Dangerous organic chemicals identified in inhalable particulate matter air pollution

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Abstract. Inhalable particulate matter (PM₁₀), comprising fine and thoracic coarse particulate matter (PM₂.5 and PM₁₀₂.5, respectively), is emitted from several sources. The sources include construction and agricultural activities, transportation, industrial processes, power plants, wildfires, household solid cookfuels and suspensions or re-suspensions from unpaved roads, mining and natural sources. Previous studies, specifically from developed countries and China have shown that PM₁₀ may contain several dangerous organic chemicals (DOCCs). However, very little is known about PM₁₀ in developing countries. Therefore this study seeks to identify the DOCCs in airborne PM₁₀ in Nagpur district, India. We collected 24-hr ambient PM₁₀ samples from urban, peri-urban and rural areas of the district during wintertime (January, 2013). The DOCCs in the PM₁₀ were identified by gas chromatography-mass spectrometry. The results revealed that polycyclic aromatic hydrocarbons (PAHs), chlorinated hydrocarbons, dioxins, furans, phthalate esters, aldehydes, ketones, phenols and organic acids are major DOCCs in the PM₁₀. Quantitative analysis of thirteen individual PAHs in the PM₁₀ revealed concentrations that greatly exceeded health-based guideline. This suggests that prolong inhalation of such PM₁₀ may pose adverse risk to the health of the population.

Keywords: polycyclic aromatic hydrocarbons (PAHs), dioxins, furans, phthalate esters, PM₁₀

1. Introduction
Inhalable particulate matter (PM₁₀), comprising fine and thoracic coarse particulate matter (PM₂.5 and PM₁₀₂.5, respectively), is emitted from several sources. The sources include construction activities, transportation, industrial processes, power plants, wildfires and household solid cookfuels [1,2]. PM₁₀ can also be suspended or re-suspended from unpaved roads, farming, mining and natural sources [3]. Atmospheric PM₁₀ may contain many chemical constituents depending on the emission source [4]. Studies have detected specific group of hazardous chemicals attached to PM₁₀ such as PAHs [5-7], nitro-PAHs [8] or chloro-PAHs [9] using either gas chromatography-mass spectrometry (GC-MS) or high performance liquid chromatography (HPLC) with fluorescence or ultraviolet visible detector. Also, using GC-MS, Bi et al. [10] identified n-alkanes and PAHs in different sub-fractions of PM₁₀ collected from urban and rural areas of Guangzhou, China. A research group in South Africa used laser induced fluorescence (LIF) and thermal desorption-gas chromatography-mass spectrometry to determine concentrations of PAHs bound to airborne particles [11,12]. Polychlorinated biphenyls...
(PCB) congeners were identified in atmospheric particles in South Korea using GC-MS [13]. GC-MS technique has also been used to identify polybrominated diphenyl ethers (PBDEs) in airborne particles from automotive shredding and metal recycling facility in Brisbane, Australia [14]. Furthermore, using high resolution GC-high resolution MS (HRGC-HRMS), some studies have detected more dangerous chemicals such as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in PM$_{10}$ in South Korea [15], Taiwan [16,17], USA [18] and Australia [19].

The aforementioned studies have provided evidence that airborne PM$_{10}$ can contain hazardous chemical constituents. The critical question however is, could all of these chemical groups (PAHs, PCBs, alkanes, PBDEs, PCDDs and PCDFs) be contained in the same PM$_{10}$? Other studies have attempted to answer this question. For instance, Ishaq et al. [9] detected PCBs, PAHs, chlorinated PAHs, polychlorinated naphthalenes (PCNs), PCDDs and PCDFs in ambient PM$_{10}$ in Stockholm, Sweden, using GC-MS and HRGC-HRMS. Mandalakis et al. [20] found aliphatic hydrocarbons, hopanes, PAHs, PCBs, PCDDs and PCDFs in ambient PM$_{10}$ in Athens, Greece, using GC-MS and GC-MS-MS techniques. Similarly, Menichini et al. [21] detected PAHs, PCBs, PCDDs and PCDFs in atmospheric particles in Rome, and in a background location in central Italy, using GC-MS and low resolution GC-high resolution MS (LRGC-HRMS). Alves et al. [22] and Pio et al. [23] found about 1050 individual organic compounds in ambient PM$_{10}$ in South European localities, including vegetation-derived alcohols and phenolic compounds, organic acids, phytosterols, and long chain alkanes and alkanones.

Using the GC-electron capture detector (GC-ECD), researchers detected several organochlorine pesticides such as dichlorodiphenyldichloro-ethylene, chlorodane, hexachloro-cyclohexane, dichlorodiphenyltrichloroethane and endosulfan in ambient particles in Turkey [24] and China [25]. The GC-ECD and GC-MS techniques were also used to determine concentrations of organohalogenated pesticides and PCBs in airborne PM in a Chinese city [26]. Qadir et al. [27] characterised the organic constituents in PM$_{10}$ in Munich, Germany by in-situ derivatization (using N-methyl-N-trimethylsilyl-trifluoroacetamide reagent) thermal desorption-GC-time of flight-MS (IDTD-GC-ToF-MS). A total of 78 organic constituent groups were identified including PAH, oxidized PAH, n-alkanes, iso and anteiso-alkanes, hopanes, cholesterol, fatty acids, resin acids, anhydrous sugars and phenolic compounds.

The aforementioned studies have shown that airborne PM$_{10}$ in developed countries and China can contain mixtures of hazardous chemical constituents. However, no information of this kind was obtainable from developing countries, including India, from the over 1400 scientific articles that were downloaded from the literature and reviewed. This indicates that there is a dearth of this information for developing countries. Therefore, in this study we seek to identify the dangerous organic chemical groups in ambient PM$_{10}$ in Nagpur – a developing district in India.

2. Methodology

2.1. Site description

Nagpur district has been extensively described previously [1,7]. In brief, the district is at the exact center of India – Latitude 21º03’N to 21º21’N and Longitude 78º57’E to 79º16’E (Figure 1). The

Figure 1: Map of India showing Nagpur district
district is the third most populous locality in the State of Maharashtra after Mumbai and Pune. Its population is about 4.7 million, with a population density of 470 persons/km². It is a developing locality with rapid urbanization and industrialization. It is also a coal mining locality that relies on coal-fired thermal power plants for power generation. It has a large vehicular fleet dependent on gasoline and diesel engines. Although, about 68% of the inhabitants live in the urban areas, there is however more villages (1859) than towns (41) in the district. Most people in the villages use unclean sources of fuel such as crop residues, animal dung, wood and coal for cooking and space heating. Nagpur district has four seasons namely: summer (April to June); monsoon (July to September), post-monsoon (October to November) and winter (December to March).

2.2. Sampling method
We sampled three locations, comprising urban (Mankapur), peri-urban (Koradi) and rural (Satak) areas in Nagpur district during the wintertime (January 2013). We collected continuous 24 hr ambient PM₁₀ samples on preheated (400°C for 5 hours) glass microfiber filters (203×254 mm diameter) using high volume air samplers (HVSs) with an average flow rate of 1000 L/min (Dutt Respirable Dust Sampler, Model: RDS-002). The HVSs were placed on unobstructed roof-tops between 3.7 and 7.6 mm high. After 24 hr sampling, sample filters were folded in half twice (with sample side inwards), wrapped in methanol pre-cleaned aluminum foil using clean forceps, labeled, and placed in an ice chest (temperature <4°C) for transportation to the laboratory. As soon as the sample filters got to the laboratory, they were placed in a freezer until extraction and analysis.

2.3. Chemical analysis
2.3.1. Sample filter extraction. The PM₁₀ sample filter from each site was transferred into a Soxhlet extractor and extracted with with 300 mL HPLC grade dichloromethane for 16 hours at about 5 cycles per hour. After extraction, the extract was allowed to cool and then dried by passing it through a drying column containing about 10 cm of anhydrous sodium sulphate (preheated to 400°C for 4 hours), and the volume was reduced to ~15 mL, using a vacuum rotary evaporator [7].

2.3.2. Instrumental analysis. We identified the hazardous chemical groups in the dichloromethane extract using optimized GC-MS (Clarus 680, PerkinElmer), with DB-5 column (30 m × 0.25 mm ID, 1 µm film thickness silicone-coated fused-silica capillary column). The carrier gas used was helium, and the GC column was temperature controlled and interfaced directly to the MS ion source. The optimised working conditions are: initial temperature held at 40°C for 4 minutes, ramped to 300°C at 10°C per minute and held for 10 minutes. Samples were injected splitless (gro-btype) with injector volume of 1 µL, and injector temperature at 290°C. Post-run time was 2 minutes with oven temperature at 300°C, and the total analytical time was 40 minutes. MS transfer line temperature was 300°C, with electron energy of 70 volts. Ionization energy was electron impact, with mass range of 35-500 amu, and a scan time of 1 second/scan.

Prior to the analysis, the MS was autotuned following the manufacturer’s specification. The autotune automatically adjusts ion source parameters within the detector using FC-43 reference gas (heptacos). Mass peaks at m/z 69, 219 and 502 were used for tuning. After the tuning was completed, the FC-43 abundances at m/z 50, 69, 131, 219, 414, 502, and 614 were further adjusted such that their relative intensities matched the selected masses of decafluorotriphenyl phosphine (DFTP). The MS was operated in the full range data acquisition (SCAN) mode with a total cycle time of 1 second per scan. Operation of the MS in the scan mode allowed monitoring of all ions and assisted with identification of possible interferences from non-target analytes due to accessibility of the complete mass spectrum in the investigative process. The MS used scans from 35 to 500 amu every 1 seconds using 70 volts (nominal) electron energy in the electron impact (EI) ionisation mode. To ensure sufficient precision of mass spectral data, the MS scan was set at five scans acquisition, while the analyte elutes from the GC. Identification of analytes in the extract was based on retention time of the resolved peaks and comparison of their mass spectrum with characteristic ions in reference mass spectrum of the NIST.
Library (total ion abundance chromatograms, mass spectral fragmentation pattern, and mass spectral library matching).

3. Results and discussion
Shown in Tables 1–3 are organic chemicals identified in the PM$_{10}$ from urban, peri-urban and rural areas in Nagpur district, India. Because we did not perform extract clean-up to separate specific chemical group, not all the compounds were adequately resolved and identified in the “full scan mode” of the GC-MS. The chromatograms (not shown) revealed clustered peaks, indicating groups of chemicals having overlapping or close retention time window. The retention time of a homologous

| S/N | Retention time | Compound name | CAS No. |
|-----|----------------|----------------|---------|
| 1   | 2.84           | 1-methyl-1-ethoxycyclobutane | 59416067 |
| 2   | 5.27           | Benzofuran, 5-methyl-, 1-oxide | 19164411 |
| 3   | 6.23           | D-Leucine | 328381 |
| 4   | 6.23           | N-acetyl-D-serine | 900126440 |
| 5   | 7.59           | 1,3-dioxolane, 4-pentyl-5-propyl-2, 2-bis (trifluoromethyl)-cis | 38274689 |
| 6   | 7.65           | Carbonic acid, decylethyl ester | 900314590 |
| 7   | 7.68           | 2-Propenoic acid, 6-methylheptyl ester | 54774913 |
| 8   | 7.80           | Cis-1-butyl-2-methylcyclopropane | 38851693 |
| 9   | 7.88           | Benzenacetic acid, 2-hexenylester, (e) | 900131771 |
| 10  | 7.91           | Octane, 2-cyclohexyl | 2883058 |
| 11  | 8.13           | Toluene | 108883 |
| 12  | 8.20           | Ethylbenzene | 100414 |
| 13  | 9.70           | Acetophenone, 2-chloro- | 532274 |
| 14  | 9.71           | Benzaldehyde | 100527 |
| 15  | 9.97           | Phenol | 108952 |
| 16  | 10.89          | Benzyl alcohol | 100516 |
| 17  | 11.50          | Spiro(2,4)hepta-4, 6-diene | 765468 |
| 18  | 11.55          | Formic acid, Phenylmethyl ester | 104574 |
| 19  | 11.78          | Benzene acetamide | 103811 |
| 20  | 15.28          | Benzaldehyde, 4-benzylxoy-2-fluoro-5-hydroxyl | 141523162 |
| 21  | 17.50          | Methyl-alpha-d-ribofuranoside | 900129831 |
| 22  | 18.27          | Benzene, 1-methyl-4-(phenylmethyl) | 620837 |
| 23  | 19.54          | Benzene, 1, 1’-methylenebis (4-methyl-) | 4957145 |
| 24  | 19.80          | Benzyl benzoate | 120514 |
| 25  | 19.80          | 4-hydroxy-8-oxo-4-phenyl-2-aza-tricyclo [3.3.1.0(3,7)] nonane-2,3-di | 900287939 |
| 26  | 20.82          | Benzaldehyde, 4-benzylxoy-2-fluoro-5-hydroxy- | 141523162 |
| 27  | 21.04          | 1,4-dimethyl-2-phenoxybenzene | 62787159 |
| 28  | 21.05          | Benzene, 1-methyl-2-(4-methylphenoxy)- | 3402720 |
| 29  | 21.26          | Benzaldehyde, 4-benzylxoy-2-fluoro-5- | 141523162 |
| 30  | 21.73          | Phenol, 2-(1-phenylethyl)- | 4237449 |
| 31  | 21.78          | Phenol, 4-(1-phenylethyl)- | 1988892 |
| 32  | 22.74          | Benzaldehyde, 4-benzylxoy-2-fluoro-5-hydroxy | 141523162 |
| 33  | 23.84          | 2-(1-benzylxoy-2-bromoethyl) oxirane | 101514163 |
| 34  | 26.57          | 1-chlorooicosane | 42217027 |
| 35  | 27.96          | Di-N-octyl phthalate | 117840 |
| 36  | 28.79          | Benz(a)anthracene-7, 12-dione | 2498660 |
| 37  | 29.45          | Tetradecane, 1-chloro- | 2425549 |
and peaks. Similarly, the presence of “di-octyl phthalate” and “benz(a)anthracene-7,12-dione” indicates that phthalate esters and PAHs are present. We attempted to see if the compounds we identified were actually fingerprints indicating the presence of the group members. We performed a two-step extract clean-up – acid-base partitioning cleanup, and

Table 2. Markers of organic chemicals in airborne PM$_{10}$ from a peri-urban area in Nagpur, India.

| S/N | Retention time | Compound name | CAS No. |
|-----|----------------|---------------|---------|
| 1   | 2.04           | 1,2,3-butatriene, 1-chloro- | 20658213 |
| 2   | 2.80           | Orthoformic acid, tri-2-butenyl ester | 14503572 |
| 3   | 5.39           | Benzofurazan, 5-methyl-, 1-oxide | 19164411 |
| 4   | 5.70           | Cysteine, 5-methyl- | 7728985 |
| 5   | 6.28           | N-acetyl-d-serine | 900126440 |
| 6   | 6.35           | Acetylcysteine | 616911 |
| 7   | 7.68           | Ethyl-2-methyl-2-tert-butyl-cyclop propane-1-carboxylate | 900144652 |
| 8   | 7.73           | Benzene, (cyclohexylmethyl)- | 4410757 |
| 9   | 7.74           | Carbonic acid, decyl ethyl ester | 900314590 |
| 10  | 7.95           | Cyclopentane, 1-hexyl-3-methyl | 61142685 |
| 11  | 7.96           | Cyclooctane | 2926648 |
| 12  | 8.24           | 1,3,5-cycloheptatriene | 544252 |
| 13  | 8.34           | Ethylbenzene | 100414 |
| 14  | 8.35           | P-xylene | 106423 |
| 15  | 8.65           | Hydroxylamine, O-(phenylmethyl) | 622333 |
| 16  | 9.68           | Benzyl benzoate | 120514 |
| 17  | 9.74           | Acetophenone, 2-chloro- | 532274 |
| 18  | 9.81           | 1,3,5-cycloheptatriene | 544252 |
| 19  | 10.00          | Phenol | 108952 |
| 20  | 10.82          | Benzene, 1’-[oxybis (methylene)] bis- | 103504 |
| 21  | 11.55          | Formic acid, phenylmethyl ester | 104574 |
| 22  | 18.06          | Benzenyl | 103297 |
| 23  | 19.53          | S,S’-methylenebis (benzylsulfone) | 6331528 |
| 24  | 19.81          | 3-hydroxybutanamide, N-phenylmethoxy | 900196741 |
| 25  | 20.82          | Benaldehyde, 4-benzyloxy-2-fluoro-5-hydroxy- | 141523162 |
| 26  | 21.04          | Benze, 1-methyl-2-(4-methyl phenoxy) | 3402720 |
| 27  | 21.78          | Phenol, 4-(1-phenylethyl)- | 1988892 |
| 28  | 22.74          | Benzene, (3-octylundecyl)- | 5637967 |
| 29  | 23.86          | Benzyloxytridecanoic acid | 900289366 |
| 30  | 24.86          | 9-octadecenoic (z)-, phenylmethyl ester | 55130160 |
| 31  | 25.21          | Octadecane, 3 ethyl-5-(2-ethylbutyl) | 55282127 |
| 32  | 26.59          | 1-chloroecosane | 42217027 |
| 33  | 27.44          | Hexadecane, 1-chloro | 4860031 |
| 34  | 27.96          | Di-N-octyl phthalate | 117840 |
| 35  | 28.45          | Dodecane, 1, 1’-thiobi | 2469456 |
| 36  | 28.50          | Benzenecarboxylic acid 2-tetradecyl ester | 900282024 |
| 37  | 28.79          | Benz(a)anthracene, 1-chloro | 2498660 |
| 38  | 28.96          | Tetradecane, 1-chloro | 2425549 |
| 39  | 29.47          | 1-octadecanesulphony chloride | 900342704 |

group of organic chemicals are usually very close. Therefore, the compounds shown in the Tables are the most abundant in the PM$_{10}$. They represent specific markers of the respective homologous groups (i.e. fingerprints), indicating that members of the group may also be present. For instance, the detection of “benzofuran 5-methyl-1-oxide” or “benzofurazan 5-methyl-1-oxide” in PM$_{10}$ from all three localities (Tables 1–3) suggests the presence of individual members of dioxins and furans, which may have been masked in the clustered (unresolved) peaks. Similarly, the presence of “di-n-octyl phthalate” and “benz(a)anthracene-7,12-dione” indicates that phthalate esters and PAHs are present.
aluminium and silica column cleanup – prior to instrumental analysis, following a method described previously [7]. The clean-up procedures were used to isolate and quantify thirteen individual PAHs in the PM$_{10}$. The result of the quantitative analysis is shown in Figure 2.
Figure 2: Concentration (ng/m$^3$) of PAHs in ambient PM$_{10}$ in Nagpur, India
We detected all thirteen PAHs investigated in the clean extract. This underscores the importance of “clean-up procedures” prior to quantitative analysis of complex organic compounds. The concentrations of all thirteen PAHs determined greatly exceeded a recent health-based guideline for atmospheric PAHs exposure in India [28]. Among all PAHs determined the concentrations of benzo[b]fluoranthene in PM$_{10}$ from the urban and peri-urban areas were the highest, while for the rural area, the concentration of anthracene was highest. Concentration of total (thirteen) PAHs in PM$_{10}$ in the urban (85.9 ng/m$^3$), peri-urban (115.2 ng/m$^3$) or rural (156.6 ng/m$^3$) areas of Nagpur district were lower than the average concentration of total PM$_{10}$-bound PAHs concentration (845 ng/m$^3$ to 1636 ng/m$^3$) in PM$_{10}$ from industrial, residential and vehicular areas of Agra, India [29]. They are also lower than the concentrations of total PAHs found in PM$_{10}$ from urban, peri-urban and rural areas of Sri Lanka [30].

The average concentration of total (thirteen) PAHs in PM$_{10}$ in Nagpur district was within the range of total PAHs concentration (0.17 ng/m$^3$ to 9200 ng/m$^3$) found in atmospheric PM$_{10}$ in some localities in Nigeria [31,32]. It however exceeded the levels found in PM$_{10}$ from some localities in Spain [33], Italy [21] or China [34-36]. It also exceeded the total concentrations of PAHs in PM$_{10}$ from a coal city in Brazil [37].

Our results have shown that atmospheric PM$_{10}$ even in developing countries can contain several dangerous chemical compounds that are detrimental to human health. The presence of all thirteen PAHs in the PM$_{10}$ in all three localities (urban, peri-urban and rural areas) has confirmed our assertion that the “benz(a)anthracene-7, 12-dione” we detected during the qualitative analysis was an indicator that PAH members were present. The same also holds true for the other dangerous organic compounds we have identified: dioxins and furans, phthalates esters, ethers, aldehydes, ketones, phenols, chlorinated hydrocarbons and organic acids. This observation is consistent with many previous reports from developed countries which found several of these toxic organic chemicals in PM$_{10}$ [9,14,20-27,38,39]. Ishaq et al. [9] reported that levels of airborne particulate organic chemicals in Stockholm, Sweden followed this order: PAHs > PCBs > PCNs >PCDDs or PCDFs > non-ortho PCBs or chlorinated PAHs. Furthermore, several studies have found high concentrations of heavy metals in airborne PM$_{10}$ in different localities within and outside India [40-46].

We did not ascertain the specific sources responsible for the individual toxic chemicals in the PM$_{10}$. However, previous studies have linked airborne PAHs to diverse combustion sources such as vehicular (gasoline and diesel engine) emissions, household combustion of solid cookfuels and other combustion or pyrolysis activities [7,20,27]. Organochlorine chemicals in air were attributed to agricultural activities, such as the use of pesticides to control agricultural pests [25,26,39]. Airborne PCBs were linked to leakages of transformer oils, volatilization from improper disposal of capacitors and burning of materials containing PCBs [20,26]. Atmospheric PCDDs and PCDFs were attributed to improper burning of wastes, particularly wastes containing chlorinated compounds [21].

4. Conclusion
Inhalable particulate matter in Nagpur, a developing district in India, contains several hazardous organic chemical groups, including PAHs, chlorinated hydrocarbons, dioxins, furans, phthalate esters, aldehydes, ketones, phenols, organic acids and heavy metals. The concentrations of individual PAHs in the particulate matter by far exceeded health-based guideline, suggesting that prolong inhalation of such particulate matter may pose adverse risk to health of the population.

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References

[1] Etchie T O Sivanesan S Adewuyi G O Krishnamurthi K Rao P S Etchie A T Pillarisetti A Arora N K and Smith K R 2017 Environ. Int. 102 143–56
[2] Etchie T O Etchie A T Adewuyi G O Pillarisetti A Sivanesan S Krishnamurthi K and Arora N K 2018 Environ. Pollut. 236 146–57
[3] Pope C A and Dockery D W 2006 J. Air Waste Manag. Assoc. 56 :709–42.
[4] United States Environmental Protection Agency (USEPA) 2011. National emission standards for hazardous air pollutants: industrial, commercial, and institutional boilers and process heaters.
Research Triangle Park, USA EPA-HQ-QAR-2002-0058.
[5] Wang Z Ren P Sun Y Ma X Liu X Na G and Yao Z 2013 Environ. Sci. Pollut. Res. 20 5753–63
[6] Zhu X, Zhou C, Henkelmann B, Wang Z, Ma X, Pfister G, Schramm K-W, Chen J, Ni Y, Wang W and Mu J 2013 Polycycl. Aromat. Compd. 33 265–88.
[7] Etchie T O Sivanesan S Etchie A T Adewuyi G O Krishnamurthi K George K V and Rao P S 2018 Chemosphere 204 277–89
[8] Inazu K Nam V D Asato T Okochi H Hisamatsu Y Kobayashi T and Baba T 2008 Polycycl. Aromat. Compd. 28 562–77
[9] Ishaq R Näf C Zebäuír Y Broman D and Järnberg U 2003 Chemosphere 50 1131–50
[10] Bi X Sheng G Peng P Chen Y and Fu J 2005 Atmos. Environ. 39 477–87
[11] Forbes P B and Rohwer E R 2009 Environ Pollut 157 2529–35
[12] Forbes P B and Rohwer E R 2010 WIT Trans. Ecol. Environ. 136 367–77
[13] Yeo H-G Choi M, Chun M-Y and Sunwoo Y 2003 Atmos. Environ. 37 3561–70
[14] Hearl L K Hawker D W Tomás L-M and Mueller J F 2013 Ecotoxicol. Environ. Saf. 92 222–8
[15] Oh J-E Chang Y-S Kim E-J and Lee D-W 2002 Atmos. Environ. 36 5109–17
[16] Chao M-R Hu C-W Ma H-W Chang-Chien G-P Lee W-J Cha ng LW and Wu K-Y 2003 Atmos. Environ. 37 4945–54
[17] Lee J H Hopke P K Holsen T M Polissar A V Lee D-W Edgerton E S Ondov J M and Allen G 2005 Aerosol Sci. Technol. 39 261–75
[18] Gullett B Touati A and Oudejans L 2008 Atmos. Environ. 42 7997–8006
[19] Black R R Meyer C P Touati A Gullett B K Fiedler H and Mueller JF 2011 Chemosphere 83 1331–8
[20] Mandalakis M Tsapakis M Tsoga A and Stephanou E G 2002 Atmos. Environ. 36 4023–35
[21] Menichini E Iacovella N Monfredini F and Turri-Baldassarri L 2007 Chemosphere 69 422–34
[22] Alves C Pio C and Duarte A 2001 Atmos. Environ. 35 5485–96
[23] Pio C Alves C and Duarte A 2001 Atmos. Environ. 35 389–401
[24] Sofuoglu A Cetin E Bozacioglu S S Sener G D and Odabasi M 2004 Atmos. Environ. 38 4483–93
[25] Yang Y Li D and Mu D 2008 Atmos. Environ. 42 677–87
[26] Xu D Dan M Song Y Chai Z and Zhuang G 2005 Atmos. Environ. 39 4119–28
[27] Qadir R M Abbaszade G Schnelle-Kreis J Chow JC and Zimmermann R 2013 Environ. Pollut. 175 158–67
[28] Etchie A T Etchie T O Shen H Pillarisetti A and Popovicheva O 2019 Ecotoxicol. Environ. Saf. 178 https://doi.org/10.1016/j.ecosynth.2019.04.028
[29] Singla V Pachauri T Satsangi A Kumari K M and Lakhan i A 2012 Polycycl. Aromat. Compd. 32 199–220
[30] Wickramasinghe A P Karunarathne D G and Sivakanesan R 2011 Atmos. Environ. 45 2642–50
[31] Ana G Sridhar MK and Emerole G O 2012 J. Air Waste Manag. Assoc. 62 18–25
[32] Salaudeen I A Sonibare O O Sojiru S and Ekundayo O 2017 Pollut. 3 561–73.
[33] Callén M S López J M Iturmendi A and Mastral A M 2013 Environ. Pollut. 183 166–74
[34] Guo H Lee S C Ho K F Wang X M and Zou S C 2003 Atmos. Environ. 37 5307–17
[35] Wang G Huang L Zhao X Niu H and D ai Z 2006 Atmos. Res. 81 54–66
[36] Wang X Y Li Q B Luo Y M Ding Q Xi L M Ma J M Li Y Liu Y P and Cheng C L 2010 Environ. Monit. Assess. 165 295–305
[37] Dallarosa J B Elba C Teixeira E C Pires M and Fachel J 2005 *Atmos. Environ.* **39** 6587–96
[38] Kouimtzis T Samara C Voutsas D Balafoutis C and Müller L 2002 Chemosphere **47** 193–205
[39] Li J Zhang G Guo L Xu W Li X Lee CSL, Ding A and Wang T 2007 *Atmos. Environ.* **41** 3889–903
[40] Singh DP, Gadi R and Mandal TK 2011 *Atmos. Environ.* **45** 7653–63
[41] Argyropoulos G Grigoratos T Voutsinas M and Samara C 2013 *Environ. Sci. Pollut. Res.* **20** 7214–30
[42] Ducret-Stich R E Tsai M-Y Thimmaiah D Künzli N Hopke P K and Phuleria H C 2013 *Environ. Sci. Pollut. Res.* **20** 6496–508
[43] Hoinaski L Franco D Stuetz R M Sivret E C and de Melo Lisboa H 2013 *Environ. Technol.* **34** 2453–63
[44] Pandey P Patel D K Khan A H Barman S C Murthy R C and Kisku G C 2013 *J. Environ. Sci. Health A* **48** 730–45
[45] Yadav S and Satsangi PG 2013 *Environ. Monit. Assess.* **185** 7365–79
[46] Tositti L Brattich E Masiol M Baldacci D Ceccato D Parmeggiani S, Stracquadanio M and Zappoli S 2014 *Environ. Sci. Pollut. Res.* **21** 872–90