Significant contributions of biomass burning to PM$_{2.5}$-bound aromatic compounds: insights from field observations and quantum chemical calculations
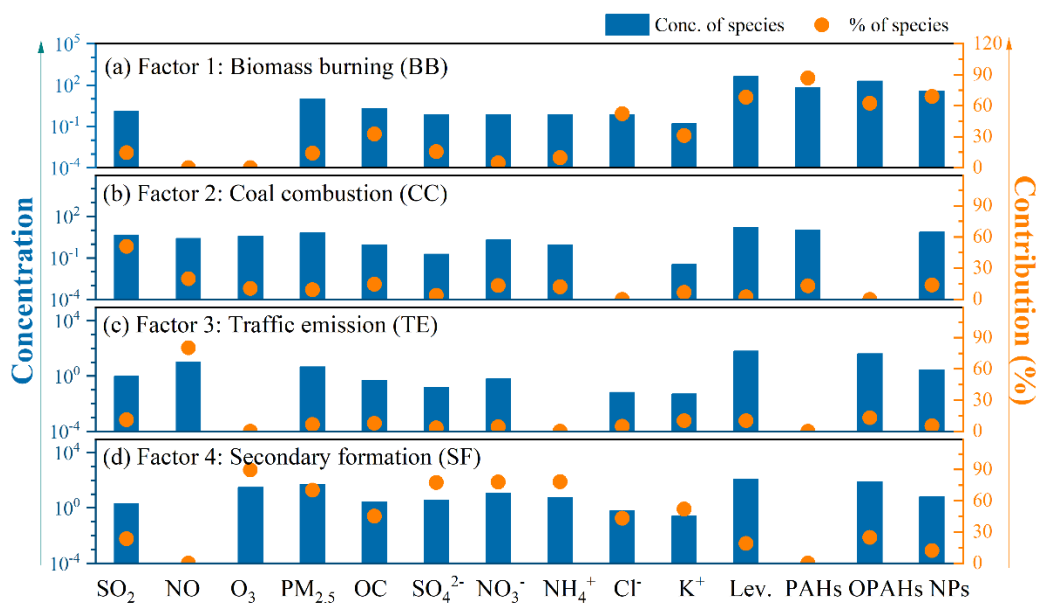
Yanqin Ren[1], Zhenhai Wu[1], Fang Bi[1], Hong Li[1], Haijie Zhang[1*], Junling Li[1], Rui Gao[1], Fangyun Long[1], Zhengyang Liu[1], Yuanyuan Ji[1*], Gehui Wang[2*]

[1] State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China
[2] Key Lab of Geographic Information Science of Ministry of Education of China, School of Geographic Sciences, East China Normal University, Shanghai 200142, China

*Corresponding authors: Dr. Haijie Zhang /Dr. Yuanyuan Ji/ Prof. Gehui Wang
E-mail address: Zhanghaijie@craes.org.cn / ji.yuanyuan@craes.org.cn / ghwang@geo.ecnu.edu.cn

Fig.S1 Source profiles of aromatic compounds obtained from PMF analysis (lev. – levoglucosan, and NPs – nitrated phenols).

Table S1. The electronic energy E_{DFT} and the Gibbs free energy G_{DFT} of reactant monomers at the M062X/6-311++G(3df,3pd) level of theory. All energies are in Hartree and $T = 298$ K.

Phase	Monomers	E_{DFT}	G_{DFT}
gas phase	OH	-75.72917436	-75.737513
	NO$_2$	-205.0652725	-205.079389
	H$_2$O	-76.42489661	-76.42151
	Nitrobenzene	-436.7193104	-436.64666
	Phenol	-307.4438958	-307.367152
	cis-HONO	-205.6987083	-205.701639
	p-Cresol	-346.7471095	-346.645291
	IM1	-306.7561086	-306.693032
	IM2	-436.0322146	-435.973217
	IM3	-346.065347	-345.97788
	IM4	-421.9825728	-421.878094
	IM5	-421.2955673	-421.203709
	4NP	-511.9504536	-511.874497
	4M5NC	-626.485922	-626.380532
liquid phase	NO$_2$	-205.0667262	-205.080949
	Phenol	-307.4507633	-307.374249
	IM1	-306.7629835	-306.700134
	IM4	-421.9910599	-421.88603
	IM5	-421.3038828	-421.212406

Table S2. The electronic energy E_{DFT}, Gibbs free energy G_{DFT} and the imaginary frequency of TS calculated for the formation of 4NP by Phenol at the M06-2X/6-311++G(3df,3pd) level of theory. All energies are in Hartree and $T = 298$ K.

phase	Steps	Molecules	E_{DFT}	G_{DFT}	v_{im} (cm^{-1})
gas phase	H-abstraction by OH	RC$_{ph-OH}$	-383.1814862	-383.099624	
		TS$_{ph-OH}$	-383.1635205	-383.085864	-1237.1969i
		IM1---H$_2$O	-383.1866979	-383.106300	
	H-abstraction by NO$_2$	RC$_{ph-NO2}$	-512.5131701	-512.435702	
		TS$_{ph-NO2}$	-512.4535054	-512.382309	-1585.4851i
		IM1---cis-HONO	-512.4624726	-512.388355	
	NO$_2$ addition	IM1+NO$_2$	-511.8213812	-511.772421	
		4NP	-511.9504536	-511.874497	
liquid phase	H-abstraction by NO$_2$	RC$_{ph-NO2}$	-512.5192961	-512.444301	
		TS$_{ph-NO2}$	-512.4621090	-512.390595	-1628.5336i
		IM1---cis-HONO	-512.4713810	-512.397119	
	NO$_2$ addition	IM1+NO$_2$	-511.8297097	-511.781083	
		4NP	-511.9625041	-511.886975	

Table S3. The electronic energy E_{DFT}, Gibbs free energy G_{DFT} and the imaginary frequency of TS calculated for the formation of 4NP by Nitrobenzene at the M06-2X/6-311++G(3df,3pd) level of theory. All energies are in Hartree and $T = 298$ K.

phase	Steps	Molecules	E_{DFT}	G_{DFT}	v_{im} (cm^{-1})
gas phase	H-abstraction by OH	RC$_{Nb-OH}$	-512.4506363	-512.375738	
		TS$_{Nb-OH}$	-512.4374359	-512.364003	-1412.9321i
		IM2---H$_2$O	-512.4617599	-512.385901	
	OH addition	IM2+OH	-511.7613890	-511.710730	
		4NP	-511.9382659	-511.862064	

Table S4. The electronic energy E_{DFT}, the Gibbs free energy G_{DFT} and the imaginary frequency of TS calculated for the formation of 4M5NC by p-Cresol at the M06-2X/6-311++G(3df,3pd) level of theory. All energies are in Hartree and $T = 298$ K.

Steps	phase	Molecules	E_{DFT}	G_{DFT}	v_{im} (cm^{-1})
Step 1: H-abstraction by OH	gas phase	RC$_{pC-OH}$	-422.4918755	-422.383209	
		TS$_{pC-OH}$	-422.4773183	-422.371344	-1188.6897i
		IM3---H$_2$O	-422.5033608	-422.395347	
Step 2: OH addition	gas phase	IM3+OH	-421.7945214	-421.715393	
		IM4	-421.9825728	-421.878094	
Step 3: H-abstraction by OH	gas phase	IM4---OH	-497.7235822	-497.612110	
		TS$_{OH}$	-497.7035890	-497.596750	-1196.772i
		IM5---H2O	-497.7267084	-497.618336	
Step 3: H-abstraction by NO$_2$	gas phase	IM4---NO$_2$	-627.0553941	-626.950478	
		TS$_{NO2}$	-626.9941024	-626.892971	-1555.5559i
		IM5---HONO	-627.0054168	-626.899673	
Step 3: H-abstraction by NO$_2$	liquid phase	IM4---NO$_2$	-627.0642238	-626.958635	
		TS$_{NO2}$	-627.0043629	-626.903942	-1613.0626i
		IM5---HONO	-627.0130492	-626.908874	
Step 4: NO$_2$ addition	gas phase	IM5+NO$_2$	-626.3608398	-626.283098	
		4M5NC	-626.485922	-626.380532	
Step 4: NO$_2$ addition	liquid phase	IM5+NO$_2$	-626.370609	-626.293355	
		4M5NC	-626.4995951	-626.394496	