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Aromatic acids as biomass-burning tracers in atmospheric aerosols and ice cores: A review[☆]

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ABSTRACT

Biomass burning (BB) is one of the largest sources of carbonaceous aerosols with adverse impacts on air quality, visibility, health and climate. BB emits a few specific aromatic acids (*p*-hydroxybenzoic, vanillic, syringic and dehydroabietic acids) which have been widely used as key indicators for source identification of BB-derived carbonaceous aerosols in various environmental matrices. In addition, measurement of *p*-hydroxybenzoic and vanillic acids in snow and ice cores have revealed the historical records of the fire emissions. Despite their uniqueness and importance as tracers, our current understanding of analytical methods, concentrations, diagnostic ratios and degradation processes are rather limited and scattered in literature. In this review paper, firstly we have summarized the most established methods and protocols for the measurement of these aromatic acids in aerosols and ice cores. Secondly, we have highlighted the geographical variability in the abundances of these acids, their diagnostic ratios and degradation processes in the environments. The review of the existing data indicates that the concentrations of aromatic acids in aerosols vary greatly with locations worldwide, typically more abundant in urban atmosphere where biomass fuels are commonly used for residential heating and/or cooking purposes. In contrast, their concentrations are lowest in the polar regions which are avoid of localized emissions and largely influenced by long-range transport. The diagnostic ratios among aromatic acids can be used as good indicators for the relative amounts and types of biomass (e.g. hardwood, softwood and herbaceous plants) as well as photochemical oxidation processes. Although studies suggest that the degradation processes of the aromatic acids may be controlled by light, pH and hygroscopicity, a more careful investigation, including closed chamber studies, is highly appreciated.

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1. Introduction

Biomass burning (BB) such as residential biofuel combustion, open burning of agricultural residues and forest fires release substantial amounts of pollutants into the atmosphere (Andreae and Merlet, 2001; van der Werf et al., 2010). These pollutants include trace gases (e.g., carbon dioxide, carbon monoxide, methane, volatile organic compounds, and precursors of O₃) and aerosols, especially organic carbon (OC) and black carbon (BC) (Chen et al.,

2017; Crutzen et al., 1979; van der Werf et al., 2010). They have potential to influence climate, regional/global air quality, the ecosystem and human health (Crutzen and Andreae, 1990; Lelieveld et al., 2015; Ramanathan et al., 2001). BB can contribute more than two thirds of the total carbonaceous aerosol emissions in regions with intense fires (e.g., South Asia) (Gustafsson et al., 2009; Venkataraman et al., 2005). Those emissions can be transported long distances and impact areas far away from the source regions (Fig. 1) (Cong et al., 2015; Fujii et al., 2015; Kawamura et al., 2012; Zhang et al., 2014). For example, a recent work revealed that BB is the major source of BC in aerosols and glaciers over the Tibetan Plateau and Himalayas (Li et al., 2016). The deposition of BC on the cryosphere can reduce the albedo and accelerate melting of snow covers and glaciers (Bond et al., 2013; Xu et al., 2009).

Organic molecular tracers play an important role in tracking and identifying the BB emissions due to their unique signatures (Simoneit, 2002; Simoneit and Elias, 2001). Biopolymers such as cellulose, hemicelluloses, lignin, suberin, sporopollenin, etc. are vital components of biomass fuels (Kawamura et al., 2012) and their thermal degradation (pyrolysis) products have been widely exploited as tracers of BB emissions. Simoneit (2002) identified various tracers of BB in smoke aerosols, including a homologous series of n-alkanes, polycyclic aromatic hydrocarbons, resin acids, anhydrous sugars from cellulose, methoxyphenols from lignin, steroids and terpenoids. Levoglucosan and its isomers (mannosan and galactosan), the pyrolysis products of cellulose and hemicelluloses have been considered as key tracers of BB in atmospheric aerosols (Bhattarai et al., 2019; Simoneit and Elias, 2001; Simoneit et al., 1999).

Lignin is the third most abundant natural polymer after cellulose and hemicelluloses and also the most abundant polymeric aromatic organic substance in the plant world (Lou et al., 2010). It is

composed of collective macromolecules that constitute the major structure of vascular plants, contributing approximately 25%–35% to softwood and 18%–25% to hardwood biomass (Hyder and Jonsson, 2012; Shakya et al., 2011). The three main aromatic alcohols (monolignols); p-coumaryl, coniferyl and sinapyl alcohols, polymerize in a random way to form lignin (Simoneit, 2002; Zakzeski et al., 2010; Zangrando et al., 2013). High temperature burning of lignin releases a variety of methoxyphenol products, such as homovanillyl alcohol, vanillin, vanillic acid, syringaldehyde,

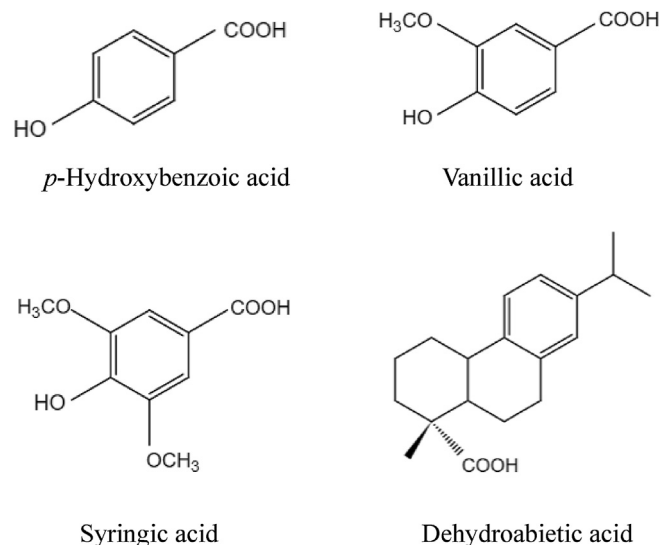


Fig. 2. Chemical structures of aromatic organic acids as BB tracers.

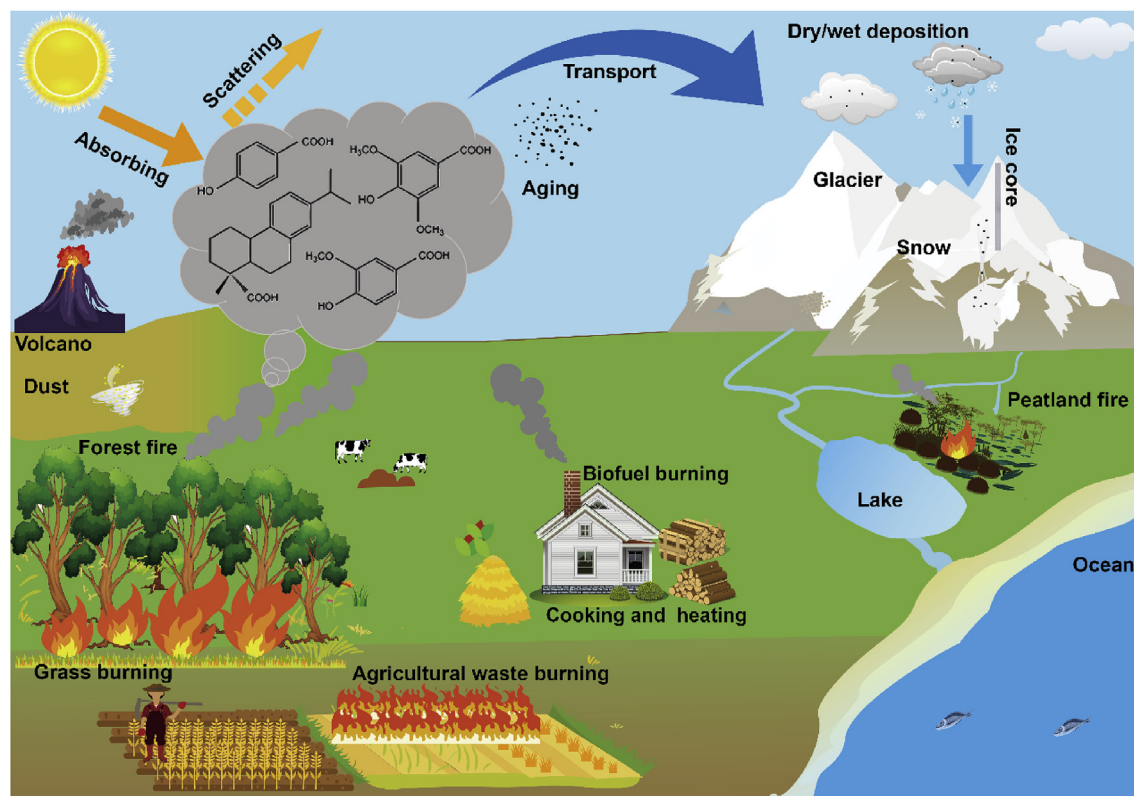


Fig. 1. Schematic overview on the sources, transport, and deposition of biomass burning (BB) emissions.

syringic acid, *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid (Oros and Simoneit, 2001a; Simoneit, 1999). Among them, vanillic, syringic and *p*-hydroxybenzoic acids (Fig. 2) are abundant products of burning and have been most frequently reported in various studies pertaining to BB emissions (Fu et al., 2011; Fu et al., 2008; Fujii et al., 2015; Simoneit, 2002; Wan et al., 2017). In addition, diterpenoid dehydroabiatic acid (Fig. 2), is the major partially altered product from resin acids, which is mainly derived from the combustion of gymnosperm (conifer fuel) (Fu et al., 2009).

Although levoglucosan is produced from the combustion and pyrolysis of cellulose and hemicelluloses and has been widely used as BB tracer, it alone cannot determine the type of vegetation burnt to produce smoke aerosols. Furthermore, recent studies have reported that levoglucosan is chemically reactive in the atmosphere (Favez et al., 2010; Hoffmann et al., 2010) and thus, its applicability as a tracer of BB emissions is questioned recently (Gensch et al., 2018; Zhao et al., 2014). On the other hand, aromatic acids are directly produced from the pyrolysis of lignin and therefore, retain the basic structure of the lignin backbone (Kuo et al., 2008). In addition, the ratio of mass concentration of two aromatic acids, for the same amount of biomass burnt, is characteristic of the biomass and more sensitive than concentration alone for source identification. Therefore, by this perspective, aromatic acids and the ratios among them have a special advantage compared to levoglucosan.

Among several aromatic acids, vanillic, syringic, *p*-hydroxybenzoic and dehydroabiatic acids have been used as tracers of BB emissions. Furthermore, they are important components in smoke from specific biomass (e.g. softwood or hardwood) but have not received much attention. Therefore, emissions and concentrations of aromatic acids in the samples highly depend on the type of biomass burnt, as well as combustion and atmospheric conditions (temperature, humidity and wind). For example, *p*-hydroxybenzoic acid is mainly derived from the burning of herbaceous plants, whereas vanillic acid is derived from both softwood and hardwood combustion. In contrast, syringic acid is more specific to hardwood burning (Simoneit, 2002; Zangrando et al., 2013) while dehydroabiatic acid is the partially altered product from burning of conifers (Fu et al., 2009). The information about pyrolysis products of lignin and resin acid have further advantages in differentiating the contribution from different types of biomass burning toward the atmospheric aerosols. The existence of different aromatic acids and their relative abundances, therefore, can help in distinguishing the type of combusted biomass (hardwood, softwood or herbaceous plants).

In addition, after deposition by dry or wet deposition following its long-distance transport, aromatic acids can be preserved as geochemical indicators in glacier snow and ice layers (Grannas et al., 2004; Grieman et al., 2015; Kawamura et al., 2012). In addition, aromatic acids display almost no apparent degradation in freezing and anaerobic conditions, therefore they are used as good proxies of historical reconstruction of BB in ice cores (Grieman et al., 2017; Kawamura et al., 2012).

In this review paper, we describe different analytical methods for measurement of the typical BB-derived organic acids in atmospheric aerosols and ice cores. We also present and compare their concentrations in various environmental matrices including urban, forest, rural, marine and polar regions. We further discuss the applicability of concentrations of aromatic acids and their ratios for source identification of different types of biomass. The application of aromatic acids in ice cores and snow samples to reconstruct historical records of BB emissions are also presented. Finally, we have summarized the importance of aromatic acids as well as limitations such as oxidation and degradation processes and provide perspectives to promote future research.

2. Determination of aromatic organic acids as BB tracers

Considering the complex matrix of samples, various analytical methods have been developed for the determination of concentrations of aromatic acids as BB tracers. Among them, gas chromatography-mass spectrometry (GC-MS) and liquid chromatography – MS (LC-MS) are the two most commonly used and suitable methods.

2.1. GC-MS

GC-MS is the most widely used method for the analysis of aromatic acids from BB. The analytical procedure involves extraction, pre-concentration, derivatization and detection (Fu et al., 2008; Myers-Pigg et al., 2016; Simoneit et al., 1993; Wang et al., 2009).

In most of the studies, atmospheric aerosols collected on a quartz filter are first extracted with organic solvents using ultrasonic agitation (Fu and Kawamura, 2011; Mikuška et al., 2017; Radzi bin Abas et al., 2004; Visentin and Pietrogrande, 2014) or hollow-fiber liquid phase microextraction (Hyder and Jonsson, 2012). The extracts are filtered to remove potential insoluble particles, and then concentrated using a rotary evaporator in vacuum and dried under an inert atmosphere (i.e. using 100% pure nitrogen gas). The dried samples are further derivatized with a trimethylsilyl reagent, which converts the active functional groups (carboxyl and hydroxyl) to esters and ethers, and finally measured by GC-MS (Rousová et al., 2018; Schummer et al., 2009). Silylation is the most prevalent derivatization method, where commonly used reagents are trimethylsilylimidazole (TMSI), trimethylchlorosilane (TMCS), *N*-methyl-trimethylsilyltrifluoroacetamide (MSTFA), *N,O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) and *N*-(*t*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide (MTBSTFA) (Fu et al., 2012a; Mikuška et al., 2017; Schummer et al., 2009; Simoneit, 2002). However, the use of a mixture of silylation reagents such as BSTFA+1%TMCS and MSTFA+1%TMCS with pyridine as a catalyst, has been recognized to improve the resolution and sensitivity on GC chromatograms as well as reproducibility of the results (Fu et al., 2012a; Simoneit, 2002). The mass spectrometry produces characteristic mass spectrum (m/z) of ions for each aromatic acid. The characteristic m/z ratio, used for the quantification of the four aromatic acids after BSTFA+1%TMCS derivatization, are as follows: m/z 225, 267 and 282 for *p*-hydroxybenzoic acid, m/z 267, 297 and 312 for vanillic acid, m/z 297, 327 and 312 for syringic acid, and m/z 239 for dehydroabiatic acid, respectively (see Fig. 3).

There has been significant advancement in the measurement of aromatic acids which do not need extraction and pre-concentration of the samples, and thus save time as well as reduce measurement cost. For example, Orasche et al. (2011) recently developed an *in-situ* derivatization method, using thermal desorption, followed by gas chromatography and time-of-flight mass spectrometry (IDTD-GC-TOFMS) for the determination of vanillic, syringic and dehydroabiatic acids. The method allows *in-situ* derivatization using MSTFA reagent and thermal desorption of polar organic acids occurring directly from particulate matter on the filters. In addition, the limit of detection (LOD) of vanillic and syringic acids (0.016 ng m^{-3} and 0.008 ng m^{-3} respectively) were much lower than that achieved using a solvent extraction method (0.046 ng m^{-3} and 0.058 ng m^{-3} , respectively) (Table 1) (Orasche et al., 2011; Qadir et al., 2013).

2.2. LC-MS

LC-MS is another powerful instrumental method for the measurement of aromatic acids as BB tracers, which is very effective and has simplified the sample preparation without derivatization.

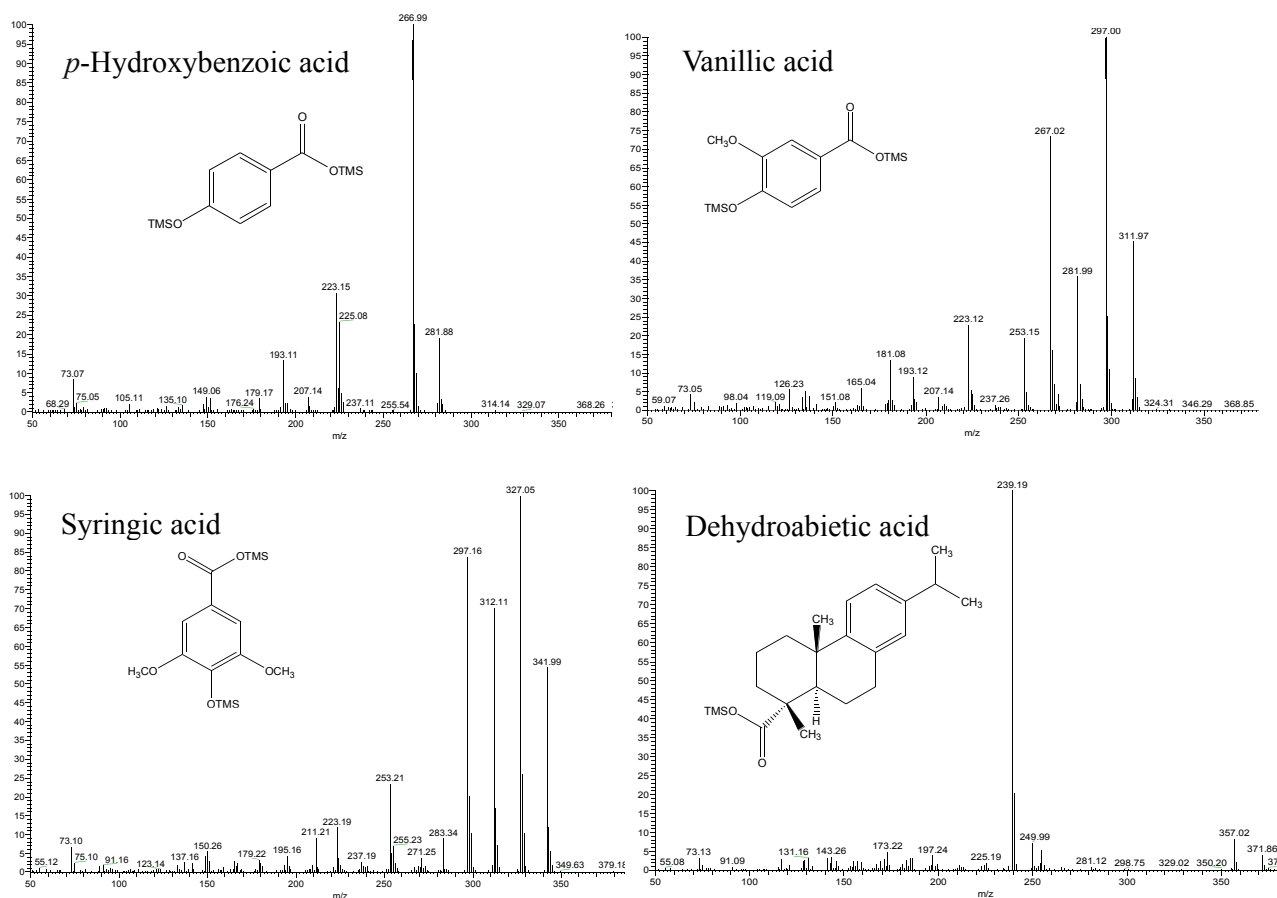


Fig. 3. Mass spectrum of *p*-hydroxybenzoic, vanillic, syringic, and dehydroabiestic acids after BSTFA+1%TMS derivatization (Gao et al., 2015).

Moreover, Hoffmann et al. (2007) developed a high-performance (HP) -LC method coupled with atmospheric pressure chemical ionization (APCI)-MS method for the measurement of aromatic acids as BB tracers. The short analysis time (15 min) with lower LOD (0.47 and 0.21 μM for vanillic and syringic acids, respectively) and high recovery (94% and 92%, respectively) make this method even more suitable for the routine analysis of aromatic acids in atmospheric aerosols or other samples (Table 1). More recently, an HPLC/(-) ESI (electrospray ionization) – MS/MS analytical method was reported for the determination of aromatic acids by Zangrando et al. (2013) and Zangrando et al. (2016). This approach helps to limit the number of validated preanalytical procedures but still detects multiple analytes of the same sample. Moreover, the approach exhibits very low LODs (0.97 fg m^{-3} for vanillic acid and 0.71 fg m^{-3} for syringic acid with assuming an average sampling volume of 11299 m^3) (Zangrando et al., 2013).

Given the simplified pretreatment and low detection limit by HPLC-MS, it has been applied to snow and ice core samples having low concentrations of aromatic acids (Grieman et al., 2015; McConnell et al., 2007; Mueller-Tautges et al., 2016). In previous work, McConnell et al. (2007) reported the direct determination of vanillic acid in polar ice core using continuous-flow ESI with tandem MS (ESI/MS/MS). Although this method provided a high temporal resolution, measured aromatic acids might have been subject to positive interferences from other co-existing organic matters because no chromatographic separation technique was used. In order to overcome this problem, Grieman et al. (2015) developed a method for analyzing aromatic acids in ice core samples by HPLC-ESI/MS/MS, thus, providing an additional selectivity

via chromatography and achieved a lower LOD of approximately 0.077 ppb (Table 1). Mueller-Tautges et al. (2016) used ultra-HPLC coupled with ESI high-resolution MS (UHPLC-ESI-HRMS) to detect *p*-hydroxybenzoic and vanillic acids in a long ice core recovered from the Swiss Alps. The LOD of vanillic acid (0.021 ppb) from this study was further lower than that from HPLC-ESI/MS/MS method (Table 1).

Besides the HPLC-MS methods mentioned above, Grieman et al. (2017) recently used an anion exchange chromatography with ESI/MS/MS detection in negative ion mode (IC-ESI-MS/MS) to carry out the analysis of *p*-hydroxybenzoic, vanillic and syringic acids from a Eurasian Arctic ice core. It has also provided better chromatographic separation and sensitivity with a lower LOD of vanillic acid (0.01 ppb) than HPLC (Table 1).

2.3. Aromatic acids as BB tracers in NIST standard reference material

Certified values for standard reference materials (SRM) of aromatic acids are very important to validate analytical methods. However, there were no such reference materials and thus, certified values for aromatic acids until Gao et al. (2018) recently determined *p*-hydroxybenzoic, vanillic, syringic and dehydroabiestic acids (average values of 26.9, 9.53, 1.13, and 7.60 $\mu\text{g g}^{-1}$, respectively in SRM 1649b using GC-MS techniques. The SRM 1649b is a reference material of atmospheric particulate matter of National Institute of Standards and Technology (NIST) (NIST, 2009) and used extensively for the PAH standards. Therefore, the SRM 1649b standard and reported values may be used for the validation of analytical

Table 1
Performance of analytical methods of aromatic acids as BB tracers in atmospheric aerosols, snow and ice cores.

Method	Vanillic acid		<i>p</i> -Hydroxybenzoic acid		Syringic acid		Dehydroabietic acid	
	LOD	Recovery (%)	LOD	Recovery (%)	LOD	Recovery (%)	LOD	Recovery (%)
Method development*								
HPLC/APCI-MS ^a	0.47 μM	94%			0.21 μM	92%		
CE/ESI-MS ^b	1.0 μM							
Off-line PILS-SPE-HPLC-MS ^c	0.04 ng	~80%						
Atmospheric aerosols								
GC/MS ^d	0.11 ng m ⁻³	79.4 ± 11.5%	0.07 ng m ⁻³	80.8 ± 9.78%			0.11 ng m ⁻³	85.4 ± 13.4%
GC/MS ^e	0.45 ng m ⁻³	80.6 ± 5.8%	0.18 ng m ⁻³	84.6 ± 7.4%				
IDTD-GC-ToF-MS ^f	0.016 ng m ⁻³				0.008 ng m ⁻³		0.010 ng m ⁻³	
SE-GC-ToF-MS ^f	0.046 ng m ⁻³				0.058 ng m ⁻³		0.009 ng m ⁻³	
HPLC/(–) ESI-MS/MS ^g	0.97 fg m ⁻³	70%			0.71 fg m ⁻³	67%		
On-line PILS-SPE-HPLC-MS ^c	0.20 ng	~80%						
Snow and ice cores								
GC/MS ^h	0.007 ppb	78 ± 15%	0.008 ppb	78 ± 18%			0.004 ppb	67 ± 40%
GC/MS ⁱ	1 ppb	87%	2 ppb	96%			4 ppb	70%
HPLC-ESI/MS/MS ^j	0.077 ppb							
UHPLC-ESI-HRMS ^k	0.021 ppb		0.009 ppb					
IC-ESI-MS/MS ^l	0.01 ppb		0.01 ppb		0.09 ppb			

* LOD and recovery are reported using aromatic acid standards only.

^a Hoffmann et al. (2007).

^b Iinuma and Herrmann (2003).

^c Parshintsev et al. (2010).

^d Wan et al. (2017).

^e He et al. (2018).

^f Orasche et al. (2011).

^g Zangrando et al. (2013).

^h Kawamura et al. (2012).

ⁱ Gao et al. (2015).

^j Grieman et al. (2017).

^k Mueller-Tautges et al. (2016).

^l Grieman et al. (2015).

methods for the measurement of aromatic acids.

3. Abundances of the aromatic acids as BB tracers in different environments

As described in the introduction section, different aromatic acids are produced by different types of BB. Therefore, they show diverse abundances with different geographic locations (Fig. 4 & Table 2). In this section, we present geographical variability in the abundance pattern of these acids in different environmental matrices whereas diagnostic ratios and degradation processes are discussed in the later sections.

Urban organic aerosols were once thought to be mainly affected by industrial emissions, traffic exhaust and coal combustion. However, BB is found to be a significant source of organic particles, accounting for up to 20–60% (by mass) of atmospheric aerosols (Streets et al., 2003; Titos et al., 2017; Zhang et al., 2017). Recently, the abundance pattern of aromatic acids and their correlation with BB tracers have clearly shown that wood burning is extensively used for heating and cooking, especially in European cities (Alves et al., 2014; Bari et al., 2010; Dvorská et al., 2011; Kubatova et al., 2002; Mikuška et al., 2017; Pietrogrande and Bacco, 2011). For example, concentrations of dehydroabietic acid in Brno (Czech Republic) were 154 ng m⁻³ in autumn and 119 ng m⁻³ in winter, whereas those of vanillic and syringic acids were 15.2 and 12.6 ng m⁻³, respectively, in autumn and 9.24 and 6.38 ng m⁻³, respectively, in winter (Mikuška et al., 2017) (Table 2). Krupal et al. (2010) and Krupal et al. (2015) also found that softwood was a prevailing type of biofuel for residential heating while hardwood was used only to a lesser extent as wood fuel in this city. Softwood was also predominantly combusted wood from other locations like Belgium (Pashynska et al., 2002; Zdrahal et al., 2002), Austria (Schmidl et al., 2008) and Norway (Yttri et al., 2007). Similarly, in

North American cities (e.g., Libby in Montana, Bakersfield and Fresno in California), concentrations of dehydroabietic acid were higher (Bergauff et al., 2008; Schauer and Cass, 2000) where people mainly make use of softwood for domestic heating, such as Douglas fir and larch. In Fresno, California, softwood burning accounted for 60% of the ambient PM_{2.5} concentration during a heavy pollution episode (December 26–28, 1995) (Schauer and Cass, 2000). Although, there are limited studies available in Asia on the measurement of aromatic acids, they also indicated that BB is an important fuel resource. For example, in Guangzhou and Baoji, China, the reported concentrations of vanillic (20 and 12 ng m⁻³, respectively), syringic (13 and 6.9 ng m⁻³) and dehydroxyboatic acids (162 and 44 ng m⁻³) were also high during winter (Table 2), indicating that biomass was still an important fuel resource (He et al., 2018; Wang et al., 2006a; Wang and Kawamura, 2005; Xie et al., 2010).

Besides the usage of urban household biofuel, aromatic acids have also been used to investigate forest fires as well as agriculture waste burning in rural areas (open BB). Vanillic, syringic and hydroxybenzoic acids were reported with high concentrations (6500 ng m⁻³, 2600 ng m⁻³ and 900 ng m⁻³, respectively) (Table 2) in aerosols collected from the northern forest reserve of Instituto Nacional de Pesquisas da Amazonia (INPA) during forest litter burning (bin Abas et al., 1995). Forest litter is a mixture of large softwood, hardwood, grasses and some leaves and gums. Thus, aerosol samples collected from forest litter burning have high concentrations of aromatic acids compared to those derived from an individual fuel.

The open burning of agricultural waste is very common in South Asia. However, there is hardly any measurement of aromatic acids in the open agricultural waste burning sources. Wan et al. (2017) recently measured aromatic acids in aerosols from a rural site (Lumbini, Nepal) of Indo-Gangetic Plain and found that the site is

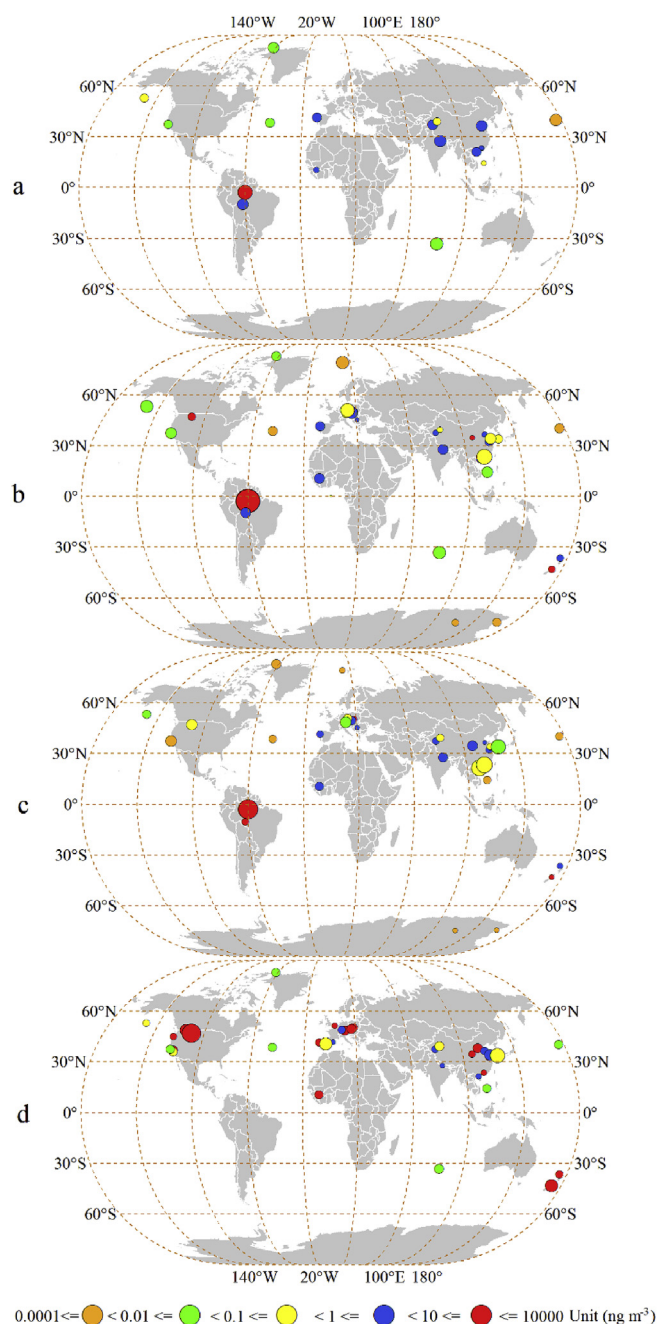


Fig. 4. The global distributions of mass concentrations of aromatic acids as BB tracers in ambient aerosols. a. *p*-hydroxybenzoic acid; b. vanillic acid; c. syringic acid; d. dehydroabietic acid.

greatly influenced by long-range transport of emissions from rice straw burning in eastern Pakistan and northwestern India during the post-monsoon season. The concentrations of *p*-hydroxybenzoic, vanillic, syringic, and dehydroabietic acids were 20.9 ± 13.5 , 17.5 ± 11.4 , 12.1 ± 8.20 , and 3.00 ± 0.71 ng m^{-3} , respectively (Table 2). Similarly, Fu et al. (2008) reported that the total concentrations of *p*-hydroxybenzoic, vanillic, syringic, and dehydroabietic acids were in the range of 1.78–57.5 ng m^{-3} with *p*-hydroxybenzoic acid as the dominant aromatic acid at Mt. Tai, which receives significant aerosols from agricultural field burning (wheat straw) in the North China Plain.

Polar regions are considered to represent pristine environments

as they are devoid of local emission sources. Due to the inherent difficulty in accessing these geographical locations, the observations on aromatic acids are rather sparse and only a few studies are available in the literature (Fu et al., 2009; Zangrando et al., 2013). The aromatic acids in polar regions are reported to have the lowest concentrations in the world. The atmospheric concentrations of *p*-hydroxybenzoic, vanillic, syringic and dehydroabietic acids at Alert in the Canadian Arctic were 0.035 ng m^{-3} , 0.02 ng m^{-3} , 0.002 ng m^{-3} , and 0.012 ng m^{-3} , respectively (Fu et al., 2009) and were mainly derived from long-range transport. Zangrando et al. (2013) documented levels of vanillic and syringic acids in size-segregated aerosols from Ny Alesund (Svalbard). The concentrations of vanillic and syringic acids were 1.77 ± 2.73 pg m^{-3} and 0.25 ± 0.21 pg m^{-3} , respectively in fine particles ($\text{PM}_{0.49}$) whereas 7.55 ± 5.25 pg m^{-3} and 0.20 ± 0.11 pg m^{-3} , respectively in coarse particles ($\text{PM}_{10-0.49}$). These levels were much lower than at Alert (Fu et al., 2009). Although high amounts of vanillic acid indicate softwood burning, however, the contribution of vanillic acid from the degradation of vanillin produced from hardwood combustion cannot be excluded. Therefore, Zangrando et al. (2013) proposed that the high level of vanillic acid in coarse particles may be formed via nucleation/coagulation processes during long-range transport.

In addition, there is a limited study on aromatic acids as BB tracers in marine aerosols. Fu et al. (2011) reported the total concentrations of *p*-hydroxybenzoic, vanillic, syringic, and dehydroabietic acids were in the range of 0.01–0.44 ng m^{-3} in aerosols collected during a round-the-world cruise from low latitudes to midlatitudes in the Northern Hemisphere. However, *p*-hydroxybenzoic acid showed the highest concentration in the western North Pacific with an average of 0.305 ng m^{-3} . Together with the special distribution of levoglucosan, measurement of aromatic acids in aerosol samples indicate that BB is an important source over marine and polar regions via long-range atmospheric transport of continental aerosols (especially from the Asian continent).

4. Historical records in ice cores

Several chemical species in glacial ice cores have been used as proxies to reconstruct the historical variability of the atmospheric composition and climate (Grieman et al., 2017; Kawamura et al., 2012; Legrand et al., 2016; McConnell et al., 2007). However, the use of aromatic acids for the historical reconstruction of fire activities has rarely been investigated. In fact, measurements of aromatic acids in ice cores have very recently been carried out. Some of these studies have detected vanillic, *p*-hydroxybenzoic and dehydroabietic acids in ice cores from Greenland (Grieman et al., 2018b; McConnell et al., 2007), the Eurasian Arctic (Grieman et al., 2017), Switzerland (Mueller-Tautges et al., 2016), Svalbard (Grieman et al., 2018a) and Northeast Asia (Kawamura et al., 2012).

In a shallow west-central Greenland ice core (~200 years), vanillic acid (~ 0.08 ng g^{-1}) was first reported as an indicator of forest fires (McConnell et al., 2007). The variability in the concentration of vanillic acid closely matched with BC before 1850 and conifer burning was attributed as the main source of BC in the ice core. Recently, a similar study was conducted in the Tune ice core from Northeastern Greenland, which is the first continuous record of vanillic acid in ice core on a millennial time-scale over the past 1700 years (268–2013 CE, common era) (Grieman et al., 2018b). The level of vanillic acid (<0.005–0.08 ppb) was higher during warmer climate periods and lower during cooler climate periods, which was also consistent with the centennial-scale variability in boreal forest fires from North America. In addition, variations in the concentration of vanillic and *p*-hydroxybenzoic acids from the Akademii Nauk ice core from the Eurasian Arctic (over the past 2600 years) (Grieman et al., 2017) and Svalbard (over the past 800

Table 2
The concentration comparison of aromatic acids as BB tracers (*p*-hydroxybenzoic, vanillic, syringic and dehydroabiestic acids) in different regions over the world (unit: ng m⁻³).

Location	<i>p</i> -Hydroxybenzoic acid	Vanillic acid	Syringic acid	Dehydroabiestic acid	Period	Type	Reference
Urban							
Libby, USA		68.4	0.5	2336.8	Winter 2008–2009	PM _{2.5}	Ward et al. (2011)
Libby, USA		55.5	1.4	353.2	Winter 2003–2004	PM _{2.5}	
Libby, USA				364	Winter 2004–2005	PM _{2.5}	Bergauff et al. (2008)
Barcelona, Spain				2.05	Summer	PM _{1.0}	van Drooge et al. (2014)
Madrid, Spain				0.65	Summer	PM _{1.0}	
Barcelona, Spain				22.85	Autumn–winter	PM _{1.0}	
Madrid, Spain				15.05	Autumn–winter	PM _{1.0}	
Brno, Czech		10.2	5.21	150	Winter 2010	PM _{2.5}	Mikuška et al. (2017)
Brno, Czech		2.71	n.d.	24.7	Spring 2010	PM _{2.5}	
Brno, Czech		4.35	n.d.	27.7	Summer 2010	PM _{2.5}	
Brno, Czech		15.2	9.24	154	Autumn 2010	PM _{2.5}	
Brno, Czech		12.6	6.38	119	Winter 2011	PM _{2.5}	
Bavaria, Germany		0.18	0.04	146	Oct. 2006 to Feb. 2007	PM _{2.5}	Qadir et al. (2013)
Bavaria, Germany		0.05	0.01	157	Oct. 2009 to Feb. 2010	PM _{2.5}	
Ghent, Belgium				20.2	Winter 1998	PM ₁₀	Kubatova et al. (2002)
Ghent, Belgium				10.3	Summer 1998	PM ₁₀	
Augsburg, Germany				18	Summer 2007	PM _{2.5}	Pietrogrande and Bacco (2011)
Augsburg, Germany				30	Winter 2008	PM _{2.5}	
Fresno, California				98.5	Dec. 26–28, 1995	–	Schauer and Cass (2000)
Fresno, California				17.8	Jan. 4–6, 1996	–	
Bakersfield, California				8.01	Dec. 26–28, 1995	–	
Bakersfield, California				16.1	Jan. 4–6, 1996	–	
Coimbra, Portugal	2.63	6.7	5.1	84	Jan. 27–Feb. 27, 2007	PM _{2.5}	Alves et al. (2014)
Christchurch, New Zealand		46	17	458	Jun. to Jul. 2004, Winter	PM ₁₀	Wang et al. (2006b)
Auckland, New Zealand		2.8	2.1	54	Jun. to Jul. 2004, Winter	PM ₁₀	
Belgrade, Serbia		1.3	1.8		Fall–winter	TSP	Zangrando et al. (2016)
Baoji, China		12	6.9	44	Winter	PM ₁₀	Xie et al. (2010)
Baoji, China		2.3	1.2	28	Spring	PM ₁₀	
Nanjing, China		5.085	3.33	17.1	Winter	PM _{2.5}	Wang and Kawamura (2005)
Nanjing, China		0.855	0.575	7.89	Summer	PM _{2.5}	
Dongguan, China	1.11	0.42	0.38		Whole year, 2012	PM _{2.5}	He et al. (2018)
Guangzhou, China	1.4	0.5	0.43		Whole year, 2012	PM _{2.5}	
Tazhong, China	0.87	0.6	2.1	0.94	Apr. 16–21, 2008	TSP	Fu et al. (2016)
Tazhong, China	0.25	0.15	0.22	0.36	Apr 16–21, 2008	PM _{2.5}	
Hetian, China	7.4	2.6	3.4	3.4	Apr.16–21, 2008	PM _{2.5}	
Nanjing, China		0.36	0.19	2.27	Daytime, Summer 2004	PM _{2.5}	Wang et al. (2006a)
Nanjing, China		1.35	0.96	13.5	Nighttime, Summer 2004	PM _{2.5}	
Nanjing, China		3.98	2.32	9.63	Daytime, Winter 2004	PM _{2.5}	
Nanjing, China		6.19	4.34	24.6	Nighttime, Winter 2004	PM _{2.5}	
Guangzhou, China				30.1	Winter	TSP	Simoneit et al. (2007)
Forest							
Amazonia	900	6500	2600		–	–	bin Abas et al. (1995)
Rondonia, Brazil	8.7	7.4	17.1		September to October 1999		Graham et al. (2002)
Rural							
Lumbini, Nepal	9.36 ± 10.8	7.59 ± 8.87	5.81 ± 6.02	1.75 ± 0.96	Apr. 2013 to Mar. 2014	TSP	Wan et al. (2017)
	16.6 ± 10.5	10.2 ± 6.89	6.81 ± 4.66	2.13 ± 1.00	Pre-monsoon		
	2.05 ± 2.07	2.26 ± 2.06	3.06 ± 3.03	1.17 ± 0.37	Monsoon		
	20.9 ± 13.5	17.5 ± 11.4	12.1 ± 8.20	3.00 ± 0.71	Post-monsoon		
	10.5 ± 9.55	12.0 ± 12.5	7.72 ± 8.72	1.94 ± 1.12	Winter		
Seiffen, Saxony, Germany		0.7	0.3		October 2007 and March 2008	PM ₁₀	Iinuma et al. (2010)
Dettenhausen, Germany				3.83	Fall–winter	PM ₁₀	Bari et al. (2010)
Nansha, Guangzhou, China	1	0.38	0.29		Whole year, 2012	PM _{2.5}	He et al. (2018)
Mountain							
Mt. Tai, China		3.2	1.7	3.4	2–5 June 2006	TSP	Fu et al. (2012b)
Mt. Tai, China		0.22	0.13	0.53	23–25 June 2006	TSP	
Mt. Tai, China	8.91	2.15	1.36	3.88	Daytime, 28 May to 28 June 2006	TSP	Fu et al. (2008)
Mt. Tai, China	8.12	2.91	1.35	1.19	Nighttime, 28 May to 28 June 2006	TSP	
Polar region							
Ny Ålesund, Svalbard, Arctic	0.0075	0.0003		19 April–24 August 2010	PM ₁₀		Zangrando et al. (2013)
Mario Zucchelli Station, Antarctica	0.0019	0.0002		2010–2011	TSP		Zangrando et al. (2016)
Dome C, Antarctica		0.0006	0.0002		2011–2012	TSP	
Dome C, Antarctica		0.0004	0.0002		2012–2013	TSP	
Alert, Canadian High Arctic	0.035	0.02	0.002	0.012	22 February–7 June 1991	TSP	Fu et al. (2009)
Ocean							
East coastal, China		0.5	0.2	8.4	Winter 2002	PM _{2.5}	Wang et al. (2007)

Table 2 (continued)

Location	<i>p</i> -Hydroxybenzoic acid	Vanillic acid	Syringic acid	Dehydroabiestic acid	Period	Type	Reference
North Pacific	0.007	0.0022	0.001	0.012	October 1989–March 1990	TSP	Fu et al. (2011)
California coast	0.012	0.031	0.005	0.014	October 1989–March 1990	TSP	
North Atlantic	0.017	0.002	0.001	0.013	October 1989–March 1990	TSP	
Indian Ocean	0.06	0.06		0.02	October 1989–March 1990	TSP	
South China Sea	0.1	0.03	0.001	0.01	October 1989–March 1990	TSP	
Western North Pacific	0.305	0.065	0.011	0.17	October 1989–March 1990	TSP	
Island							
Gosan site, South Korea		0.27	0.1	0.79	Springtime 2005	TSP	Wang et al. (2009)
Weizhou Island, China	6.07	1.57	0.6	1.28	Daytime, March–April 2015	PM _{2.5}	Zheng et al. (2018)
Weizhou Island, China	6.42	2.25	0.98	2.1	Nighttime, March–April 2015	PM _{2.5}	
Background							
Kern Wildlife, California				0.249	Dec 26–28, 1995		Schauer and Cass (2000)
Kern Wildlife, California				0.268	Jan 4–6, 1996		
Oporto, Portugal	5.65	5.8	3.2	72	January–February 2007	PM _{2.5}	Alves et al. (2014)
Oregon, USA				33.3	Fall	TSP	Simoneit et al. (2007)
Industrial area							
Ostrava-Radvanice		233	186	243	Winter 2012, (26 January- 14 February)	PM _{2.5}	Mikuška et al. (2015)
Ostrava-Radvanice		55.5	39.9	104	Winter 2012 (15 February - 21 February)	PM _{2.5}	
Nanhai, Foshan, China	2	0.96	0.99		Whole year, 2012	PM _{2.5}	He et al. (2018)
Pasture							
Rondônia, Brazil	32	22.1	38.7		1–29 Oct. 1999		Graham et al. (2002)

years) (Grieman et al., 2018a) also revealed a connection between fires and large-scale climate variability over millennial timescales. Together with the air mass back trajectories, it indicated that Europe and Siberia are the principle source regions of wildfire emissions arriving to the Northern Hemisphere (Grieman et al., 2018a).

With regard to ice cores from Switzerland, a 60-year ice core from Grenzglacier in southern Swiss Alps was analyzed (Mueller-Tautges et al., 2016). The levels of *p*-hydroxybenzoic and vanillic acids were within the range of BDL (below detection limit, 0.0087 ng g⁻¹) to 0.151 ng g⁻¹ and BDL (0.021 ng g⁻¹) to 0.36 ng g⁻¹ respectively. The concentrations were elevated during 1950s–1970s and exhibited good correlation with the burned area from fires in southern Switzerland.

Aromatic acids have also been successfully used to reconstruct the historical records of BB and boreal forest fires during a period of 300 years in an ice core taken from Kamchatka Peninsula, North-east Asia (Kawamura et al., 2012). The levels of vanillic acid ranged from BDL to 0.248 ng g⁻¹, *p*-hydroxybenzoic acid from BDL to 0.127 ng g⁻¹ and dehydroabiestic acid from BDL to 1.741 ng g⁻¹. Dehydroabiestic acid showed a gradual increase in concentration during the 1990s with a significant peak in 1970. Similarly, vanillic and *p*-hydroxybenzoic acids showed much higher concentrations during the 1700s and twentieth century when there were sporadic peaks occurring in 1705, 1759 and 1949. These results indicate that boreal fires of confiner forests in the Far East and Siberia broke out more frequently during the last century.

In the Tibetan Plateau, snow pit samples (0–117 cm) were collected from the Zhadang Glacier and were analyzed for *p*-hydroxybenzoic, vanillic, and dehydroabiestic acids (Gao et al., 2015). The concentrations of these acids ranged from 0.033 to 0.568, 0.015–0.361, BDL–0.490 ng mL⁻¹, respectively. These snow-pit samples have high concentrations of BC and water-soluble organic carbon on the glacier surface in the Tibetan Plateau. Together with high concentration of aromatic acids, it clearly revealed that there was a remarkable proportion of carbonaceous materials originating from BB emission (Gao et al., 2015). These findings open a promising window for a rich record of variations in vegetation-burning-derived aerosol signals (i.e. aromatic acids)

that could be preserved in ice cores. Therefore, measurement of aromatic acids in ice cores and snow have the potential to enhance our understanding of BB influences on climate on a regional scale.

5. Diagnostic ratios

The concentrations of an individual aromatic acid in aerosols depend on the amount, burning conditions and type of biomass. For example, low concentrations of syringic acid is resulted probably from the low amount of hardwood combustion emissions while high concentrations of *p*-hydroxybenzoic acid prove the dominant share from the burning of herbaceous plants (Myers-Pigg et al., 2016). Moreover, the ratio of two aromatic acids, for the same amount of biomass burnt, becomes characteristics of the given biomass and is more sensitive than concentration alone. Therefore, mass ratios of different aromatic acids have been suggested as more important indicators to distinguish the vegetation burnt (Myers-Pigg et al., 2016; Simoneit, 1999; Simoneit et al., 1993; Zangrando et al., 2016).

Among them, the concentration ratio of vanillic acid/syringic acid (VA/SyA) have been widely used for identifying the BB source in aerosols (Fine et al., 2002; Fujii et al., 2015; Myers-Pigg et al., 2016; Nolte et al., 2001; Oros et al., 2006; Shakya et al., 2011; Simoneit et al., 1999; Wan et al., 2017). We have summarized the typical ranges of VA/SyA ratios for different potential sources (hardwood, softwood and herbaceous plants or gramineae, and other BB sources) over the world in Fig. 5 and Table S1. The VA/SyA ratios for hardwood ranged from 0.12 to 4.00 and for softwood ranged from 8.57 to 11.9 whereas the ratios for herbaceous plants or gramineae lies in between the two types of the fuels (range: 0.40–5.03, Fig. 5 and Table S1). Therefore, overlapping ratios makes it sometime difficult to apportion the sources, especially there are more than two emission sources. Wan et al. (2017) reported VA/SyA ratios in aerosols from Lumbini, South Asia, ranging from 0.39 to 2.56 with an average of 1.28 ± 0.50, which suggested hardwood and herbaceous plants (crop residue) are likely sources for the BB aerosols. Fujii et al. (2015) reported VA/SyA ratios of 1.70 ± 0.36 in Malaysia during Indonesian peatland fires, which is about three times higher than the ratios (0.59 ± 0.27) of VA/SyA on normal days,

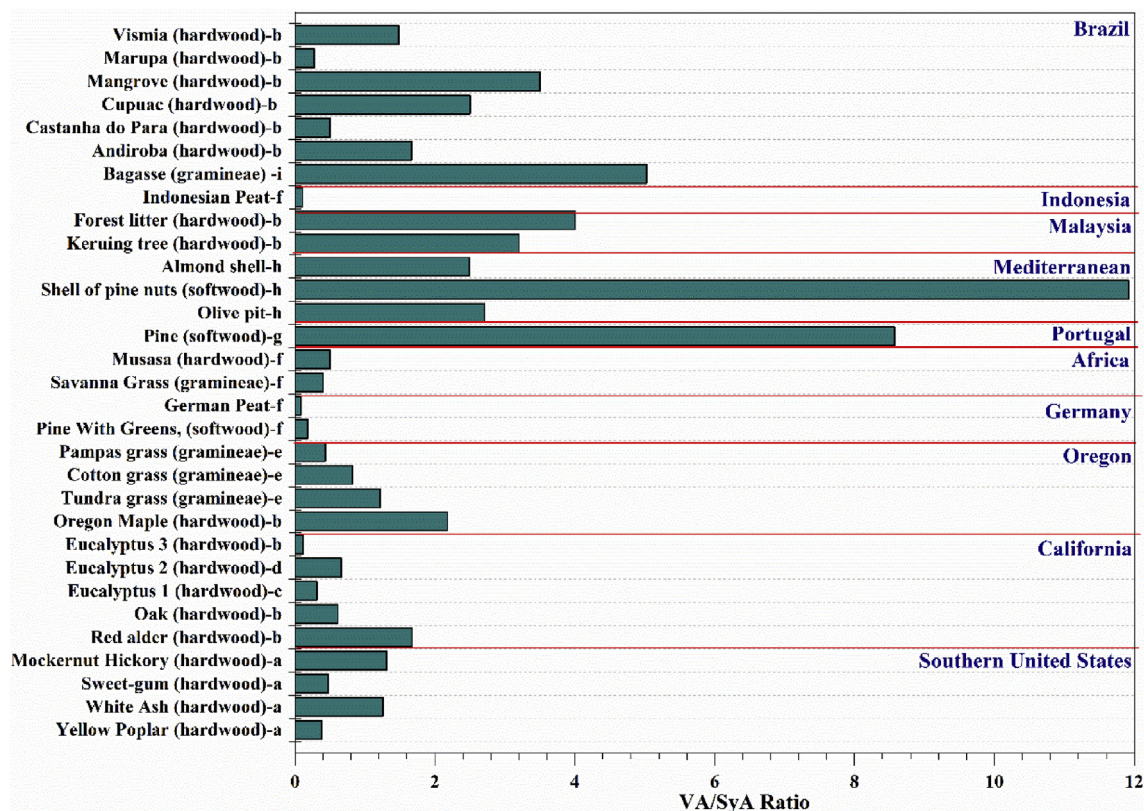


Fig. 5. Comparison of VA/SyA mass ratios obtained from hardwood, softwood, gramineae and other burning sources. Data from a: Fine et al. (2002), b: Simoneit et al. (1999), c: Nolte et al. (2001), d: Oros and Simoneit (2001b), e: Oros et al. (2006), f: Iinuma et al. (2007), g: Goncalves et al. (2010), h: Alves et al. (2017), i: dos Santos et al. (2002).

providing a good indicator of the influence of the Indonesian peatland fires.

Recently, the vanillic/*p*-hydroxybenzoic acid (VA/*p*-HBA) ratio was also used to distinguish BB types (Grieman et al., 2017; Iinuma et al., 2007; Rogge et al., 1998; Simoneit et al., 1999). From the perspective of emission factors, some laboratory investigations of burning different biomass fuels have demonstrated varying emissions of aromatic acids. For example, combustion of conifers resulted in higher VA levels than *p*-HBA and thus, higher VA/*p*-HBA ratios (Iinuma et al., 2007; Nolte et al., 2001; Oros and Simoneit, 2001b; Otto et al., 2006; Rogge et al., 1998). Pine wood burned in Europe yielded a VA/*p*-HBA ratio of 8.75 (Iinuma et al., 2007) whereas the VA/*p*-HBA ratio was 19.75 obtained after burning ponderosa pine (Oros and Simoneit, 2001b). In contrast, burning of herbaceous plants resulted in higher yields of *p*-HBA than VA, e.g., Iinuma et al. (2007) found that German peat fires produced much more *p*-HBA than VA. In addition, North American tundra grass fires released *p*-HBA with hardly no VA (Oros and Simoneit, 2001b; Otto et al., 2006). More recently, VA/*p*-HBA ratio was also determined in an Eurasian Arctic ice core (Grieman et al., 2017) and the VA/*p*-HBA ratios in the ice core correlated with the fires of Siberian forests and tundra lands, particularly the three peaks of major preindustrial burning were perceived very well in the ice core records.

The ratios of aromatic acids to other products (aromatic aldehydes) from pyrolysis of lignin are also useful for oxidation processes and transport to characterize the fate of BB polymers under various environmental conditions. For example, the ratios of vanillic and syringic acids with vanillin (VAN) and syringaldehyde (SyAH) were further used to diagnose the sources of atmospheric aerosols. The VAN and SyAH can be oxidized to VA and SyA with ozone, via the heterogeneous reactions, in the presence or absence

of solar light. However, the ozonolysis produces more VA and SyA in sunlight compared to that under total darkness (Net et al., 2011). Therefore, VA/VAN and SyA/SyAH ratios indicate the degree of oxidation of aromatic aldehydes and their subsequent transformation into aerosols (Net et al., 2011). Zangrando et al. (2016) pointed out the average VA/VAN and SyA/SyAH ratios at a coastal site were prominently much lower than that at the Dome C plateau location, demonstrating the existence of much more oxidized aerosols at Dome C.

6. Degradation and hygroscopic properties

The aromatic organic acids carry the imprints of major plant classes and therefore, relative amounts of various phenolic compounds can be used as tracers for BB types. However, some chemical reactions such as photochemical degradation may take place in the atmosphere depending on temperature, pH, aerosol vapor content and cation concentrations, which would influence the lifetimes and yield intermediates of aromatic organic acids (Grieman et al., 2017; Hays et al., 2002; Schauer et al., 2001). For example, in the tropospheric actinic window, vanillic acid can absorb light and therefore be photochemically active which in turn induces further modifications of the aerosols (Net et al., 2011). However, no reaction products were observed during the ozonolysis of vanillic and syringic acids under experimental conditions (i.e., in total darkness and under illumination with simulated solar light at 297 K) (Net et al., 2011).

Santos and Duarte (2015) and Santos et al. (2016a) investigated the oxidation processes (Fenton-like reaction in aqueous phase and the absence of light) of vanillic, syringic and *p*-hydroxybenzoic acids. The extent of the oxidation of the acids increased with a

decrease of pH from neutral to acidic in atmospheric vapor. However, for vanillic acid, a neutral pH was not able to promote the oxidation. In the absence of light, aromatic acids might have a different behavior depending on reactivity and availability of atmospheric vapor (Santos and Duarte, 2015). In addition, the main intermediate products of oxidation reaction are small aromatic compounds (Santos et al., 2016b). These results suggest that it should be important in the future to assess if the intermediate products of oxidation processes are less or more hazardous than their precursors to foresee consequences for the environment.

Recent studies have pointed out that aerosols with vanillic, syringic and *p*-hydroxybenzoic acids generally do not hygroscopically grow (under relative humidity conditions up to 95%) (Mochida and Kawamura, 2004). However, the reaction of methoxyphenols with triplet excited states of organic compounds ($^3C^*$) and OH radicals form highly oxygenated species (Smith et al., 2014; Yu et al., 2014) with higher hygroscopicity (Li et al., 2014). Liu and Zeng (2018) investigated the heterogeneous kinetics of vanillic acid in OH-initiated reactions at 40% relative humidity and 25 °C temperature, and found that OH radicals are critical in determining the lifetimes of vanillic acid in atmosphere.

There are also some studies on the degradation of resin acids. Corin et al. (2000) proposed that they are resistant to chemical degradation in the atmosphere. However, dehydroabietic acid can be degraded under UV light when dissolved in water, which indicates that it can be affected by relative humidity (Corin et al., 2000; Vicente and Alves, 2018). Thus, ambient observations of dehydroabietic acid should represent the lower limit of impact from softwood combustion. According to Mazzoleni et al. (2007), the moisture content of biofuel might play a remarkable role in the concentration of the resin acids with respect to other carbonaceous compounds. Lai et al. (2015) conducted a laboratory study on the OH-initiated degradation kinetics of dehydroabietic acid and found that the atmospheric lifetime of dehydroabietic acid varied from 2.3 ± 0.2 to 4.4 ± 0.8 days under different environmental conditions (the influence of temperature of 25 °C, relative humidity of 40% and mixing state with $(NH_4)_2SO_4$ and soot).

Since most of the aromatic organic acids showed different degradation mechanisms and hygroscopic properties under different environment conditions, it is necessary to improve the knowledge for more effective means of source apportionment and their uses as BB tracers.

7. Summary and perspectives

Aromatic acids as BB tracer (*p*-hydroxybenzoic, vanillic, syringic and dehydroabietic acids) are ubiquitous in atmospheric aerosols, with concentrations generally decreasing from urban to polar regions. The highest concentration of aromatic acids occurred in aerosols from forest litter burning over Amazonia. Most of the aromatic acids were reported in urban sites, where biomass was used for residential heating and cooking. In remote and polar regions, concentrations of aromatic acids are mostly influenced by long-range atmospheric transport. In snow and ice cores, historical records of *p*-hydroxybenzoic and vanillic acids have revealed the influence of the areas with significant BB and to reconstruct paleo-fire records. In addition, they also helped to improve our understanding of the link between fires and large-scale climate variability. The diagnostic ratios among aromatic acids has been used as good indicators for the amounts and types of biomass (hardwood, softwood and herbaceous plants), as well as photochemical oxidation processes. However, the degradation processes of aromatic acids have not been clearly understood up to now. Further, the possible effects of variable factors such as light, pH and hygroscopicity still need to be investigated in future.

Climatic changes such as more severe and widespread droughts are implicated in global BB (wildfire) variations and are expected to increase BB emissions over the coming decades (Andreae and Merlet, 2001; Flannigan et al., 2013; Jolly et al., 2015). The BB emissions would lead to an increase in GHGs as well as aerosol pollution and deterioration in air quality not limited to only emission source regions but remote areas by long-range transportation. Therefore, the aromatic acids are expected to be more widely used for biomass burning studies in the future. There are additional areas which need to strengthen for the better applicability of aromatic acids. Firstly, the analytical methods need to be improved for simultaneous determination of aromatic acids with high sensitivity and lower detection limits. For ice core analysis, high-resolution methods and reduction of samples need to be considered. Secondly, since there is an overlap in ratio of aromatic acids derived from different BB and the diagnostic ratios among aromatic acids from direct emissions are critical for more effective BB source apportionments, it is necessary to increase the study on the emission characteristics of the aromatic acids in specific biomass categories from different locations, especially in South Asia and Africa. Thirdly, additional aromatic acids and/or other tracers need to be identified to distinguish the type of biomass burnt. These can be used to enable more quantitative interpretation in ice cores for better understanding of the paleo-fire and climate variability.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2019.01.028>.

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