

# Non-target screening of organic pollutants and target analysis of halogenated polycyclic aromatic hydrocarbons in the atmosphere around metallurgical plants by high-resolution GC/Q-TOF-MS

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## Research

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## Abstract

**Background** The 16 priority polycyclic aromatic hydrocarbons (PAHs) issued by US Environmental protection agency are a major focus in atmosphere in previous studies. Much more PAH congeners or their substitutes could be produced during combustion or thermal industrial processes and released into the atmosphere. However, a full screening of various organic pollutants in air surrounding important industrial sources have not been conducted. Identifying and characterizing organic pollutants in air is essential to accurate risk assessment. This study conducted non-target screening of organic pollutants and simultaneous target analysis of emerging contaminants including 8 polychlorinated naphthalenes and 30 higher cyclic halogenated PAHs by high-resolution gas chromatography quadrupole time-of-flight mass spectrometry (GC/Q-TOF-MS) and applied to the air samples collected surrounding metallurgical plants. Emerging organic chemicals of high toxicity in air were identified.

**Results** We identified and characterized 187 organic chemicals categorized as PAHs, alkylated polycyclic aromatic compounds (PACs), heterocyclic PACs, and aliphatic hydrocarbons in atmosphere around industrial sources. Some of these identified chemicals, such as phthalic acid esters, dimethylbenz[a]anthracene, and hydroquinone with alkane substituents are of potential high toxicities and have not been the focus of previous studies of airborne contaminants. Moreover, hydroquinone with alkane substituents may be critical intermediates and precursors of an emerging contaminant- environmentally persistent free radicals. Thus, the presences of those identified highly toxic chemicals in the air merits attention. Moreover, 38 chlorinated and brominated PAHs as target compounds were accurately quantitated by using isotopic dilution method by application of GC/Q-TOF-MS, and the findings were similar to those of high-resolution magnetic mass spectrometry.

**Conclusion** In this study, both non-target screening of organic pollutants and target analysis of halogenated PAHs in air were achieved by GC/Q-TOF-MS. The method could be of significance for simultaneous analysis of those trace pollutants containing multiple congeners. Specific pollutants of potential high toxicity in atmosphere around industrial sources were identified. Those knowledge could be helpful for comprehensively recognizing the organic contaminants in air surrounding metallurgical plants and better understanding their potential health risks.

## Background

The 16 priority polycyclic aromatic hydrocarbons (PAHs) issued by US Environmental protection agency (EPA) are a major focus of efforts to assess the risks of pollutants in atmosphere to human health [1]. However, besides the 16 priority PAHs, much more PAH congeners or their substitutes are also produced during combustion or thermal industrial processes and released into the atmosphere [2]. Taken polychlorinated naphthalenes (PCNs) as an example, they can be unintentionally produced and emitted to the air. PCNs are on the list of persistent organic pollutants (POPs) covered under the Stockholm Convention because of their toxicity, persistence, bio-accumulation, and long-range transport in the environment [3, 4]. Halogenated PAHs, which exert similarly toxic effects, can also be formed during activities such as incineration of municipal solid waste and secondary copper smelting [5, 6]. Chlorinated and brominated PAHs (Cl/Br-PAHs) with three to five rings are considered more toxic than their parent chemicals [7-9]. Those less focused PAH congeners or their substitutes might be important pollutants or precursors for highly toxic air contaminants. Therefore, pollutants of high concentrations and toxicities in atmosphere need to be recognized and further intensive studied.

Metallurgical plants have been identified to be important sources of unintentional POPs, and can release trace levels but carcinogenic polychlorinated dibenzo-*p*-dioxins and dibenzofurans, polychlorinated biphenyls, and PAHs [10, 11]. Incomplete combustion of the organic residues, such as cables, paint and heavy oil in the raw materials used for metallurgical plants and the formation during cooling stage of flue gas is the inherent cause for toxic pollutant emissions [12, 13]. Studies characterizing and measuring the levels of these dioxins and dioxin-like compounds of trace levels in the environment surrounding metallurgical plants have been widely conducted by gas chromatography coupled with magnetic sector high-resolution mass spectrometry (GC-HRMS) for the accurate qualification and quantification [14, 15]. GC-HRMS is typically run in selected ion monitoring mode to achieve high sensitivity and selectivity, meeting the analytical requirements of trace levels of specific POPs in air [8, 10, 11, 16]. GC/MS, GC/MS/MS and GC/HRMS have been used for the analysis of halogenated PAHs, among which GC/HRMS in selected ion mode is the most widely applied method currently [14]. GC×GC/TOF-MS or fourier transform ion cyclotron resonance mass spectrometry have been applied for non-target analysis of soil and biota samples, and high levels of several halogenated PAH congeners were detected [14]. Besides the well-known dioxins and PAHs, it is believed that numerous other toxic organic pollutants could simultaneously be formed during the metallurgical processes. However, comprehensive recognition of the pollutant components in environment surrounding the industrial sources were still unknown. Screening of more organic pollutants such as PAH congeners and their substitutes should be conducted for better understanding the potential impact of source emissions on surrounding environment. High-resolution GC quadrupole time-of-flight (GC/Q-TOF-MS) mass spectrometry has great potential for the non-target analysis of GC-amenable compounds. The same full-spectrum accurate mass data enable both quantitation of priority targets and reliable screening of more compounds, especially those present in trace amounts.

In this study, we developed a high-resolution GC/Q-TOF-MS method to comprehensively measure and identify organic pollutants such as PAHs, alkylated polycyclic aromatic compounds (PACs), heterocyclic PACs in air. Novel PACs of high toxicity and concentrations in the air samples will be identified and focused with the aim of obtaining comprehensive overview of various organic chemicals in the air surrounding the metallurgical plants. We also conducted a simultaneous analysis of targeted halogenated PAHs including PCNs regulated by the Stockholm Convention by GC/Q-TOF-MS. The method by application of GC/Q-TOF-MS could be useful for simultaneous analysis of those trace pollutants containing multiple congeners. The knowledge obtained in this study could be helpful for recognizing and characterizing the organic contamination in air and better understanding their potential health risks.

## Methods And Materials

Air samples were collected from an area surrounding metallurgical plants including iron ore sintering plants and steel making plants by high-volume air samplers (Echo Hi-Vol, Tecora, Milan, Italy) at a flow rate of 0.24 m<sup>3</sup> min<sup>-1</sup> for 24 h, according to US EPA method TO-9A. The air volume was approximately

1,000 m<sup>3</sup>. Cleaned quartz fiber filters (102 mm diameter, baked in muffle furnace at 450 °C for 6 h) and polyurethane foam (63 mm diameter, 76 mm length, purified by accelerated solvent extraction with acetone and hexane) were used to gather particle phase and gas phase of the air samples, respectively. The collected air samples were wrapped with aluminum foil and retained in polyethylene valve bags. Prior to extraction, the samples were spiked with labeled standards (2 ng of a mixture of three PAHs, 2 ng of a mixture of six halogenated PAHs and 2 ng of a mixture of six PCNs) for target analysis of halogenated PAHs. The spike of label internal standards into the samples were used for accurate qualification and quantification of target compounds. Moreover, the labelled internal standards could be helpful for preliminarily estimating the relative abundance of non-target compounds by comparing their peak areas with that of labeled internal standards. The signal-to-noise ratio and the recoveries of labelled standards can meet the accurate identification of target compounds and the semi-quantification of non-target chemicals. The samples were extracted by accelerated solvent extraction with dichloromethane and hexane (1:1). The extraction solution was concentrated and then cleaned using an activated silica gel column [14]. The sample solution was then concentrated by rotary evaporator and nitrogen gas and the elution was concentrated to approximately 20 µL. Fly ashes from the metallurgical plants were also collected and analyzed by gas chromatography-Orbitrap mass spectrometry in our previous studies [6]. The non-target screening results were compared between that in air samples and in fly ashes samples to show their different distribution characteristics.

Data were acquired using an Agilent 7890B GC instrument coupled to an Agilent 7250 high resolution Q-TOF-MS platform equipped with a multimode inlet (Agilent Technologies, Santa Clara, CA, USA). The electron ionization full-spectrum mode of the GC/Q-TOF-MS system enabled target and non-target acquisition using the same method. The resolution of the mass analyzer was set at >25,000 (full width at half maximum) at  $m/z$  271.9867. A DB-5ms UI (60 m-0.25 mm-0.25 µm) column was used to separate all targeted and untargeted chemicals. Table S1 lists the detail parameters of analytical settings. The data were acquired and processed using MassHunter Qualitative Analysis (version B.08.00) and Quantitative Analysis (version B.09.00) software (Agilent Technologies). Unknowns Analysis software (version B.09.00) with the SureMass deconvolution algorithm, on the basis of the exact mass number, was used for non-target analysis. Initial compound identification was performed by spectrum comparison with data from the NIST17 EI library. Hexane solution was analyzed by the same methods as a solvent blank to exclude interferences from systematic errors.

Target analysis of the 38 Cl/Br-PAHs, including eight PCNs congeners and 30 Cl/Br-PAHs congeners, were conducted using isotope dilution GC/Q-TOF-MS. The compounds were measured by calibration curves with <sup>13</sup>C-labeled compounds as internal standards (shown in Table 1 and 2). Most calibration concentrations were 5–800 ng/mL. The lowest level of calibration solution (5 ng/mL) was sequentially injected eight times and the RSDs of almost all congeners ranged from 2.0%-14.4%, all below 15% over the range. The signal-to-noise ratios of these congeners at the lowest concentration in the calibration curve were all >10. These calibration curves were used to quantitate the target Cl/Br-PAHs congeners in the air samples. Relative response factors (RRFs) equation were used and measured for accurate quantification of the target congeners on the basis of the Method 1613 developed by the United States Environmental Protection Agency for dioxins: (see Equation 1 in the Supplemental Files)

where A1x and A2x are the peak areas of quantitative and qualitative ion of target congeners, respectively; A11 and A21 are the peak areas of quantitative and qualitative ion of <sup>13</sup>C-labeled internal standard, respectively; Cx and C1 are concentration of target congeners and the corresponding <sup>13</sup>C-labeled internal standard (pg/m<sup>3</sup>). The RRFs ranged from 1.21-1.65, and the variable deviation ranged from 8.3-14.6%.

## Results And Discussion

### General characteristics of organic pollutants in air

Target priority PAHs were quantified using a calibration curve with labeled internal standards. The concentrations of target priority PAHs ranged from 0.12 to 101.2 pg/m<sup>3</sup>. We used SureMass signal processing of GC/Q-TOF-MS data to deconvolute the components and MassHunter Unknowns Analysis software to identify untargeted PAHs to briefly understand the components of pollutants in the air surrounding industries. Compounds were identified and verified via the NIST17 library using the exact mass of the molecular ion or characteristic fragments (mass error <10 ppm) and isotopic distribution as the criteria parameters. Fig. 1. shows an example compound, 9H-Fluorene, 9-methylene-. Altogether, we identified and verified 187 organic chemicals using GC/Q-TOF-MS. Among these organic chemicals, 146 were aromatic hydrocarbons (Table 1) and 41 were aliphatic hydrocarbons (Table S2).

**Table 1.** Aromatic hydrocarbons in air samples screened by gas chromatography quadrupole time-of-flight mass spectrometry.

No.	Retention time	Name	Match Factor	Formula	Area	No.	Retention time	Name	Match Factor
8.565	Naphthalene-D <sub>8</sub> (standard)	91.3	C <sub>10</sub> D <sub>8</sub>	141601	73	36.878	Benzo[b]fluorene	81.8	C <sub>17</sub> H <sub>12</sub>
1	8.611	Naphthalene	96.1	C <sub>10</sub> H <sub>8</sub>	239308	74	36.954	Isopropyl-methylphenanthrene	84.0
2	10.065	Acenaphthylene	73.0	C <sub>12</sub> H <sub>8</sub>	205121	75	37.061	Benzo[b]fluorene	94.0
3	10.156	Naphthalene, methyl-	91.8	C <sub>11</sub> H <sub>10</sub>	154350	76	37.391	Benzo[b]fluorene	75.4
4	10.434	Naphthalene, methyl-	88.7	C <sub>11</sub> H <sub>10</sub>	105858	77	37.635	Ethyl-methylanthracene	72.1
5	11.524	Biphenyl	92.5	C <sub>12</sub> H <sub>10</sub>	126399	78	37.667	Benzo[b]fluorene	95.7
6	11.874	Diphenyl ether	78.2	C <sub>12</sub> H <sub>10</sub> O	54297	79	37.895	Pyrene, methyl-	95.0
7	12.103	Naphthalene, dimethyl-	75.2	C <sub>12</sub> H <sub>12</sub>	122059	80	38.066	Phenanthro[b]pyran	90.0
8	12.499	Naphthalene, dimethyl-	84.8	C <sub>12</sub> H <sub>12</sub>	111953	81	38.133	Butanal, [(tetrahydro-pyran-yl)oxy]-	72.5
9	12.533	Dimethyl phthalate	89.6	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	238035	82	38.248	Benzene, methyl-[(propylphenyl)ethynyl]-	65.7
10	12.642	Naphthalene, ethenyl-	74.5	C <sub>12</sub> H <sub>10</sub>	5510	83	38.685	Pyrene, methyl-	82.4
11	12.853	Naphthalene, dimethyl-	83.5	C <sub>12</sub> H <sub>12</sub>	77767	84	38.961	Pyrene, methyl-	94.2
12	13.215	Acenaphthylene	94.9	C <sub>12</sub> H <sub>8</sub>	364045	85	39.290	Azulene, dimethyl-phenyl-	67.3
13	13.704	Biphenyl, methyl-	86.5	C <sub>13</sub> H <sub>12</sub>	92301	86	39.490	Phenanthro[b]pyran	67.9
13.812	Acenaphthene-D <sub>10</sub> (standard)	91.2	C <sub>12</sub> D <sub>10</sub>	369692	87	40.152	Isopropyl-methylphenanthrene	66.0	C <sub>18</sub> H <sub>18</sub>
14	13.956	Isopropenyl-naphthalene	66.1	C <sub>13</sub> H <sub>12</sub>	116949	88	41.002	Pyrene, dimethyl-	68.4
15	14.750	Dibenzofuran	86.4	C <sub>12</sub> H <sub>8</sub> O	360672	89	41.528	Pyrene, dimethyl-	68.6
16	14.938	Naphthalene, trimethyl-	89.7	C <sub>13</sub> H <sub>14</sub>	85943	90	42.133	Isopropyl-dimethylphenanthrene	75.4
17	15.325	Naphthalene, trimethyl-	78.9	C <sub>13</sub> H <sub>14</sub>	99806	91	42.163	Hexanedioic acid, bis(ethylhexyl) ester	87.5
18	15.463	Naphthalene, trimethyl-	86.3	C <sub>13</sub> H <sub>14</sub>	68935	92	42.227	Pyrene, dimethyl-	74.2
19	15.883	Diethyl Phthalate	89.7	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub>	405710	93	42.903	Cyclopenta(cd)pyrene, dihydro-	81.0
20	16.517	Phenylene	78.4	C <sub>13</sub> H <sub>10</sub>	578874	94	43.149	Cyclopenta[cd]pyrene	81.7
21	16.992	Methanesulfonic acid, tetrahydrocyclohepta[de]naphthalen-8-yl ester	66.5	C <sub>15</sub> H <sub>16</sub> O <sub>3</sub> S	75251	95	43.189	Bicyclohex-en-one, diphenyl-	66.3
22	17.433	Xanthene and isomers	90.9	C <sub>13</sub> H <sub>10</sub> O	180355	96	43.817	Naphthalene, (methylphenylethenyl)-	65.2
23	17.892	Xanthene and isomers	92.3	C <sub>13</sub> H <sub>10</sub> O	253558	97	44.058	Cyclohexane, triphenyl-	83.5
24	18.184	Xanthene and isomers	77.0	C <sub>13</sub> H <sub>10</sub> O	90325	98	44.623	Cyclopenta[cd]pyrene	90.4
25	19.369	Tetramethylnaphthalene	66.8	C <sub>14</sub> H <sub>16</sub>	58051	99	44.800	Triphenylene	94.1
26	19.525	Methyl pentyl phthalate	95.3	C <sub>14</sub> H <sub>18</sub> O <sub>4</sub>	412765	100	44.973	Benzo[c]phenanthrene	87.2
27	19.949	Methanone, (methylphenyl)phenyl-	66.9	C <sub>14</sub> H <sub>12</sub> O	68883	101	45.088	Triphenylene	96.6
28	20.023	Fluorene, methyl-	91.9	C <sub>14</sub> H <sub>12</sub>	159814	102	45.481	Benzo[b: b']bisbenzofuran	84.1
29	20.384	Fluorene, methyl-	80.0	C <sub>14</sub> H <sub>12</sub>	174927	103	46.468	Bis(ethylhexyl) phthalate	72.2
30	20.777	Naphthofuran, dimethyl-	66.4	C <sub>14</sub> H <sub>12</sub> O	163081	104	46.477	Phthalic acid, di(hex-yl) ester	80.2
31	21.520	Phenol, (phenylethenyl)-, (E)-	69.6	C <sub>14</sub> H <sub>12</sub> O	139556	105	46.724	Naphtho[klmn]xanthene	80.0
32	21.722	Dibenzothiophene	68.2	C <sub>12</sub> H <sub>8</sub> S	129680	106	47.679	Tribenzo[a,c,e]cycloheptene	81.0
22.448	Phenanthrene-D <sub>10</sub> (standard)	76.5	C <sub>14</sub> D <sub>10</sub>	247131	107	47.958	Chrysene, methyl-	67.2	C <sub>19</sub> H <sub>14</sub>
33	22.616	Diphenylacetylene	95.3	C <sub>14</sub> H <sub>10</sub>	2571463	108	48.110	Tribenzo[a,c,e]cycloheptene	80.3
34	23.001	Fluorene, methylene-	94.2	C <sub>14</sub> H <sub>10</sub>	354107	109	48.195	Chrysene, methyl-	81.5
35	23.721	Acetyl-trimethylhydroquinone	68.5	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	73506	110	48.431	Tribenzo[a,c,e]cycloheptene	92.0
36	23.793	Acetyl-trimethylhydroquinone	68.1	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	50813	111	48.752	Cyclopenta[a]pyrene	85.4
37	24.255	Carbazole	88.1	C <sub>12</sub> H <sub>9</sub> N	277626	112	48.958	Cyclopenta[a]pyrene	80.9
38	24.355	Benzenedicarboxylic acid, bis(methylpropyl) ester	94.9	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	2801977	113	49.054	Binaphthalene	82.2
39	24.868	Indene, phenylmethylene-	89.8	C <sub>16</sub> H <sub>12</sub>	85131	114	49.097	Benz[a]anthracene, methyl-	73.5
40	25.966	Phthalic acid, butyl isopropyl ester	76.6	C <sub>15</sub> H <sub>20</sub> O <sub>4</sub>	96433	115	49.123	Cyclopenta[a]pyrene	84.3
41	26.331	Indene, phenyl-	92.6	C <sub>15</sub> H <sub>12</sub>	340666	116	49.514	Binaphthalene	83.5
42	26.540	Phenanthrene, methyl-	94.1	C <sub>15</sub> H <sub>12</sub>	506636	117	49.835	Phenanthrene, phenyl-	85.6
43	26.905	Indene, phenyl-	89.7	C <sub>15</sub> H <sub>12</sub>	161893	118	50.664	Benzenoanthracene, dihydro-	73.7
44	27.109	Cyclobuta[jk]phenanthrene	90.5	C <sub>15</sub> H <sub>10</sub>	407602	117	51.042	Benz[a]anthracene, dimethyl-	68.2
45	27.138	Anthracene, methyl-	74.4	C <sub>15</sub> H <sub>12</sub>	18604	120	51.253	Benz[a]anthracene,	78.0

46	27.352	Phenanthrene, methyl-	93.0	C <sub>15</sub> H <sub>12</sub>	357052	121	51.342	dimethyl-Benzenedicarboxylic acid, bis(ethylhexyl) ester	92.0
47	27.624	Dibutyl phthalate	94.7	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	2996424	122	52.368	Benzo[a]pyrene	79.6
48	28.863	Indene, phenylmethylene-	91.2	C <sub>16</sub> H <sub>12</sub>	375666	123	52.528	Benzo[e]pyrene	95.2
49	30.091	Phenanthrene, dimethyl-	82.1	C <sub>16</sub> H <sub>14</sub>	108908	124	52.922	Benzo[e]pyrene	94.2
50	30.311	Phenanthrene, dimethyl-	71.4	C <sub>16</sub> H <sub>14</sub>	128812	125	53.491	Dinaphtho[b: d]furan	77.5
51	31.123	Naphthalene, phenyl-	70.2	C <sub>16</sub> H <sub>12</sub>	263619	126	53.584	Dinaphtho[b: d]furan	88.8
52	31.373	Phenanthrene, ethyl-	75.9	C <sub>16</sub> H <sub>14</sub>	43955	127	53.856	Benzo[e]pyrene	93.8
53	31.618	Pyrene, tetrahydro-	71.0	C <sub>16</sub> H <sub>14</sub>	330800	128	53.906	Dinaphtho[b: d]furan	79.8
54	32.081	Fluoranthene	93.5	C <sub>16</sub> H <sub>10</sub>	2476032	129	54.136	Perylene	93.7
55	32.241	Phenanthrene, dimethyl-	80.8	C <sub>16</sub> H <sub>14</sub>	24320	130	54.499	Dinaphtho[b: d]furan	72.0
56	32.550	Naphthalene, phenylmethyl-	76.8	C <sub>17</sub> H <sub>14</sub>	137771	131	54.605	Benzo[a]pyrene	88.7
57	32.878	Fluoranthene	92.6	C <sub>16</sub> H <sub>10</sub>	566651	132	55.341	Terphenyl, phenyl-	85.0
58	33.140	Naphthalene, phenylmethyl-	79.8	C <sub>17</sub> H <sub>14</sub>	59763	133	55.557	Indeno[b]phenanthrene	74.4
59	33.519	Fluoranthene	73.9	C <sub>16</sub> H <sub>10</sub>	113988	134	56.189	alpha.H-Trisnorhopane	71.8
60	33.947	Fluoranthene	93.4	C <sub>16</sub> H <sub>10</sub>	2015556	135	57.038	Oxo-phenyl-(hydroxyphenyl)-dihydropyrimidine	75.0
61	34.015	Benzo[b]naphtho[d]furan	89.8	C <sub>16</sub> H <sub>10</sub> O	505271	136	57.722	Oxo-phenyl-(hydroxyphenyl)-dihydropyrimidine	70.4
62	34.082	Diacetyldiphenylmethane	68.0	C <sub>17</sub> H <sub>16</sub> O <sub>2</sub>	78418	137	59.799	Benzo[ghi]perylene	65.6
63	34.580	Benzo[kl]xanthene	87.0	C <sub>16</sub> H <sub>10</sub> O	397033	138	60.185	.beta.-iso-Methyl ionone	73.8
64	34.771	Pentadiyn-one, bis(methylphenyl)-	65.6	C <sub>19</sub> H <sub>14</sub> O	207966	139	60.457	Benzo[ghi]perylene	90.3
65	34.902	Ethyl-methylanthracene	76.7	C <sub>17</sub> H <sub>16</sub>	332863	140	61.129	Benzo[ghi]perylene	91.1
66	35.217	Benzo[b]naphtho[d]furan	91.0	C <sub>16</sub> H <sub>10</sub> O	497015	141	61.357	Pentacene	80.0
67	35.406	Ethyl-methylanthracene	77.4	C <sub>17</sub> H <sub>16</sub>	98062	142	62.064	Pentacene	83.1
68	35.902	Benzo[kl]xanthene	86.3	C <sub>16</sub> H <sub>10</sub> O	256306	143	62.314	Dibenz[a,j]anthracene	70.3
69	36.160	Benzanthrene	78.0	C <sub>17</sub> H <sub>12</sub>	308803	144	63.013	Benzo[ghi]perylene	86.5
70	36.224	Propanedioic acid, (dihydro-methyl-phenyl-naphthalenyl)-, dimethyl ester	75.0	C <sub>22</sub> H <sub>22</sub> O <sub>4</sub>	143602	145	64.809	Benzo[ghi]perylene, methyl-	74.8
71	36.436	Phenanthrene, trimethyl-	78.1	C <sub>17</sub> H <sub>16</sub>	131081	146	66.526	Benzo[ghi]perylene, methyl-	84.7
72	36.805	Benzo[b]fluorene	82.6	C <sub>17</sub> H <sub>12</sub>	135890				

Fly ashes are considered to be important matrix for catalyzing the organic pollutant formations during thermochemical processes. General characteristics of organic pollutants in air were summarized and compared to that in fly ashes.<sup>6</sup> As shown in Fig. 2, the compound composition of air and the fly ash were different, and pollutants in air are more diverse than that in fly ash samples. Comparison between the screening results of air samples and fly ash samples from industrial sources showed that aliphatic hydrocarbons are more abundant in air. Few aliphatic hydrocarbons have been reported in fly ash from industrial sources [6]. Halogenated PACs are easily released from industrial activities [6], but PAHs and alkylated or heterocyclic PACs are more common in air samples. Physical properties including subcooled vapor pressure and  $\log k_{oa}$  of the contaminants in air were predicted in this study and compared to the pollutants in the fly ash samples from multiple industries reported in our previous studies [6]. Even though pollutants in air were much more numerous than that in fly ash, the deviation degree of the physical properties were smaller for pollutants in air than that in fly ashes (shown in Fig. 2). The deviation degree of pollutants in fly ashes were greater than that in air, most of which were of higher subcooled vapor pressure and lower  $\log k_{oa}$  than that of pollutants in air. Therefore, some pollutants in fly ashes with higher subcooled vapor pressure and lower  $k_{oa}$  from multiple industries might release into the air. Those pollutants of high subcooled vapor pressure and toxicity should be focused during the disposal of fly ash. Normal distribution test of subcooled vapor pressure of pollutants in air and fly ashes were also conducted (Fig. 2C). Results showed that the subcooled vapor pressure of pollutants in the air fit the lognormal distribution pattern, indicating the multiple influence factors on the pollutants in the air. Pollutants in air originated from numerous sources, but the pollutants in fly ashes were relatively simple due to high-temperature combustion processes. This might contribute to the abnormal distribution of the organic pollutants in fly ashes. It was suggested that the pollutants with relatively higher subcooled vapor pressure and lower  $\log k_{oa}$  in the fly ashes need to be concerned because their potential adverse impacts on the air pollutions.

#### Aromatic hydrocarbons in air by non-target analysis of GC/Q-TOF-MS

Most of the 16 priority PAHs were detected in the air samples surrounding industrial sources. Fluoranthene was a major contributor to the atmospheric PAH burden, and its peak areas accounted for 59% of the total peak areas of the 16 PAHs. A similar finding was also found by the comparison of PAHs in different areas in Indian, and the results showed that fluoranthene in the industrial sites was significantly higher than those in commercial sites [17]. Other studies concluded that atmospheric fluoranthene concentrations may have sources other than motor vehicles [18, 19]. Fluoranthene may therefore be considered an important indicator of industrial emissions. Higher molecular weight parent PAHs such as benzo[ghi]perylene, triphenylene, perylene, and benzo[a]pyrene were also abundant in the samples, and these compounds are typically formed via combustion at elevated temperatures [20]. The results are different from the

PAHs dominance in the air from residential areas [21], indicating the remarkable influence of pyrogenic processes on the surrounding air of thermal industries. Benzo[a]pyrene was reported to be photo-reactive and thus unstable in air. Benzo[a]pyrene cannot undergo long distance migration and is normally in relatively low abundance in air samples [22]. Therefore, detection of Benzo[a]pyrene in air can be used as an indicator of emissions from local sources. Perylene was confirmed to be dominant precursor of PCNs during combustion or other industrial thermal processes [23, 24]. Therefore, these parent PAHs with high levels in air surrounding thermal industries need further attention.

Chemical substitution in PAH molecules can substantially affect their carcinogenic potential [25]. However, PAH derivatives in the environment have been studied less than the 16 priority pollutants. We have detected multiple novel aromatic hydrocarbons and substitutes of the 16 PAHs such as isopropyl-methylphenanthrene, methylphenanthrene, and ethyl-methylanthracene. Some PAH derivatives, including methyl-, dimethyl-, trimethyl-, tetramethyl-, and ethenyl- substitutes, may be more toxic than their parent compounds and contribute a large part of toxicity of the atmospheric pollutants [2]. Toxicities of several novel PAH derivatives were calculated and shown in Table S3. Chemical substitution in PAH molecules such as Fluorene, 9-methylene were of relatively higher toxicities compared to benz[a]pyrene. 7,12-dimethylbenzo[a]anthracene, whose toxic equivalency factor was reported to be 20 times that of its parent and twice that of benzo[a]pyrene [2], but this compound is typically ignored in routine tests of PAHs in air samples. Dimethylbenzo[a]anthracene was screened out in this study, even though the methyl substitution position cannot be elucidated according to the screening result, alkyl derivatives of PAHs such as 7,12-dimethylbenzo[a]anthracene in the air need further attention.

Concentrations of phthalic acid esters such as dibutyl phthalate, dibutyl phthalate, bis(2-methylpropyl) ester-1,2-Benzenedicarboxylic acid, di(hex-3-yl) ester phthalic acid (Table 1) were higher than those of other chemicals, and their peak areas contributed 19% of all 147 chemicals detected. Phthalic acid esters are widely used as plasticizers in various industries and have been detected in water, soil, and air, because they are not chemically bound to polymers and can therefore be easily released into the environment [26]. The oral chronic reference dose of p-phthalic acid was calculated as 1 mg/kg/day, approximately four orders of magnitude higher than that of the widely recognized toxic benzo[a]pyrene ( $3 \times 10^{-4}$  mg/kg/day) [27], and its highest peak areas in the air samples we collected indicated higher inhalation exposure. Six phthalic acid esters have been listed as priority controlled toxic pollutants by the US and European agencies considering the corroborated endocrine disrupting toxicity, and three phthalic acid esters—dimethyl phthalate, diethyl phthalate, and di-n-octylphthalate—are regulated in surface and drinking water in China [28, 29], but phthalic acid esters in the air around industrial plants has not yet become a focus of study. Our findings were in accordance with those of previous studies, which reported higher concentrations at industrial sites than at residential and trafficked areas [30]. Workers and residents in areas contaminated by phthalic acid esters will be exposed to high levels over time [31], so control of phthalic acid esters in industrial areas is essential.

We detected heteroatom-substituted polycyclic aromatic compounds, which are often neglected in studies of environmental pollution even though their toxicity is comparable to that of PAHs [32]. Oxygenated PAHs have one or more carbonyl oxygens in the aromatic ring structure and are more mobile in the environment than PAHs because of their polarity properties, easily moving from air to surface water [32]. Therefore, oxy-PAHs should be taken into consideration when assessing risks of PAHs in the air. Oxygenated PAHs have also been reported in diesel exhaust [33], stack gas from combustion processes [34], and fly ash from various industries [35]. Hydroquinone, a toxic phenolic organic compound, has been found in various industrial effluents [36-38]; In this study, 42 oxy-PAHs including phenols, xanthenes, furans, aldehydes and quinones were detected. The oxy-PAHs are emitted from similar primary sources of PAHs. Both oxy-PAHs and PAHs were products of incomplete combustions. In addition, chemical or photo-oxidation of PAHs can also form oxy-PAHs in the environment [2]. Therefore, oxy-PAHs can widely occur in diesel exhaust, stack gas or fly ash from thermal processes, soils and air [2]. Oxy-PAHs such as hydroquinone with alkane substituents was detected. Apart from the known hematotoxicity and carcinogenicity of hydroquinone [39], it may also be a critical intermediate and precursor of an emerging toxic pollutants in the air—the environmentally persistent free radicals, which has already been found in the atmospheric particles [40-42]. Semiquinone free radicals and cyclopentadiene radicals attached to airborne fine particles were considered as the dominant composition of EPFRs in the air and are believed to persist in the air for a long time [42-47]. Hydroquinone molecules with alkane substituents and phenol substitutes may be precursors or products in the formation or transformation of environmentally persistent free radicals in airborne particles [48], and therefore the levels and characteristics of hydroquinone and environmentally persistent free radicals in the air should be correlated and merits further attention. Oxygenated PAHs such as benzobisbenzofuran and dibenzofuran were also detected, and may subsequently chlorinate to polychlorinated dibenzofurans. We also identified nitro- and sulfurized PAHs such as dibenzothiophene and carbazole, which have acute or long-term hazardous to the aquatic life. Furthermore, they may be further chlorinated to the toxic polychlorinated dibenzofurans, polychlorinated dibenzothiophenes, and polychlorinated carbazoles [49, 50]. This highlights the importance of studying high molecular weight PAHs, alkylated PAHs, and heteroatom-substituted PAHs in the air, beyond the standard focus on the 16 priority pollutants.

#### **Occurrences of chlorinated and brominated PAHs in air by target analysis of GC/Q-TOF-MS**

Cl/Br-PAHs are halogenated derivatives of PAHs, which can be emitted as by-products of thermal industries and formed through photochemical reactions in the air [51]. Because of the large numbers of Cl/Br-PAHs congeners and extremely trace levels in environmental media, it is difficult to accurately quantify and characterize these compounds. In addition, there are no standardized methods for extraction and instrument analysis of Cl/Br-PAHs. Existing accurate analysis for multiple Cl/Br-PAH congeners is mainly conducted by HRMS [52]. We used GC/Q-TOF-MS to analyze 21 chlorinated PAHs (including eight PCNs) and 17 brominated PAHs and quantitated them with 12 labeled internal standards (Fig. 3A). Mass spectrum parameters were shown in Table 2. The calibration curve range was set to 5–500 pg/ $\mu$ L. The lowest calibration solution (5 pg/ $\mu$ L) was sequentially injected eight times to evaluate the stability of the analysis and calculate the instrument limit of quantitation. The relative standard deviations of almost all congeners were lower than 10%. The limit of quantitation was calculated by these standard deviations times 10 and ranged from 1.0-7.2 pg/ $\mu$ L (shown in Table 2). An accurate mass extraction window  $\pm$  15 ppm was used to eliminate the matrix noise. Two labelled compounds were added to the final extract prior to injection to assess the recoveries of 12 internal standards (ISTDs). The recoveries of 6 PCN internal standards (ISTD 1-6 in Table 2) relative to  $^{13}\text{C}$ -labelled 1,2,3,4,5,7-hexachloro-naphthene were calculated to be in the range of 28.9-81.6%. Recoveries of the Cl/Br-PAHs internal standards (ISTD 7-12) relative to  $^{13}\text{C}$ -labelled 7,12-dichlorobenzo[a]anthracene were calculated to be in range of 18.9-80.3%. Fig. 3B shows the extracted ions chromatograms of specific Cl/Br-PAHs in air samples. Fig. 3C shows the

chromatograms of specific PCNs homologs, indicating sufficient resolution and sensitivity of the GC/Q-TOF-MS method for the synchronization analysis of those trace pollutants containing multiple congeners. Further studies can be conducted on the development of simultaneous analysis of the widely concerned persistent organic pollutants of trace levels in the environment.

**Table 2.** Quantitative method performance for chlorinated and brominated polycyclic aromatic hydrocarbons.

Compound Name	Retention time/min	Quantitative Ion	Qualitative Ion	Internal standard (ISTD)	LOQ/ pg uL <sup>-1</sup>	
Chlorinated naphthalene (ap)	2-Cl-Nap	11.66	162.0231	164.0202	ISTD 1	3.0
	1,5-diCl-Nap	15.96	195.9841	197.9812	ISTD 1	3.5
	1,2,3-TriCl-Nap	22.38	229.9451	231.9422	ISTD 1	2.6
	1,2,3,5-TetraCl-Nap	27.81	265.9033	263.9062	ISTD 2	2.1
	1,2,3,5,7-PentaCl-Nap	32.47	299.8643	301.8614	ISTD 3	2.4
	1,2,3,4,6,7-HexaCl-Nap	39.94	333.8253	335.8224	ISTD 4	2.7
	1,2,3,4,5,6,7-HeptaCl-Nap	47.91	367.7863	365.7892	ISTD 5	3.5
	OctaCl-Nap	52.92	403.7444	401.7473	ISTD 6	5.0
	ISTD 1_1,3,5,7-TetraCl-Nap- <sup>13</sup> C	24.92	275.9368	273.9397		
	ISTD 2_1,2,3,4-TetraCl-Nap- <sup>13</sup> C	28.39	275.9368	273.9397		
	ISTD 3_1,2,3,5,7-PentaCl-Nap- <sup>13</sup> C	32.45	309.8978	311.8948		
	ISTD 4_1,2,3,5,6,7-HexaCl-Nap- <sup>13</sup> C	39.98	343.8588	345.8559		
	ISTD 5_1,2,3,4,5,6,7-HeptaCl-Nap- <sup>13</sup> C	47.90	377.8199	379.8169		
ISTD 6_OctaCl-Nap- <sup>13</sup> C	52.92	413.7779	411.7809			
Bromacenaphthene	23.54	231.9882	233.9862	ISTD 7	2.1	
Bromofluorene	26.74	243.9882	245.9862	ISTD 7	2.9	
1-Chlorophenanthrene	29.29	212.0389	214.0358	ISTD 7	1.6	
2-Chlorophenanthrene	29.59	212.0389	214.0358	ISTD 7	1.0	
1-Chloroanthracene	29.59	212.0389	214.0358	ISTD 8	1.5	
2-Chloroanthracene	30.01	212.0389	214.0358	ISTD 8	3.3	
1,2-Dichlorofluorene	30.62	233.9998	235.9968	ISTD 8	2.3	
1,2-Dibromacenaphthylene	30.70	309.8811	307.8831	ISTD 8	4.2	
Bromophenanthrene	33.06	257.9867	255.9883	ISTD 9	2.7	
Bromophenanthrene	33.47	257.9867	255.9883	ISTD 9	3.3	
Bromophenanthrene	33.47	257.9867	255.9883	ISTD 9	4.7	
Bromoanthracene	33.70	257.9867	255.9883	ISTD 9	3.8	
Bromoanthracene	34.02	257.9867	255.9883	ISTD 9	3.9	
1,2-Dichloroanthracene	36.08	245.9998	247.9968	ISTD 9	1.5	
1,9,10-Dichloroanthracene	36.59	245.9998	247.9968	ISTD 9	2.6	
1,10-Dichlorophenanthrene	37.07	245.9998	247.9968	ISTD 9	2.8	
1,2-Dibromofluorene	38.37	323.8967	325.8947	ISTD 9	2.9	
Bromofluoranthene	42.99	279.9883	281.9862	ISTD 10	2.7	
1,1,5-Dibromoanthracene	43.94	335.8967	337.8947	ISTD 10	3.6	
1,10-Dibromoanthracene	44.31	335.8967	337.8947	ISTD 10	3.2	
Bromopyrene	44.80	279.9883	281.9862	ISTD 10	3.9	
1,10-Dibromophenanthrene	44.87	335.8967	337.8947	ISTD 10	2.9	
Bromopyrene	45.02	279.9883	281.9862	ISTD 10	2.3	
1,2-Dichlorofluoranthene	46.03	269.9998	271.9969	ISTD 10	4.5	
1,9,10-tetrachloroanthracene	51.35	315.9189	313.9218	ISTD 11	4.5	
Bromotriphenylene	52.81	306.0039	308.0019	ISTD 12	4.0	
1,2-Dibromopyrene	53.21	359.8967	361.8947	ISTD 12	4.5	
1-Chlorobenzo[a]pyrene	59.39	286.0544	288.0515	ISTD 12	7.2	
ISTD 7_9-chlorophenanthrene- <sup>13</sup> C	29.56	218.0589	220.0559			
ISTD 8_2-chloroanthracene- <sup>13</sup> C	30.01	218.0589	220.0559			
ISTD 9_9-bromophenanthrene-D <sub>9</sub>	33.20	265.0447	267.0427			
ISTD 10_1-chloropyrene- <sup>13</sup> C	41.16	242.0589	244.0559			
ISTD 11_7-chlorobenz[a]anthracene- <sup>13</sup> C	50.63	268.0745	270.0716			
ISTD 12_7-bromobenz[a]anthracene- <sup>13</sup> C	53.23	312.0240	314.0220			

The total concentration of the 13 chlorinated PAHs and 17 brominated PAHs (shown in Table 2) in air samples was 818.9 and 294.9 pg/m<sup>3</sup>, respectively. These levels are similar to those estimated previously in our laboratory by isotope dilution high-resolution gas chromatography and HRMS (987.4 pg/m<sup>3</sup> for 13 chlorinated PAHs and 429.6 pg/m<sup>3</sup> for 17 brominated PAHs) in air [49]. Concentrations of chlorinated PAHs were approximately three times higher than those of brominated PAHs, because chlorine levels are typically higher than bromine levels in the natural environment and in thermal-related activities. Monochlorinated anthracene was the most abundant congener, contributing 20%–50% of the total chlorinated PAHs in the samples, and its fractions were higher than those of dichlorinated or tetrachlorinated anthracene, indicating that chlorination may not be favored during the formation of the chlorinated compound. Less-chlorinated polychlorinated naphthalene congeners were dominant in the gas phase, while more highly chlorinated congeners dominated the particle phase. For example, 70% of 2-chloronaphthalene was in the gas phase. 54% of more highly chlorinated congeners (hexa- to octa-) existed in the particle phase. The phenomenon may be contributed by the physicochemical properties of Cl/Br-PAHs that highly chlorinated congeners with lower vapor pressure tend to be absorbed into the particle phase.

## Conclusions

Non-target screening of organic pollutants and simultaneous target detection of halogenated PAHs by GC/Q-TOF-MS mass spectrometry were achieved by GC/Q-TOF-MS and applied to the air samples collected surrounding metallurgical plants. Emerging pollutants of trace levels in the air including 8 polychlorinated naphthalenes (PCNs) and 30 higher cyclic halogenated PAHs as target compounds were accurately quantitated. In addition, 187 organic chemicals categorized as PAHs, alkylated polycyclic aromatic compounds (PACs), heterocyclic PACs, and aliphatic hydrocarbons in the air samples were identified by non-target screening. Some specific compounds such as phthalic acid esters, dimethylbenz[a]anthracene, which were of high toxicity and concentration, indicated the influence of industrial sources on the surrounding atmosphere. Hydroquinone with alkane substituents in the air were not reported previously, except for the known hematotoxicity and carcinogenicity, they may be critical intermediates and precursors of an emerging toxic pollutants in air-the environmentally persistent free radicals. The toxicological significance of these pollutants is often neglected in studies of airborne contaminants around industries and requires recognition.

## Abbreviations

PAHs: Polycyclic aromatic hydrocarbons;

GC/Q-TOF-MS: High-resolution gas chromatography quadrupole time-of-flight mass spectrometry;

PACs: Polycyclic aromatic compounds;

EPA: Environmental protection agency;

PCNs: Polychlorinated naphthalenes;

POPs: Persistent organic pollutants;

Cl/Br-PAHs: Chlorinated and brominated PAHs;

GC-HRMS: Gas chromatography coupled with magnetic sector high-resolution mass spectrometry;

RRFs: Relative response factors.

## Declarations

### Ethics approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

### Availability of data and material

All data generated or analysed during this study are included in this published article.

### Competing interests

The authors declare that they have no competing interests.

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### Authors' contributions

GL contributed to general planning of the research. LY and GL collected the samples and performed the sample extraction. LY, JW and ZC performed the non-target screening and target analysis by GC/Q-TOF-MS. CL and MS contributed to the deconvolution and identification of chemicals. LY wrote the draft. GL and MZ critically revised the manuscript.

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## Figures

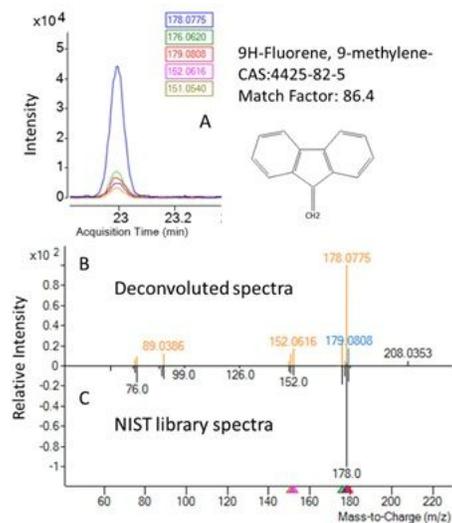


Figure 1

Example of deconvolution function for 9-methylene-9H-fluorene (CAS: 4425-82-5) detected by gas chromatography quadrupole time-of-flight mass spectrometry. (A) Co-elution plot of first five main deconvoluted fragment ions in an air sample. (B) The mass spectra after deconvolution. (C) NIST spectrum for 9-methylene-9H-fluorene. The match factor was calculated by MassHunter Unknown Analysis software (Agilent Technologies).

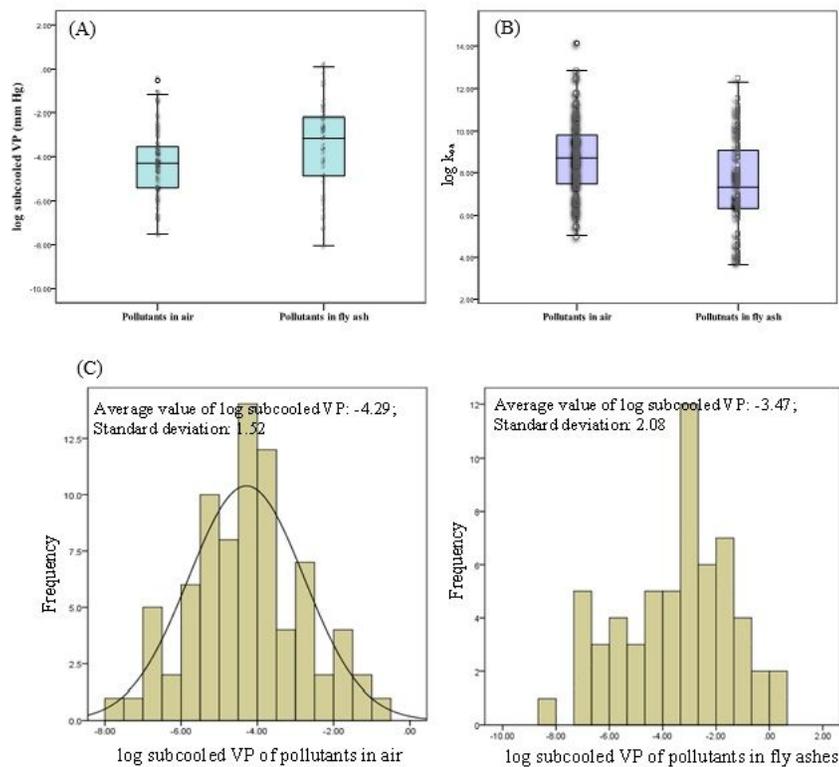
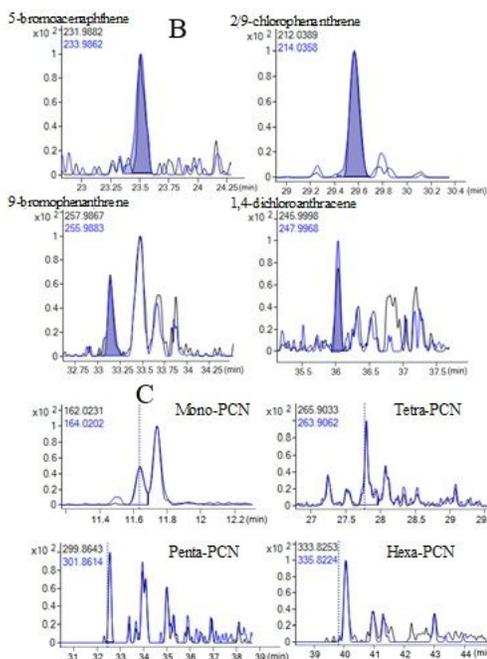
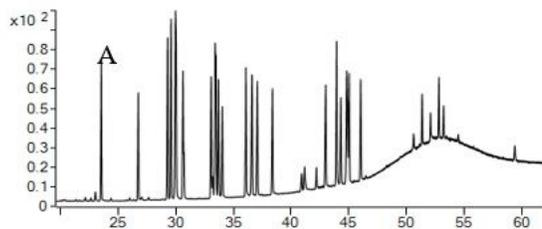


Figure 2

Properties including (A) subcooled vapor pressure (VP), (B) log  $K_{oa}$  of pollutants in air and fly ash samples and the (c) normal distribution test of log subcooled VP.



**Figure 3**

(A) Total ion chromatogram. (B) Extracted ion chromatograms of chlorinated and brominated polycyclic aromatic hydrocarbon standards. (C) Extracted ion chromatograms of specific polychlorinated naphthalene homologs in air samples.

## Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Equation1.pdf](#)
- [AdditionalInformationESEUD2000096.pdf](#)