the Moderate Resolution Imaging Spectroradiometer (MODIS) direct broadcast burned area product. In Asia, approximately 730 Tg of biomass is burned each year, of which forest burning accounts for approximately 45%, with an annual EC emission of 0.45 Tg [112].

3.4. Emissions of Volatile Organic Compounds

A growing number of studies suggest that VOCs have significant direct and indirect adverse effects. The short-term exposure to specific VOCs groups and species might increase cardiorespiratory risks, carcinogenic hazard, and impacts on the circulation system [61,113]. VOCs are essential precursors of O₃ and secondary organic aerosols [114]. O₃ is a powerful reactive oxidant that is harmful to human and ecosystem health [115].

In the past two decades, biomass burning contributes 10–30% of the total emission of VOCs in many regions, which is the second largest anthropogenic source of VOCs [115,116]. According to the source apportionment result in China (Figure 4), the contribution of biomass burning to VOCs was 27%, 13%, and 11% in Beijing, Pearl River Delta, and Lin'an [33,110,117,118].

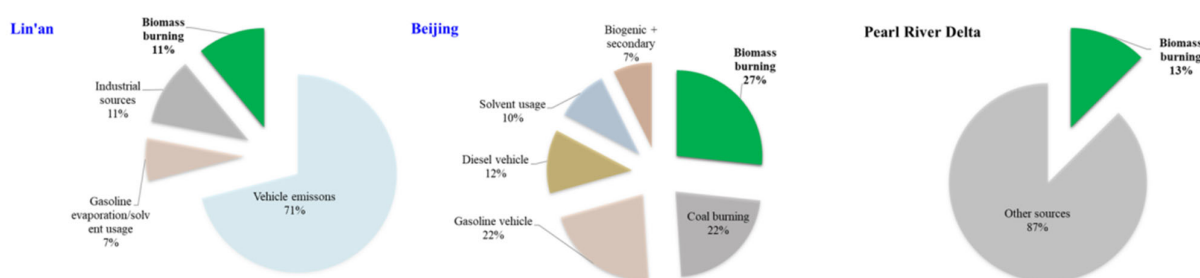


Figure 4. Contributions of biomass to VOCs.

Compared with some other emission sources, emissions from biomass burning presented significant variations among different seasons [119]. Because domestic fuel consumption is strongly dependent on seasons, the daily temporal variation in domestic burning varies throughout the year [120]. In rural Northeast China, biomasses are the dominant contributor to domestic burning, contributing to 83.3% of the total emission of VOCs, whereas coal contributed to 16.7% [121]. Hence, to control VOCs pollution during heating seasons in Northeast China, biomass burning should be taken into account.

The volatile organic compounds (VOCs) associated with biomass burning were characterized in China, including two types of combustion (stove and open fire burning). Measurements were emphasized for five typical kinds of biomass (residues of rice, wheat, beans, rapeseed, and wood) [33]. To compare the VOCs composition from the burning of different biomasses, VOCs source profiles of the burning of different biomasses were obtained according to emission factors of each group of VOCs (Figure 5) [116]. The most VOCs emitted from wheat straw burning (7.57 g/kg), where emissions were almost twice as much as other varieties. The emission factors of straw and firewood burning for total VOCs were 4.37 ± 2.23 g/kg and 2.12 ± 0.77 g/kg, respectively [122]. The emissions from straw burning were higher than those from firewood burning. Among the VOCs emitted by civil biomass combustion, the most abundant species were aromatic hydrocarbons and aldehydes, both with a content of more than 25%. Straw and firewood combustion showed similar distributions of other species except for the large differences in the content of halogenated hydrocarbons and nitriles [122].

Emission factors affected the reliability of emission inventory significantly, according to the methods of sampling and testing, as well as the influence of environmental conditions (e.g., temperature and humidity). Hence, uncertainties in estimating the emission of VOCs from biomass burning are due to the lack of local emission factors and source profiles. Measurement errors could induce large uncertainties in the emission factors of VOCs biomass burning, ranging over two orders of magnitude [123]. Although it did not play a dominant role on an annual scale, biomass burning mostly occurred during the pre-cultivation and harvesting seasons, usually causing severe regional air pollution [124].

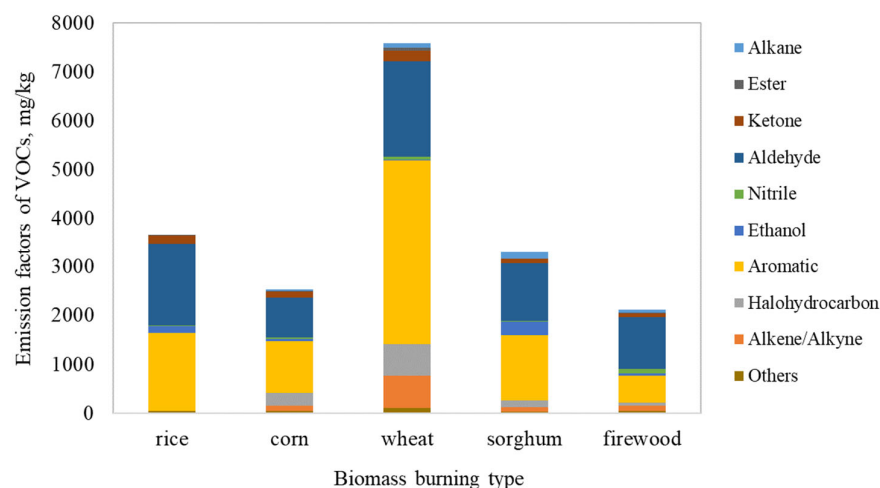


Figure 5. Emission factors of VOCs from different types of biomass.

Emission factors of VOCs from the burning of crop residues ranged from 0.18 to 26.57 g/kg, influenced significantly by stove types and ambient temperatures. CO/CO₂ ratios (30.9×10^{-3} to 77.1×10^{-3}) of the kang stove (a commonly used stove in northern China for heating beds) were lower than those from a cookstove (98.3×10^{-3} to 349.5×10^{-3}). As a result, a kang stove is cleaner and has better efficiency compared to a cookstove. The bigger combustion chamber of a kang stove allows more air/oxygen inlet, which reduces the proportion of incomplete combustion [125]. Moreover, lower ambient temperature resulted in lower combustion efficiency, which may lead to more condensation of gaseous organic compounds on the surface of particulate matter.

Overall, characteristics of four toxic substances emitted from biomass burning are discussed, associated with technical parameters and types of biomasses. For instance, emissions from old stoves are 2–4 times higher than those from new stoves [78,83,84]. Emission factors of PAHs from stoves were 1–2 orders of magnitude higher than those from open fires. The toxicity of substances relates to the amount of significant emissions. Older stoves, equipped with chimneys and higher thermal efficiencies, result in higher toxic emissions. Burning various types of biomass corresponds to higher emissions of certain toxic substances. Heavy metal emissions from oil crop straw are significantly higher than those from firewood [67]. Cd and Zn are less dependent on the type of biomass. EC emissions can be reduced by pelleting and carbonizing, with a reduction rate of 93% [117]. Moreover, measurement errors could induce large uncertainties, e.g., the emission factors of VOCs by biomass burning ranging over two orders of magnitude [123]. Hence, research design is equally important.

4. Conclusions

The emission of toxic substances from biomass burning is assignable. Biomass burning is the second largest solid fuel source in developing countries, which contributed to 32.1% of the emission of household PAHs, approximately 42% of black carbon emissions on a global scale, and 10–30% of the total emissions of VOCs in many regions over the past two decades.

The targeted released toxic substances of this study are seriously hazardous to human health. Heavy metals are very difficult to biodegrade. They can interact with proteins and enzymes in the human body, causing chronic poisoning. PAHs induce carcinogenicity, immunotoxicity, and reproductive development toxicity by entering the organism through metabolic activation with various enzymes in the organism, inducing cancer [12]. EC damages lung functions and enters the blood, inducing both cardiovascular and pulmonary diseases. VOCs directly hurt the liver, kidney, brain, and nervous system. Moreover, VOCs affect human health indirectly as precursors of ozone formation. Exploring the impacts of biomass types and technical parameters on toxic emissions could provide

scientific implications for the abatement of toxic substances and introduction of overall health protection.

Different biomass burning technologies and biomass types lead to a massive gap of toxic substances emissions. The design of stoves and combustion modes (household stove, open fire in field, wild fire, etc.) could cause multiple or even orders of magnitude differences in emission factors. Temperature and oxygen supply in the stove could significantly affect the completeness of burning, and then influence the emission of heavy metals, PAHs, EC, and VOCs. The properties of various biomasses are different. For instance, the burning of rice straw emitted higher Pb, Cr, Cd, As, Mn, and Cu, compared with wheat straw and cornstalk, but, comparatively, emitted lower Hg [91]. The emission factors of EC and VOCs from crop residue burning are approximately three and five times higher than those from firewood, respectively [38,122].

The abatement of toxic emissions and introduction of personal protection are possible ways to reduce health risks. Abatement could be conducted on the sources of toxicity, such as the design of stoves or the retrofitting with after treatment devices. However, most of the stoves worldwide are working without after treatment at all. The open burning of crop residues still contributes large amounts of toxic and air pollutants. In addition to the traditional methods (ban burning or burn in turn), the development of in situ emission control technologies would help with the control of open burning. The proper utilization of biomasses, such as biomass pellet pressing or carbonizing, would increase thermal efficiency and reduce toxic emissions. For personal protection, the risks could be reduced by shortening the exposure duration, dressing up with helpful wears, etc. Furthermore, there are gaps in the research. The efficiency and economic control technologies of biomass stoves, the research and development of high efficiency biomass stoves, the quantitative research of biomass mixed fuel combustion, and the control of open fire combustion still need further research.

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