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

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$^3$ min$^{-1}$ for 24 h, according to US EPA method TO-9A. The air volume was approximately 1,000 m$^3$. 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 13C-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)

$$\text{RRF} = \frac{A_{1x} - A_{11}}{A_{2x} - A_{21}}$$

where $A_{1x}$ and $A_{2x}$ are the peak areas of quantitative and qualitative ion of target congeners, respectively; $A_{11}$ and $A_{21}$ are the peak areas of quantitative and qualitative ion of 13C-labeled internal standard, respectively; $C_x$ and $C_1$ are concentration of target congeners and the corresponding 13C-labeled internal standard (pg/m3). 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/m³. 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 |
|-----|----------------|------|--------------|---------|------|
| 8.565 | Naphthalene-D₉ (standard) | 91.3 | C₁₀D₈ | 141601 | 73 |
| 1 | 8.611 | Naphthalene | 96.1 | C₁₀H₈ | 239308 |
| 2 | 10.065 | Acenaphthylene | 73.0 | C₁₂H₈ | 205121 |
| 3 | 10.156 | Naphthalene, methyl- | 91.8 | C₁₁H₁₀ | 154350 |
| 4 | 10.434 | Naphthalene, methyl- | 88.7 | C₁₁H₁₀ | 105858 |
| 5 | 11.524 | Biphenyl | 92.5 | C₁₂H₁₀ | 126399 |
| 6 | 11.874 | Diphenyl ether | 78.2 | C₁₂H₁₀O | 54297 |
| 7 | 12.103 | Naphthalene, dimethyl- | 75.2 | C₁₂H₁₂ | 122059 |
| 8 | 12.499 | Naphthalene, dimethyl- | 84.8 | C₁₂H₁₂ | 111953 |
| 9 | 12.533 | Dimethyl phthalate | 89.6 | C₁₀H₁₀O₄ | 238035 |
| 10 | 12.642 | Naphthalene, ethenyl- | 74.5 | C₁₂H₁₀ | 5510 |
| 11 | 12.853 | Naphthalene, dimethyl- | 83.5 | C₁₂H₁₂ | 77767 |
| 12 | 13.215 | Acenaphthylene | 94.9 | C₁₂H₈ | 364045 |
| 13 | 13.704 | Biphenyl | 86.5 | C₁₃H₁₂ | 92301 |
| 13.812 | Acenaphthene-D₉/D₁₀ (standard) | 91.2 | C₁₂D₁₀ | 369692 | 87 |
| 14 | 13.956 | Isopropenyl napththalene | 66.1 | C₁₃H₁₂ | 116949 |
| 15 | 14.750 | Dibenzo furan | 86.4 | C₁₂H₁₂O | 360672 |
| 16 | 14.938 | Naphthalene, trimethyl- | 89.7 | C₁₃H₁₄ | 85943 |
| 36.878 | Benzo[b]fluorene | 81.8 | C₁₇H₁₂ | 335917 |
| 74 | 36.954 | Isopropyl-methylphenanthrene | 84.0 | C₁₈H₁₈ | 801787 |
| 75 | 37.061 | Benzo[b]fluorene | 94.0 | C₁₇H₁₂ | 867951 |
| 76 | 37.391 | Benzo[b]fluorene | 75.4 | C₁₇H₁₂ | 4944 |
| 77 | 37.635 | Ethyl-methylanthracene | 72.1 | C₁₇H₁₆ | 142691 |
| 78 | 37.667 | Benzo[b]fluorene | 95.7 | C₁₇H₁₂ | 787979 |
| 79 | 37.895 | Pyrene, methyl- | 95.0 | C₁₇H₁₂ | 373719 |
| 80 | 38.066 | Phenanthro[b]pyran | 90.0 | C₁₇H₁₂O | 509329 |
| 81 | 38.133 | Butanal, [(tetrahydro-pyran-yl)oxy]- | 72.5 | C₉H₁₆O₃ | 10978 |
| 82 | 38.248 | Benzene, methyl-[(propyl phenyl)ethyl]- | 65.7 | C₁₈H₁₈ | 156776 |
| 83 | 38.685 | Pyrene, methyl- | 82.4 | C₁₇H₁₂ | 39736 |
| 84 | 38.961 | Pyrene, methyl- | 94.2 | C₁₇H₁₂ | 455096 |
| 85 | 39.290 | Azulene, dimethyl-phenyl- | 67.3 | C₁₈H₁₆ | 161426 |
| 86 | 39.490 | Phenanthro[b]pyran | 67.9 | C₁₇H₁₂O | 233150 |
| 87 | 40.152 | Isopropyl- | 66.0 | C₁₈H₁₈ | 50960 |
| 88 | 41.002 | Pyrene, dimethyl- | 68.4 | C₁₈H₁₄ | 199615 |
| 89 | 41.528 | Pyrene, dimethyl- | 68.6 | C₁₈H₁₄ | 266527 |
| 90 | 42.133 | Isopropyl-dimethylphenanthrene | 75.4 | C₁₉H₂₀ | 194982 |
| No. | Retention Time | Compound Description | Molecular Formula | Molecular Weight |  
|-----|----------------|----------------------|-------------------|------------------|  
| 17  | 15.325         | Naphthalene, trimethy l- | C_{13}H_{14}       | 180.20           |  
| 18  | 15.463         | Naphthalene, trimethy l- | C_{13}H_{14}       | 180.20           |  
| 19  | 15.883         | Diethyl Phthalate      | C_{12}H_{14}O_{4}  | 205.24           |  
| 20  | 16.517         | Phenanthrene          | C_{13}H_{10}      | 184.20           |  
| 21  | 16.992         | Methanesulfonic acid, tetrahydroyclocloptetadeinaphthalen-8-yl ester | C_{13}H_{16}O_{3} | 255.28           |  
| 22  | 17.433         | Xanthene and isomers  | C_{13}H_{10}O      | 203.20           |  
| 23  | 17.892         | Xanthene and isomers  | C_{13}H_{10}O      | 203.20           |  
| 24  | 18.184         | Xanthene and isomers  | C_{13}H_{10}O      | 203.20           |  
| 25  | 19.369         | Tetramethylthylanthrene | C_{14}H_{16}      | 216.24           |  
| 26  | 19.525         | Methylpentylphthalate  | C_{14}H_{18}O_{4}  | 262.28           |  
| 27  | 19.949         | Methaneone, (methylphenyl)p-phenyl- | C_{14}H_{12}O      | 214.20           |  
| 28  | 20.023         | Fluorene, methyl-     | C_{14}H_{12}       | 202.20           |  
| 29  | 20.348         | Fluorene, methyl-     | C_{14}H_{12}       | 202.20           |  
| 30  | 20.777         | Naphthalene, dimethyl- | C_{14}H_{12}O      | 208.20           |  
| 31  | 21.520         | Phenol, (phenylethenyl)-, (E)- | C_{14}H_{12}O      | 200.20           |  
| 32  | 21.722         | Dibenzothiophen       | C_{12}H_{8}S       | 192.20           |  
| 91  | 42.163         | Hexane dioic acid, bis(ethylhexyl)ester | C_{22}H_{42}O_{4} | 344.32           |  
| 92  | 42.227         | Pyrene, dimethyl-     | C_{18}H_{14}       | 266.20           |  
| 93  | 42.903         | Cyclophenta(cd)p-phenyrene, dihydro- | C_{18}H_{12}       | 246.20           |  
| 94  | 43.149         | Cyclophenta[c]p-phenyrene | C_{18}H_{10}       | 230.20           |  
| 95  | 43.189         | Bicycloex-ene, diphenyl- | C_{18}H_{14}O_{4}  | 324.32           |  
| 96  | 43.817         | Naphthalene, (methylphenylethynyl)- | C_{19}H_{16}       | 266.20           |  
| 97  | 44.058         | Cyclohexane, triphenyl- | C_{24}H_{24}       | 336.32           |  
| 98  | 44.623         | Cyclophenta[c]p-phenyrene | C_{18}H_{10}       | 230.20           |  
| 99  | 44.800         | Triphenylene         | C_{18}H_{12}       | 246.20           |  
| 100 | 44.973         | Benzo[c]phenylene     | C_{18}H_{12}       | 246.20           |  
| 101 | 45.088         | Triphenylene         | C_{18}H_{12}       | 246.20           |  
| 102 | 45.481         | Benzo[b]-b'bisbenzo furan | C_{18}H_{10}O_{2}  | 266.20           |  
| 103 | 46.468         | Bis(ethyhexyl)phthalate | C_{24}H_{38}O_{4}  | 440.40           |  
| 104 | 46.477         | Phthalic acid, di(hexyl)ester | C_{20}H_{30}O_{4}  | 344.32           |  
| 105 | 46.724         | Naphthalene[kl]xa nthene | C_{18}H_{10}O_{2}  | 266.20           |  
| 106 | 47.679         | Tribenzox[a,c,e]c     | C_{19}H_{14}       | 282.28           |
|   | Compound                              | MW (g/mol) | Formula       | CAS Number | T/R  | 50%  | MW (g/mol) | Formula       | CAS Number |
|---|---------------------------------------|------------|---------------|------------|------|------|------------|---------------|------------|
| 22.448 | Phenanthrene-<sub>D<sub>10</sub></sub> (standar d) | 267.41     | C<sub>14</sub>H<sub>10</sub>D<sub>10</sub> | 107 | 108 | 109 | 110 | 111 | 112 | 113 | 114 | 115 | 116 | 117 | 118 | 119 | 120 | 121 | 122 |
| 33 | Diphenyl acetylene                   | 226.22     | C<sub>14</sub>H<sub>10</sub> | 95.3 | 354107 | 80.3 | C<sub>19</sub>H<sub>14</sub> | 171678 |
| 34 | Fluorene, methylene                 | 217.22     | C<sub>14</sub>H<sub>10</sub> | 94.2 | 2571463 | 81.5 | C<sub>19</sub>H<sub>14</sub> | 51069  |
| 35 | Acetyl-trimethy l hydroquinone       | 222.32     | C<sub>11</sub>H<sub>14</sub>O<sub>3</sub> | 68.5 | 735068  | 92.0 | C<sub>19</sub>H<sub>14</sub> | 346092 |
| 36 | Acetyl-trimethy l hydroquinone       | 222.32     | C<sub>11</sub>H<sub>14</sub>O<sub>3</sub> | 68.1 | 508132  | 85.4 | C<sub>19</sub>H<sub>12</sub> | 250792 |
| 37 | Carbazole                            | 168.22     | C<sub>12</sub>H<sub>9</sub>N | 88.1 | 277626  | 80.9 | C<sub>19</sub>H<sub>12</sub> | 232886 |
| 38 | Benzene dicarbox ylic acid, bis(methylpropyl) ester | 293.32     | C<sub>16</sub>H<sub>22</sub>O<sub>4</sub> | 94.9 | 2801977 | 84.3 | C<sub>19</sub>H<sub>12</sub> | 185894 |
| 39 | Indene, phenylm ethylene             | 152.22     | C<sub>16</sub>H<sub>12</sub> | 89.8 | 85131   | 73.5 | C<sub>19</sub>H<sub>14</sub> | 197814 |
| 40 | Phthalic acid, butyl isopropyl ester | 188.32     | C<sub>13</sub>H<sub>20</sub>O<sub>4</sub> | 76.6 | 96433   | 84.3 | C<sub>19</sub>H<sub>12</sub> | 238148 |
| 41 | Indene, phenyl-                      | 152.22     | C<sub>16</sub>H<sub>12</sub> | 92.6 | 340666  | 83.5 | C<sub>20</sub>H<sub>14</sub> | 121290 |
| 42 | Phenanthrene, methyl-               | 168.22     | C<sub>13</sub>H<sub>12</sub> | 94.1 | 506636  | 85.6 | C<sub>20</sub>H<sub>14</sub> | 169928 |
| 43 | Indene, phenyl-                      | 152.22     | C<sub>16</sub>H<sub>12</sub> | 89.7 | 161893  | 73.7 | C<sub>20</sub>H<sub>14</sub> | 15568  |
| 44 | Cyclobuta[jk]prenthrene              | 190.22     | C<sub>15</sub>H<sub>10</sub> | 90.5 | 407602  | 68.2 | C<sub>20</sub>H<sub>16</sub> | 19493  |
| 45 | Anthracene, methyl-                  | 156.22     | C<sub>15</sub>H<sub>12</sub> | 74.4 | 18604   | 78.0 | C<sub>20</sub>H<sub>16</sub> | 178610 |
| 46 | Phenanthrene, methyl-                | 164.22     | C<sub>15</sub>H<sub>12</sub> | 93.0 | 357052  | 92.0 | C<sub>24</sub>H<sub>38</sub>O<sub>4</sub> | 1465392 |
| 47 | Dibutyl phthalate                    | 244.32     | C<sub>16</sub>H<sub>22</sub>O<sub>4</sub> | 94.7 | 2996424 | 79.6 | C<sub>20</sub>H<sub>12</sub> | 97032  |
| 48 | 28.863 | Indene, phenylmethylene | 91.2 | C\textsubscript{16}H\textsubscript{12} | 375666 |
| 49 | 30.091 | Phenanthrene, dimethyl | 82.1 | C\textsubscript{16}H\textsubscript{14} | 108908 |
| 50 | 30.311 | Phenanthrene, dimethyl | 71.4 | C\textsubscript{16}H\textsubscript{14} | 128812 |
| 51 | 31.123 | Naphthalene, phenyl-ethyl | 70.2 | C\textsubscript{16}H\textsubscript{12} | 263619 |
| 52 | 31.373 | Phenanthrene, ethyl | 75.9 | C\textsubscript{16}H\textsubscript{14} | 43955 |
| 53 | 31.618 | Pyrene, tetrahydro-ro- | 71.0 | C\textsubscript{16}H\textsubscript{14} | 330800 |
| 54 | 32.081 | Fluoranthene | 93.5 | C\textsubscript{16}H\textsubscript{10} | 2476032 |
| 55 | 32.241 | Phenanthrene, dimethyl | 80.8 | C\textsubscript{16}H\textsubscript{14} | 24320 |
| 56 | 32.550 | Naphthalene, phenyl-ethyl | 76.8 | C\textsubscript{17}H\textsubscript{14} | 137771 |
| 57 | 32.878 | Fluoranthene | 92.6 | C\textsubscript{16}H\textsubscript{10} | 566651 |
| 58 | 33.140 | Naphthalene, phenyl-ethyl | 79.8 | C\textsubscript{17}H\textsubscript{14} | 59763 |
| 59 | 33.519 | Fluoranthene | 73.9 | C\textsubscript{16}H\textsubscript{10} | 113988 |
| 60 | 33.947 | Fluoranthene | 93.4 | C\textsubscript{16}H\textsubscript{10} | 2015556 |
| 61 | 34.015 | Benzo[b]naptho[d]furan | 89.8 | C\textsubscript{16}H\textsubscript{10}O | 505271 |
| 62 | 34.082 | Diacetyl diphenyl methane | 68.0 | C\textsubscript{17}H\textsubscript{16}O | 78418 |
| 63 | 34.580 | Benzo[k]xanthene | 87.0 | C\textsubscript{16}H\textsubscript{10}O | 397033 |
| 64 | 34.771 | Pentadien-one, bis(methylphenyl)- | 65.6 | C\textsubscript{19}H\textsubscript{14}O | 207966 |
| 65 | 34.902 | Ethylmethyla | 76.7 | C\textsubscript{17}H\textsubscript{16} | 332863 |
| No. | MW  | Compound Name                                      | C  | H  | O   | Experimental value | Predictive value |
|-----|------|----------------------------------------------------|----|----|-----|--------------------|------------------|
| 66  | 35.217 | Benzo[b]naphtho[d]furanethrene                     | C_{16}H_{10}O | 91.0 | 497015 |
| 67  | 35.406 | Ethylmethylanthracene                               | C_{17}H_{16} | 77.4 | 98062  |
| 68  | 35.902 | Benzo[k]xanthrene                                   | C_{16}H_{10}O | 86.3 | 256306 |
| 69  | 36.160 | Benzanthrene                                        | C_{17}H_{12} | 78.0 | 308803 |
| 70  | 36.224 | Propane dioic acid, (dihydro-methyl-phenyl-naphthalenyli), dimethyl ester | C_{22}H_{22}O_4 | 75.0 | 143602 |
| 71  | 36.436 | Phenanthrene, trimethyl-                             | C_{17}H_{16} | 78.1 | 131081 |
| 72  | 36.805 | Benzo[b]fluorenene                                  | C_{17}H_{12} | 82.6 | 135890 |
| 141 | 61.357 | Pentacene                                           | C_{22}H_{14} | 80.0 | 277114 |
| 142 | 62.064 | Pentacene                                           | C_{22}H_{14} | 83.1 | 155782 |
| 143 | 62.314 | Dibenz[a,j]anthracene                               | C_{22}H_{14} | 70.3 | 13213 |
| 144 | 63.013 | Benzo[g,h]perylene                                  | C_{22}H_{14} | 86.5 | 982552 |
| 145 | 64.809 | Benzo[g,h]perylene, methyl-                         | C_{23}H_{14} | 74.8 | 80372  |
| 146 | 66.526 | Benzo[g,h]perylene, methyl-                         | C_{23}H_{14} | 84.7 | 134744 |

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. 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 was 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-methylantracene. 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-dimethylbenz[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-dimethylbenz[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 (3×10^-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.

**Occurences 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/µL. The lowest calibration solution (5 pg/µL) 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/µL (shown in Table 2). An accurate mass extraction window ± 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 $^{13}$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 $^{13}$C-labelled 7,12-dichlorobenz[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 µL⁻¹ |
|---------------|--------------------|------------------|----------------|--------------------------|-------------|
| 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         |
| 1,2,3,4,5,6-TetraCl-Nap | 22.38 | 229.9451         | 231.9422       | ISTD 1                   | 2.6         |
| 1,2,3,5,6-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         |
| 1,2,3,4,5,6,7-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         |
| Nap-OctaCl-Nap | 52.92              | 403.7444         | 401.7473       | ISTD 6                   | 5.0         |
| ISTD 1,3,5,7-TetraCl-Nap-¹³C | 24.92 | 275.9368         | 273.9397       | ISTD 2                   | 2.3         |
| ISTD 2,1,2,3,4-TetraCl-Nap-¹³C | 28.39 | 275.9368         | 273.9397       | ISTD 2                   | 2.3         |
| ISTD 3,1,2,3,5,7-PentaCl-Nap-¹³C | 32.45 | 309.8978         | 311.8948       | ISTD 3                   | 3.3         |
| ISTD 4,1,2,3,5,6,7-HexaCl-Nap-¹³C | 39.98 | 343.8588         | 345.8559       | ISTD 4                   | 3.3         |
| ISTD 5,1,2,3,4,5,6,7-HeptaCl-Nap-¹³C | 47.90 | 377.8199         | 379.8169       | ISTD 5                   | 3.3         |
| Nap-OctaCl-Nap-¹³C | 52.92              | 413.7779         | 411.7809       | ISTD 6                   | 3.3         |
| napthaene     | 23.54              | 231.9882         | 233.9862       | ISTD 7                   | 2.1         |
| napthene      | 26.74              | 243.9882         | 245.9862       | ISTD 7                   | 2.9         |
| chloroanthrene| 29.29              | 212.0389         | 214.0358       | ISTD 7                   | 1.6         |
| 1-chloroanthrene | 29.59        | 212.0389         | 214.0358       | ISTD 7                   | 1.0         |
| chloroanthracene | 29.59            | 212.0389         | 214.0358       | ISTD 8                   | 1.5         |
| chloroanthracene | 30.01            | 212.0389         | 214.0358       | ISTD 8                   | 1.5         |
| 1,2-chlorofluorene | 30.62            | 233.9998         | 235.9968       | ISTD 8                   | 2.3         |
| 1,2-dibromoacenaphthylene | 30.70    | 309.8811         | 307.8831       | ISTD 8                   | 4.2         |
| naphthalene   | 33.06              | 257.9867         | 255.9883       | ISTD 9                   | 2.7         |
| naphthalene   | 33.47              | 257.9867         | 255.9883       | ISTD 9                   | 3.3         |
| naphthalene   | 33.47              | 257.9867         | 255.9883       | ISTD 9                   | 4.7         |
| naphthalene   | 33.70              | 257.9867         | 255.9883       | ISTD 9                   | 3.8         |
| naphthalene   | 34.02              | 257.9867         | 255.9883       | ISTD 9                   | 3.9         |
| 1,2-dichloroanthracene | 36.08          | 245.9998         | 247.9968       | ISTD 9                   | 1.5         |
| i,9,10-dichloroanthracene | 36.59       | 245.9998         | 247.9968       | ISTD 9                   | 2.6         |
| 0-dichloroanthracene | 37.07            | 245.9998         | 247.9968       | ISTD 9                   | 2.8         |
| 1,2-dibromofluorene | 38.37          | 323.8967         | 325.8947       | ISTD 9                   | 2.9         |
| naphthene     | 42.99              | 279.9883         | 281.9862       | ISTD 10                  | 2.7         |
| i,1,5-dibromoantrachene | 43.94        | 335.8967         | 337.8947       | ISTD 10                  | 3.6         |
| 0-dibromoantrachene | 44.31            | 335.8967         | 337.8947       | ISTD 10                  | 3.2         |
| naphthene     | 44.80              | 279.9883         | 281.9862       | ISTD 10                  | 3.9         |
| 0-dibromoantrachene | 44.87            | 335.8967         | 337.8947       | ISTD 10                  | 2.9         |
| naphthene     | 45.02              | 279.9883         | 281.9862       | ISTD 10                  | 2.3         |
| i-dichloroantrachene | 46.03          | 269.9998         | 271.9969       | ISTD 10                  | 4.5         |
| i,9,10-tetrachloroantrachene | 51.35        | 315.9189         | 313.9218       | ISTD 11                  | 4.5         |
| naphthylenene | 52.81              | 306.0039         | 308.0019       | ISTD 12                  | 4.0         |
| i-dibromopyrene | 53.21            | 359.8967         | 361.8947       | ISTD 12                  | 4.5         |
| chlorozen[a]pyrene | 59.39            | 286.0544         | 288.0515       | ISTD 12                  | 7.2         |
| D 7-9-chloroantrachene-¹³C | 29.56          | 218.0589         | 220.0559       | ISTD 1                   | 4.5         |
| D 8-2-chloroantrachene-¹³C | 30.01          | 218.0589         | 220.0559       | ISTD 1                   | 4.5         |
| D 9-9-bromophenanthrene-D₉ | 33.20       | 265.0447         | 267.0427       | ISTD 1                   | 4.5         |
| D 10-1-chloroantrachene-¹³C | 41.16          | 242.0589         | 244.0559       | ISTD 1                   | 4.5         |
| D 11-7- | 50.63              | 268.0745         | 270.0716       | ISTD 1                   | 4.5         |
| D 12-7-53.23 | 312.0240         | 314.0220         | 314.0220       | ISTD 1                   | 4.5         |
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$^3$, 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$^3$ for 13 chlorinated PAHs and 429.6 pg/m$^3$ 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 physiochemical 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 koa 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.

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