

## **Persistent Organic Pollutants in Smoke Particles Emitted During Open Burning of Municipal Solid Wastes**

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There has been growing concern about the potentially harmful effects on human health of toxic agents known to be present in our urban atmosphere. Fine organic particle emissions from open burning of waste carbonaceous material account for significant proportions of particle-bound persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine (OC) pesticides released in the atmosphere. Many of these anthropogenic compounds, are classified as possible mutagenic and carcinogenic and have caused worldwide concern as toxic environmental contaminants (Menzie et al. 1992; Lutz and Schlatter 1993; Hardell et al. 1997). Further, particle-bound airborne contaminants deposit more efficiently in the human respiratory system, which raises serious concern about the potential hazard of these pollutants to the public health. In Alexandria, Egypt's second largest city, important potential sources of organic pollutants arise from combustion of domestic waste in largely uncontrolled situations, which although intermittent in nature can have a very marked effect on air quality. The arid climate aggravates the high pollution levels, resulting in enormous levels of suspended particulate matter.

Much less work has been carried out to determine the contribution of open burning of municipal solid wastes (MSW) to the atmospheric burden of PAHs and OC compounds adsorbed onto particulate matter. Once comprehensive information on the molecular composition of such emissions is available, it may be possible to estimate the contribution of municipal solid waste burning operations to the atmospheric particulate matter burden by molecular tracer techniques. In this study, the molecular composition of PAHs, PCBs, and OC insecticide residues in smoke particles emitted during open burning of municipal solid wastes is examined. Source samples are analyzed by high-resolution gas chromatography (HRGC) and gas chromatography/mass spectrometry (GC/MS) techniques in order to identify and quantify organic pollutants and key molecular marker compounds emitted during the combustion process.

## MATERIALS AND METHODS

Sampling of atmospheric particles were carried in conditions of atmospheric stability, in the absence of precipitation and with a wind speed less than  $4 \text{ m s}^{-1}$ . The average minimum and maximum temperatures were  $23^{\circ}\text{C}$  and  $30^{\circ}\text{C}$ , respectively. Two consecutive samples were collected 100 m directly downwind of an open burning MSW site located in southwest Alexandria. A flow controlled low volume air sampler with precombusted glass fiber filter ( $400^{\circ}\text{C}$ , 8 h) was used. The pump was situated at 3 m above the ground level to avoid any significant interference from the ground. The average sampling volume was  $75 \text{ m}^3$ . The filters were stored in a freezer ( $-18^{\circ}\text{C}$ ) until the analysis in the laboratory. Suspended particulate samples were extracted with high purity dichloromethane for 15 min by sonication and concentrated in Kuderna-Danish tubes. The procedure used for separation and quantification of PAHs, PCBs and chlorinated pesticides has been described elsewhere (Wade et al. 1988). Briefly, the extracts were fractionated by alumina:silica gel (80-100 mesh) chromatography and sequentially eluted from the column with 50 mL of pentane (aliphatic fraction) and 200 mL of 1:1 pentane-dichloromethane (aromatic/PCB/pesticide fraction). The fractions were then concentrated to 1 ml using Kuderna-Danish tubes heated in a water bath at  $60^{\circ}\text{C}$ . Surrogate standards were added to the sample prior to extraction and were used for quantification.

Aromatic hydrocarbons were separated and quantified by GC/MS (HP-5890-GC and HP5970-MSD). The samples were injected in the spitless mode onto a  $0.25\text{-mm} \times 30\text{-m}$  ( $0.32\text{-}\mu\text{m}$  film thickness) DB-5 fused silica capillary column (J & W Scientific, Inc) at an initial temperature of  $60^{\circ}\text{C}$ , the temperature was programmed to increase  $12^{\circ}\text{C min}^{-1}$  to  $300^{\circ}\text{C}$  and was held at the final temperature for 6 min. The mass spectral acquired using selected ions for each of the PAH analytes. The GC/MS was calibrated by injection of a standard component mixture at five concentrations ranging from  $0.01 \text{ ng } \mu\text{l}^{-1}$  to  $1 \text{ ng } \mu\text{l}^{-1}$ . Sample component concentrations were calculated from the average response factor for each analyte. Analyte identifications were based on correct retention time of the quantitation ion (molecular ion) for the specific analyte and confirmed by the ratio of the confirmation ion. The surrogate standards for the PAHs analysis were  $\text{d}_8$ -naphthalene,  $\text{d}_{10}$ -acenaphthene,  $\text{d}_{10}$ -phenanthrene,  $\text{d}_{12}$ -chrysene, and  $\text{d}_{12}$ -perylene. To monitor the recovery of the surrogates,  $\text{d}_{10}$ -fluorene was added prior to GC-MS analysis. Surrogate compounds recoveries were as follows:  $\text{d}_8$ -naphthalene (59-66%),  $\text{d}_{10}$ -acenaphthene (61-67%),  $\text{d}_{10}$ -phenanthrene (54-59%),  $\text{d}_{12}$ -chrysene (79-106%), and  $\text{d}_{12}$ -perylene (46-74%).

The pesticides and PCBs were separated by gas chromatography in the spitless mode using an electron capture detector (ECD). A  $30 \text{ m} \times 0.32 \text{ mm i.d.}$  fused silica column with DB-5 bonded phase (J & W Scientific, Inc) provided component separations. A sample containing only PCBs was used to confirm the identification of each PCB congener. The chromatographic conditions for the pesticide-PCB analysis were  $100^{\circ}\text{C}$  for 1 min, then  $5^{\circ}\text{C min}^{-1}$  to  $250^{\circ}\text{C}$ , hold for 1 min, and then

10°C min<sup>-1</sup> to 300°C and a final hold of 5 min. The surrogates DBOFB (dibromooctafluorobiphenyl), PCB-103, and PCB-198 were added to the samples prior to extraction. The internal standard, TCMX (tetrachloro-*m*-xylene), was added prior to GC/ECD analysis. The QA/QC procedures included analysis of matrix spikes, duplicates, laboratory blanks and SRMs (Wade and Cantillo, 1994). Surrogate compounds recoveries were as follows: DBOFB (91-94%), PCB-103 (94-96%), and PCB-198 (97-101%). For data presentation all concentrations were assigned a value of 0.25 ng/g<sup>-1</sup> dry weight as the estimated average detection limit. The instrument was calibrated by injection of the standards component mixture at three to five different concentrations, prior to analysis of the samples.

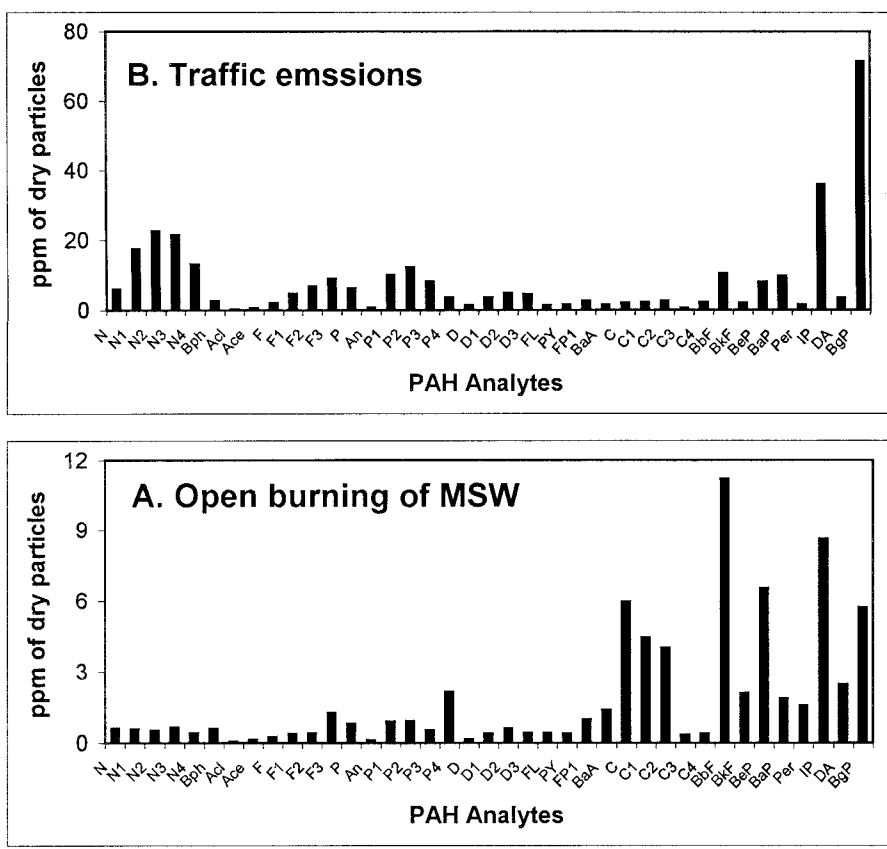
## RESULTS AND DISCUSSION

Due to various factors during PAH emission and atmospheric transport process from open burning of MSW, the range of total PAH concentration was quite scattered being 18,600 – 124,000 ng g<sup>-1</sup> (Table 1). Figure 1A depicts graphically the average composition of individual PAH homologous. The abbreviations used to represent them in the latter figure are listed in Table 2.

**Table 1.** Concentrations of particle-bound PAHs, PCBs, and chlorinated pesticides.

POPs	Concentration Range	
	ng g <sup>-1</sup> dry particles	ng m <sup>-3</sup> of air
ΣPAHs	18,600-124,000	14,100-81,400
ΣPCBs	420-2,280	318-1,500
2,4'-DDT + 4,4'-DDT	36.6-110	27.6-72.5
Chlordane-related compounds	<0.25-47.7	<0.25-31.4
CBs	50.1-76.0	33.0-57.5
HCHs	31.7-46.4	24.0-30.6
Pentachloranisole	20.3-25.4	13.3-19.2
Chlorpyrifos	<0.25-38.9	<0.25-25.6
Mirex	<0.25-19.5	<0.25-12.8
Endosulfan	<0.25-46.4	<0.25-30.5

Thirty-nine PAHs have been quantified in the samples investigated in this study. The GC/MS analytical results indicated that the PAHs consists of five families of compounds: naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, and chrysenes, each consisting of an unsubstituted or parent compound and a homologous series of alkylated compounds, as well as higher molecular weight five and six membered ring PAHs. Hydrocarbons with a higher degree of condensation (four-ring PAH and higher) were the most dominant components and were responsible for more than 80% of the total concentration of PAHs. Benzo[b]fluoranthene, indeno[1,2,3-cd]pyrene, benzo[e]pyrene, Benzo(g,h,i)perylene and chrysenes were the most abundant PAHs.



**Figure 1.** PAH fingerprints in particulates from open burning of MSW and traffic emissions in Alexandria City. PAHs identification codes are listed in Table 2.

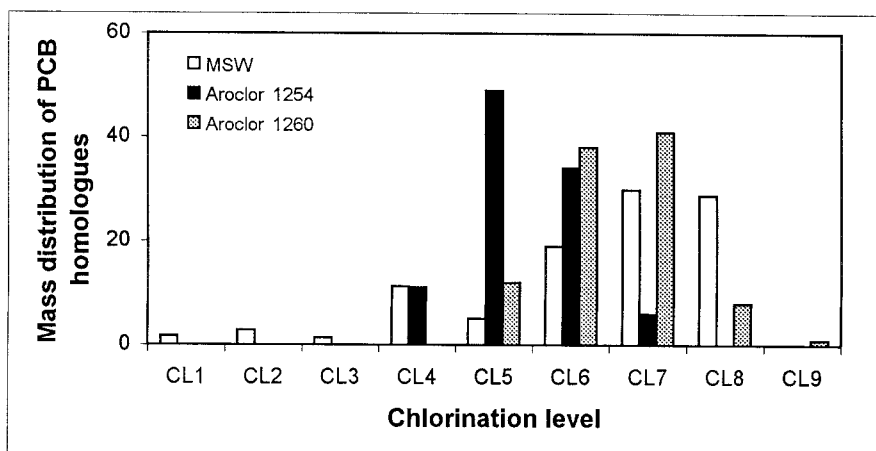
Studies performed during the last decades showed that PAHs have significant variation in their composition for different combustion sources and their fingerprints if available can be used in the sources identification models (Gordon 1988). Nevertheless, the data presented in Figure 1A suggest a PAH composition in refuse combustion particles that is markedly different from the composition found in other combustion sources such as biomass burning (Jenkins et al. 1996), wood and duff burning (Freeman and Cattell 1990; Tan et al. 1992), diesel and gasoline exhausts (Westerholm et al. 1991; Rogge et al. 1993; Li et al. 1996); and other pollution sources (Daisey et al. 1986; Li and Kamens 1993). Figure 1 also shows the differences in particle-bound composition of PAH homologues emitted from open burning of MSW and particle-bound PAHs composition from emissions of heavy traffic by gasoline and diesel powered vehicles in central Alexandria, sampled under similar metrological conditions (Barakat 2002). In smoke particles from open fires of wastes benzo[b]fluoranthene, indeno[1,2,3-cd]pyrene, benzo[e]pyrene, and chrysene stand out as predominant species. A notable feature of

**Table 2.** Polycyclic aromatic hydrocarbon identified in air samples.

PAH analyte	Code	PAH analyte	Code
Naphthalene	N	C2 dibenzothiophenes	D2
C1 naphthalenes	N1	C3 dibenzothiophenes	D3
C2 naphthalenes	N2	Fluoranthene	FL
C3 naphthalenes	N3	Pyrene	PY
C4 naphthalenes	N4	C1 fluoranthene-pyrenes	FP1
Biphenyl	Bph	Benz[a]anthracene	BaA
Acenaphthylene	AcI	Chrysene	C
Acenaphthene	Ace	C1 chrysenes	C1
Fluorene	F	C2 chrysenes	C2
C1 fluorenes	F1	C3 chrysenes	C3
C2 fluorenes	F2	C4 chrysenes	C4
C3 fluorenes	F3	Benzo[b]fluoranthene	BbF
Phenanthrene	P	Benzo[k]fluoranthene	BkF
Anthracene	An	Benzo[e]pyrene	BeP
C1 phenanthrenes-anthracenes	P1	Benzo[a]pyrene	BaP
C2 phenanthrenes-anthracenes	P2	Perylene	Per
C3 phenanthrenes-anthracenes	P3	Indeno[1,2,3-cd]pyrene	IP
C4 phenanthrenes-anthracenes	P4	Dibenz[ah]anthracene	DA
Dibenzothiophene	DBT	Benzo[ghi]perylene	BgP
C1 dibenzothiophenes	D1		

PAH mixtures in particle-bound PAHs from traffic exhaust is the relatively high abundance of indeno[1,2,3-cd]pyrene and benzo[ghi]perylene which are likely to be of pyrolytic origin from vehicular exhausts emission. Many studies have suggested that some specific PAH or ratios between PAH compounds may be used for source identification. Cretney et al. (1985) proposed that the ratio of (BbF + BkF) to BgP can be used to distinguish between domestic fires and automobiles. This ratio was found to be 2.3 for refuse combustion particles and 0.18 for gasoline and diesel combustion particles. Moreover, the relative abundance of total methyl-dibenzothiophenes to that of methylphenanthrenes, clearly distinguished between PAHs in particulates from MSW fires and traffic exhausts (0.31 as compared to 1.52, respectively).

The range of total PCB concentration was quite scattered being 420 – 2,279 ng g<sup>-1</sup> (Table 1). The mean PCB homologues distribution (Figure 2) shows that the relative composition of the PCB congeners was clearly dominated by the hexa-, hepta-, and octa-chlorinated biphenyls with these three homologues representing approximately 80% of the total. The PCB-homologue distributions of particle-phase samples do not reflect the composition of commercial PCB mixtures of the higher chlorinated Aroclor 1254 and 1260 (Figure 2). The type of pattern depicted in Figure 2 is also different from those observed by other researchers in ambient air samples (Lee et al. 1996; McConnell et al. 1998) and contaminated sediments and



**Figure 2.** The mass distribution of PCB-homologues (%) in particulates from open burning of MSW, and in Aroclor 1254 and 1260.

soils (Iwata et al. 1995; Tolosa et al. 1995). This shift in congener profile toward higher molecular weight congeners may be more a result of increased sampling temperature, which increases the vapor phase concentrations of the lower vapor pressure compounds (Hoff et al. 1992). From the 96 PCB congeners analyzed the maximum average levels correspond to PCB 171/202, and PCB 194. PCBs 129, 205, 197 and 138/160, exhibited intermediate concentration levels, which, with the exception of PCB 138 and 194, exhibit low to medium toxicity levels (Ahlborg et al. 1994). Finally, PCB 156, PCB 77, PCB 105, PCB 126, and PCB 169, the most toxic congeners analyzed, are present at the lowest levels.

Organochlorine insecticide were detected in smoke particle from open burning of MSW (Table 1). Total DDT concentrations, i.e. the sum of 2,4'-dichlorodiphenyltrichloroethane (DDT) and 4,4'-DDT ranged from 36.6 to 110 ng g<sup>-1</sup> dry wt. Breakdown products of DDT i.e., 2,4'- and 4,4'-dichlorodiphenyldichloroethane (DDD) and 2,4'- and 4,4'-dichlorodiphenyltrichloroethene (DDE), were not detected in the sample analyzed indicating recent usage of DDTs. Concentration of total chlordane-related compounds range from below detection limit (<0.25 ppb) to 47.7 ng g<sup>-1</sup> dry wt. Total chlordane is reported as the sum of heptachlor and its epoxide,  $\gamma$ -, and  $\alpha$ -chlordane, oxychlordane and cis- and trans-nonachlor. The chlorinated benzenes (CBs) 1,2,4,5- and 1,2,3,4- tetrachlorobenzene, and pentachlorobenzene may be metabolites of the commercial pesticide hexachlorobenzene (HCB) or other CBs, e.g. pentachlorophenol (Wang and Jones 1994). The sum of the concentrations of these CBs ranged from 50.1 to 76.0 ng g<sup>-1</sup> dry wt. Hexachlorohexanes (HCHs) concentrations (sum of  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -isomers) range from 31.7 to 46.4 ng g<sup>-1</sup>. Chlorpyrifos, endosulfan II, mirex and chlorpyrifos were also detected in smoke particles (Table 2). Concentrations of dieldrin, aldrin, and endrin were below detection limits.

It should be noted that semivolatile organic compounds such as insecticides, PCBs, and PAHs are present in the atmosphere as vapors and associated with suspended particles. Bidleman et al. (1987) found that CBs, HCHs and chlordanes are so volatile that at 20°C less than 1% are filter-retained; while this fraction increased slightly for Aroclor 1254, DDTs (2.0 and 8.9%, respectively). Given the difference in ambient temperature, vapour-to-particle ratios of POPs are expected to be far higher in the hotter climate of Alexandria.

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