

# Occurrence and Characteristics of Persistent Organic Pollutants (POPs) in the Ambient Air of Riyadh City, Saudi Arabia: A Step toward the Clean Air Act

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## Abstract

Little research has been done on the occurrence and concentration of persistent organic pollutants (POPs), including polycyclic aromatic hydrocarbons (PAHs), pesticides and polychlorinated biphenyls (PCBs), in the ambient air of Saudi Arabia. POPs emissions are an environmental pressure that can negatively impact human health. Saudi Arabia has undergone significant agricultural and industrial development and economic growth over the past three decades and this has resulted in increased air pollution. As a result, there are elevated concentrations of PAHs, pesticides and PCBs in the ambient air of Riyadh city. The average total pesticide concentration ranged from 1.92 to 8216 ng/m<sup>3</sup>. These relatively high concentrations suggest the heavy use of pesticides around Riyadh, as well as possibly long-range atmospheric transport. The average total PAH concentration ranged from 17.85 to 1002.8 ng/m<sup>3</sup>, while the total PCB concentration ranged from 0.32 to 20.08 ng/m<sup>3</sup>. Some of the POPs were of local and regional origin, while other POPs may be the result of long-range atmospheric transport. Saudi Arabia is focused on reducing the emission of POPs through concerted efforts at both the national and international levels.

## 1. Introduction

Ambient air quality refers to the air in our immediate surroundings and describes the level of air pollutants in that particular region. Poor ambient air quality means pollutant levels are high enough to raise concern for human health. Ambient air quality is measured near ground level, away from direct sources of pollution. Harmful emissions into the air represent an environmental pressure that adversely affects human health and productivity. Organic geochemistry and environmental chemistry have been used to assess the presence and occurrence of anthropogenic and natural organic compounds in ambient air.

Polycyclic aromatic hydrocarbons (PAHs), pesticides and polychlorinated biphenyls (PCBs) are persistent organic pollutants (POPs) whose presence in the particulate matter of ambient air has profound environmental and human health concerns. POPs are organic compounds

that resist biological and chemical degradation, including photolytic breakdown. They are characterized by low water solubility and high lipid solubility, leading to their bioaccumulation in fatty tissues [Jones and de Voogt, 1999]. POPs persist in the environment, may undergo atmospheric long-range transport, bioaccumulate in human and animal tissue, biomagnify in food chains, [Aristizábal, et al., 2011] and have potential significant impacts on human health and the environment [Jones and de Voogt, 1999]. They are also semi-volatile, enabling them to move long distances in the atmosphere before deposition occurs. Some of POPs, such as PCBs, persist in the environment for periods of years and may bioconcentrate by factors of up to 70,000 fold [Bieser et. al., 2012, Jones and de Voogt, 1999].

The background concentrations of POPs and the seasonal variation of their concentrations are two factors to consider when estimating population exposure via inhalation. Information on the seasonality of POP concentrations is available for urban air, but is missing for background areas. The PAH concentration trends throughout the year was investigated at several urban sites [Menichini, 1992; Brown et al., 1996; Dorr et al., 1996; Valerio et al., 1996; Menichini et al., 1999; Lodovici et al., 2003] Measurements of PAH emissions from air pollution sources originating from different types of activities have also been investigated [Rogge et al., 1991, 1993a-d, 1994, 1997a, b, 1998; Schauer et al., 1996, 1999a, b, 2001, 2002a, b].

The World Health Organization (WHO) recognizes the importance of monitoring particulate matter in ambient air in order to protect public health. The WHO air quality guidelines (AQG) recommend standards that every government should consider when formulating policy targets after evaluating the local conditions. Limit values for PM10 in ambient air were set in many countries considering the WHO reference values [WHO, 1997, 2000, 2003, 2005; US EPA, 1987, 1999, 2009; Sloss and Smith, 2000]. A limit value of 20  $\mu\text{g}/\text{m}^3$  (annual limit) and 50  $\mu\text{g}/\text{m}^3$  (24h mean) for PM10 in ambient air was recommended by WHO [WHO, 2005].

The objectives of this work were to identify, characterize and determine the POP concentrations in the ambient air of the city of Riyadh, Saudi Arabia and to highlight the policy implications for POPs and possible scenario for the Clean Air Act for policy makers in Saudi Arabia. To do this, particulate matter samples were collected from ambient air in Riyadh from December 2010 to January 2011 and analyzed for PAHs, pesticides and PCBs.

## **2. Material and Methods**

### **2.1 Sampling Site**

The sampling location was selected to represent the Riyadh metropolitan area of about more than 90  $\text{km}^2$  (Figure 1). The site was located at the College of Food and Agriculture Sciences of King Saud University (KSU, 24° 43' 30.53"N, 46° 37' 06.74"E), Riyadh, away from areas subjected to point source emissions or unusual aerosol transport conditions. The air sampler was on the roof top of the two story building for the ease of access, power supply and security reasons.

### **2.2 Sampler**

A high volume air sampler (Precision Hi-Volume Air Sampler, GCA Corp., Precision Scientific Group, and 3737 West Cortland St., Chicago, IL, USA) was used to collect particulate matter with 10  $\mu\text{m}$  size cutoff (PM<sub>10</sub>). The sampler was fitted with quartz microfiber filters (QMA, 20.3 x 25.4 cm). A batch of 21 samples was collected with the HVS at a flow rate of 1.2 m<sup>3</sup>/min for typically 24 h on consecutive days from December 13, 2010 to January 2, 2011.

## 2.3 Sample preparation

### 2.3.1 Extraction

In brief, the wrapped aluminum foil filter samples were removed from the freezer at the time of sample preparation and allowed to warm to room temperature for approximately 1 h in sealed Polytetrafluoroethylene (PTFE) bags. Then, a quarter of the filter was cut, weighed on an analytical balance, then folded and placed in a 100mL stainless steel Accelerated Solvent Extractor (ASE) cell (Dionex, Sunnyvale, CA, USA). Approximately, 0.5 g GF (blank) was also weighed, folded and placed in the ASE cell. Prior to use, each ASE cell had been pre-cleaned by rinsing with organic solvents and baking over-night. Each ASE cell was filled with anhydrous sodium sulfate and 15  $\mu\text{L}$  of isotopically labeled recovery surrogates in 1.25-10 ng/ $\mu\text{L}$  solutions, (equivalent to 12.5-150 ng) which distributed equally among the tops of the cells. Then, cells were capped, put in the extractor and extracted with dichloromethane (DCM) (100 °C, 1500 psi, 2 cycles of 5 minutes, 150 % flush volume). The extract was concentrated to 0.5 mL in the TurboVap II (Zymark, Hopkinton, MA) with nitrogen, and solvent exchanged to hexane. The sample was spiked with isotopically labeled PAHs for quantifying the recovery.

### 2.3.2 Clean-up and purification

Interferants were removed from the extracts using silica adsorption chromatography utilizing a solid phase extraction (SPE) cartridge packed with 20 g silica. The silica columns were eluted in three fractions with 50 ml hexane for the first fraction (F1), 100 ml dichloromethane (DCM) for the second fraction (F2) and 50 ml ethyl acetate for the third fraction (F3). Extract volumes were reduced using a TurboVap II. The target fractions (F1-F3) were concentrated to 0.3 ml with ethyl acetate rinses under a gentle stream of nitrogen and spiked with 15  $\mu\text{L}$  of a 10 ng/ $\mu\text{L}$  isotopically labeled internal standard solution prior to analysis. Blank extracts were carried through the entire method together with batches of 3 to 5 samples.

### 2.3.3 Analysis

Analyte separation, detection, and identification were performed by gas chromatography – mass spectrometry (GC-MS) on an Agilent (Palo Alto, CA) 6890N gas chromatograph equipped with an Agilent HP-5MS column (30m x 0.25 mm x 0.25  $\mu\text{m}$  film thickness) and 5973N mass selective detector. Persistent organic pollutants (POP) concentrations in filter extracts were determined by GC-MS in the selected-ion-monitoring (SIM) mode using electron impact (EI) and negative chemical ionization (NCI) mass spectrometry. The target analyte list was comprised of 83 PAHs, 50 pesticides and pesticide degradation products, 6 PCBs, and isotopically labeled surrogates and internal standards. Target analyte loss was corrected for surrogate recovery by using target analyte to surrogate response ratios in calibration curves. The mean recovery over the entire analytical method for all surrogates in all samples was more than 59%.

### 3. Theoretical framework:

POPs are defined within the Stockholm convention in terms of persistence, bioaccumulation, and adverse health effects. Increasing levels of large-scale application agro-chemicals and stationary and mobile emission sources have been found in regions isolated from their use and production. The PM<sub>10</sub> fraction was chosen for analysis because they result from primary emission or indirectly from secondary emission. Therefore, the identification and source apportionment of these emissions need to be quantified and regulated toward a clean air environment.

### 4. Results

The sampling location, general characteristics of the particulate matter (PM<sub>10</sub>) and metrological conditions for Riyadh are given in Table 1 and Figure 1. The analytical characteristics and concentrations of the POPs determined by GC-MS in the EI and CI SIM modes are shown in Table 2 and Figures 2 and 3. The concentrations of PAHs, pesticides and PCBs in ng/m<sup>3</sup> in PM<sub>10</sub> of Riyadh city during December 2010 are given in Figure 3 and summarized in Table 2. The mean concentration for all reported individual PAHs ranged from 18±8 - 1003±597 ng/m<sup>3</sup>. The minimum and maximum concentrations for PAHs were 4-134 ng/m<sup>3</sup> and 40-2281 ng/m<sup>3</sup>, respectively. Total PAHs (TPAHs) ranged from 1762-13470 ng/m<sup>3</sup>, with a mean concentration of 5938±2766 ng/m<sup>3</sup>. Retene was detected in all samples. The mean concentration for all reported individual pesticides in GC-MS-EI in SIM mode ranged from 2±5 - 833±2202 ng/m<sup>3</sup>. The minimum and maximum ranges for pesticides in GC-MS-EI in SIM mode are 0-108 ng/m<sup>3</sup> and 16-10398 ng/m<sup>3</sup>, respectively (Table 2 and Figure 3). The mean concentration for all reported individual pesticides in GC-MS-CI in SIM mode ranged from 1±1 - 20±24 ng/m<sup>3</sup>. The minimum and maximum ranges for pesticides in GC-MS-CI in SIM mode were 0-7 ng/m<sup>3</sup> and 1-122 ng/m<sup>3</sup>, respectively (Table 2 and Figure 3). The mean concentration for all PCBs congeners in GC-MS-CI in SIM mode ranged from 1±1 - 8±6 ng/m<sup>3</sup>. The minimum and maximum ranges for pesticides in GC-MS-CI in SIM mode were 0-2 ng/m<sup>3</sup> and 4-51 ng/m<sup>3</sup>, respectively (Table 2 and Figure 3).

### 5. Discussion

There was significant variation in the POPs concentrations over the sampling month period. High standard deviations reflect the high variability in daily concentrations. The lowest total ambient concentrations of PAHs, pesticides and PCBs were 1762, 933, 11, 4 ng/m<sup>3</sup>, respectively, while the highest were 13470, 31005, 166, and 31 ng/m<sup>3</sup>, respectively (Figure 3). The standard deviations of the compound concentrations were large compared to the means, resulting in coefficients of variation > 1.0, indicating highly variable data. All POPs concentrations exceeded the limits recommended by the international organizations. (WHO, 2005, UNEP 2002, 2005 and USEPA 2009). The mean PM<sub>10</sub> concentration in the ambient air of Riyadh (576 µg/m<sup>3</sup>) exceed the limit regulated by the WHO (50 µg/m<sup>3</sup> 24-hour mean. (WHO, 2005))

Riyadh is rapidly increasing in population to approximately 5.33 million (<http://www.cdsi.gov.sa>), and hence the number of vehicles on the roads is also rising. In 2010, about 4.8 million cars were registered in Riyadh by the Ministry of Interior - General Directorate of Traffic, (<http://www.cdsi.gov.sa/yb46/Tabels/Chapter5/Table5-32.xls>). This dramatic increase in traffic load resulted in a considerable increase in vehicle engine

emissions, one major source of PAHs and PCBs (Rogge et al 1993a; Gogou, et al., 1994; Zhou et al., 2009; Robinson et al., 2006, Schauer, et al., 1996, 1999b, 2002b, Broz, et al., 2000). Similarly, there is a significant increase in pesticides consumption during the past decade. A total of 324555 ton of pesticides were used to treat an area of 2143228 Hectare during 2000-2010 (<http://www.moa.gov.sa/files/stat24/5/16.htm> 2010). The climate of Saudi Arabia is an important factor in increasing pollution. It is located in a dry region where precipitation rarely occurs, with an annual mean rainfall of 7.2 mm and surface winds are inactive almost all year. Land topography also affects air pollution. Most of the area of Saudi Arabia is desert, which results in a high concentration of wind transported dust into the air sheds of inhabited areas. Air pollution increases with the growing socio-economic development and traffic is a major source. Figure 3 and Table 2 show the distribution of PAHs in the Riyadh PM samples. Although the qualitative composition of PAHs in Riyadh aerosol PM is similar to those of other urban areas, the concentration of specific components exhibit distinct variation. They also contained 3 ring PAHs. Riyadh PM Samples had a total PAH concentrations two orders of magnitude higher than those of rural samples reported for coastal cities in the eastern Mediterranean (Gogou et al., 1994).

The PAHs, pesticides and PCBs concentration levels correlates well with the PM10 concentrations during collection period (Figure 2a and 2b). PAHs from pyrogenic sources have enhanced concentrations of compounds, such as anthracene, phenanthrene, fluoranthene and pyrene. These results demonstrated that the contribution of PAHs from pyrogenic sources was minor. The PAHs in the PM10 were mainly from traffic-related emissions based on the assessment using the diagnostic ratios. Nevertheless, these ratios should be considered with caution. Retene was present in all PM samples. It is an incomplete combustion product of compounds from conifer wood biomass (Ramdahl, 1983; Simoneit, 2002), and is a tracer for forest fires or an indicator of residential wood stoves (Standley and Simoneit, 1987), as well as here for fires by Saudi's in desert-camping during winter and spring. The minor contribution of retene to the total PAH concentrations suggests transboundary transport from surrounding suburb or more remote areas. Pesticides concentrations reached alarming levels. There is a significant concentration of accumulated pesticides of 16-10398 ng/m<sup>3</sup> over the years. This concentration suggests an excessive use of pesticides with minor contribution from trans-boundary transported pesticides. Pesticides enter the atmosphere via drift, volatilization and wind erosion and are removed from the atmosphere via dry deposition and precipitation. More persistent compounds such as total DDTs, triallate, lindane, chlorpyrifos and endosulfan can recycle numerous times in this manner. Some of the more volatile compounds, such as trifluralin and triallate, are not efficiently removed from the atmosphere via precipitation because they are not water soluble. Alachlor, atrazine, simazine, malathion, triallate and pepulate were measured in high concentrations that reached 242-833 ng/m<sup>3</sup>.

There has been continuous and rapid growth of the Saudi economy over the past three decades (early 80s). Significant and rapid urbanization and industrialization, is taking place specifically in the capital city of Riyadh. The Saudi government developed a regulatory and institutional framework for environmental management in order to reverse environmental deterioration. Saudi Arabia needs to develop, enforce and implement a clean air act which requires the application of maximum achievable control technology for hazardous air pollutants, including POPs. Major sources to be regulated under this authority include municipal, medical, and hazardous waste incineration; pulp and paper manufacturing; and certain metals production, petrochemical industries and refining processes. However, the environmental management system and policy implementation are still far from being effective and efficient owing to weak monitoring and insufficient public involvement in

Saudi Arabia (World Bank, 1997; OECD, 2006). Like many countries [Patankar, Trivedi, 2011], the government of Saudi Arabia, represented by the ministry of Agriculture and the ministry of Health, should improve management practices in agriculture, disease vector control and other relevant areas to reduce or eliminate POPs, including unintentionally-produced POPs (uPOPs) generated from vehicle engines emission (Broz et al., 2000), open and uncontrolled burning (Chen et al., 2010), and other hazardous pesticide use, including those traded and used illegally (if any). They are requested to develop and implement POPs waste management and eradication plans, primarily for PCBs and pesticides. Methods to reduce and phase-out POPs, and other chemicals of concern, may be introduced to industry, including the informal sector (Dvorak et al., 2010). Possible approaches might include; risk based management and process optimization (e.g. cleaner production, chemical leasing) (Heidi et al., 2006). The Presidency of Metrology and Environment (PME) of Saudi Arabia may develop and implement, in partnership with key stakeholders, effective planning tools for the environmentally sound management of chemicals, taking into consideration all stages of the chemical's life cycle. Through collaborative efforts with neighboring Gulf Corporation Countries (GCC), an implementation of a regional plan to address POPs and other chemicals of concern involving different stockholders including people (Dong et al., 2011), making optimal use of regional resources and knowledge could be possible.

## **6. Conclusions:**

The findings reveal the presence of some POPs in the ambient air of Riyadh city at elevated concentrations. Some are locally originated, while others are suggested to be long-range transported. Petrochemical industry, road traffic and agribusiness may be responsible for most of air pollution in Saudi Arabia. Efforts are underway by the authorities to monitor and regulate harmful emissions. Initiatives for research and development toward the clean air act have been launched.

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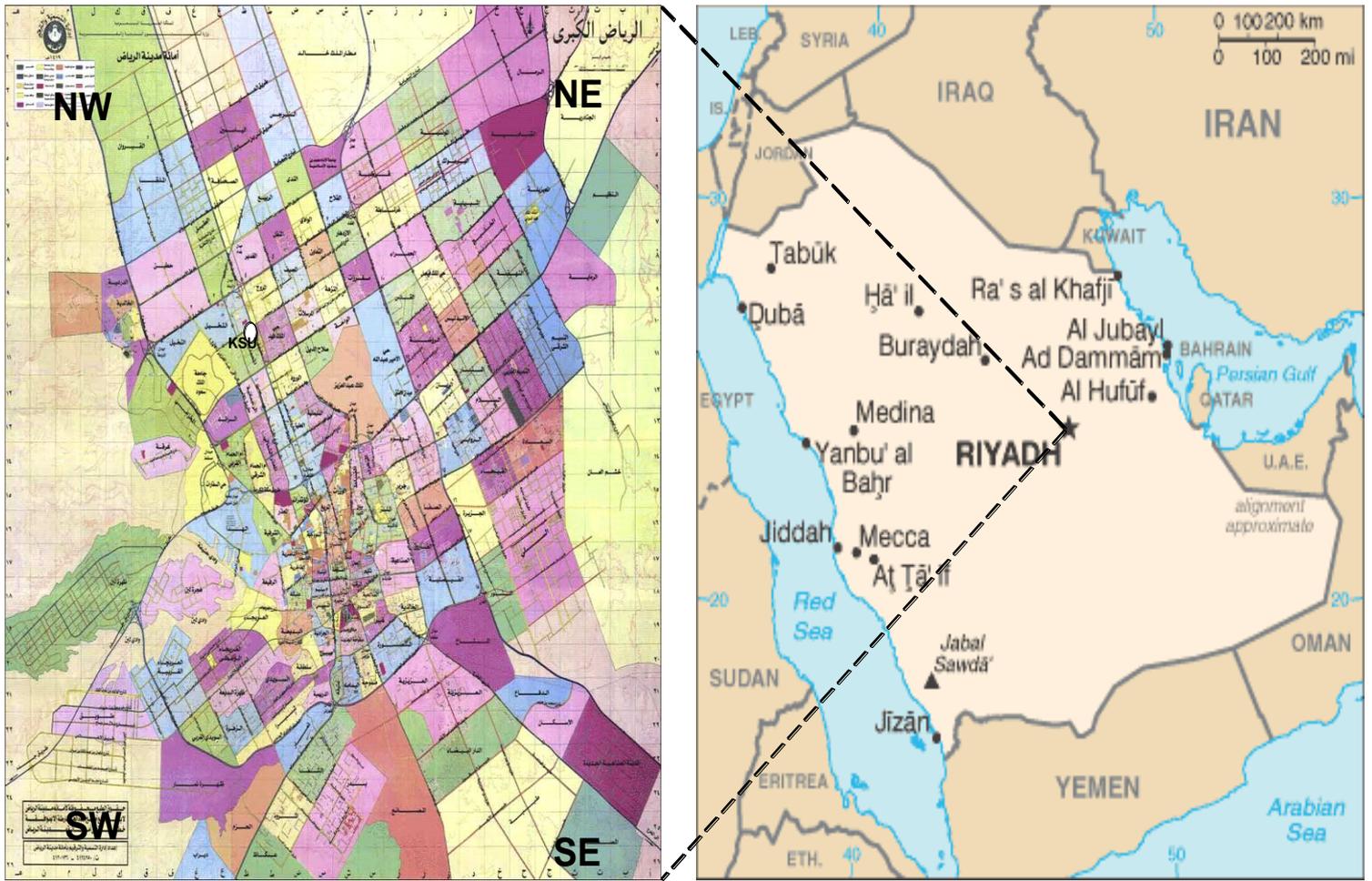


Figure 1 Map of Saudi Arabia showing Riyadh city, with enlargement of the urban area showing the sampling location

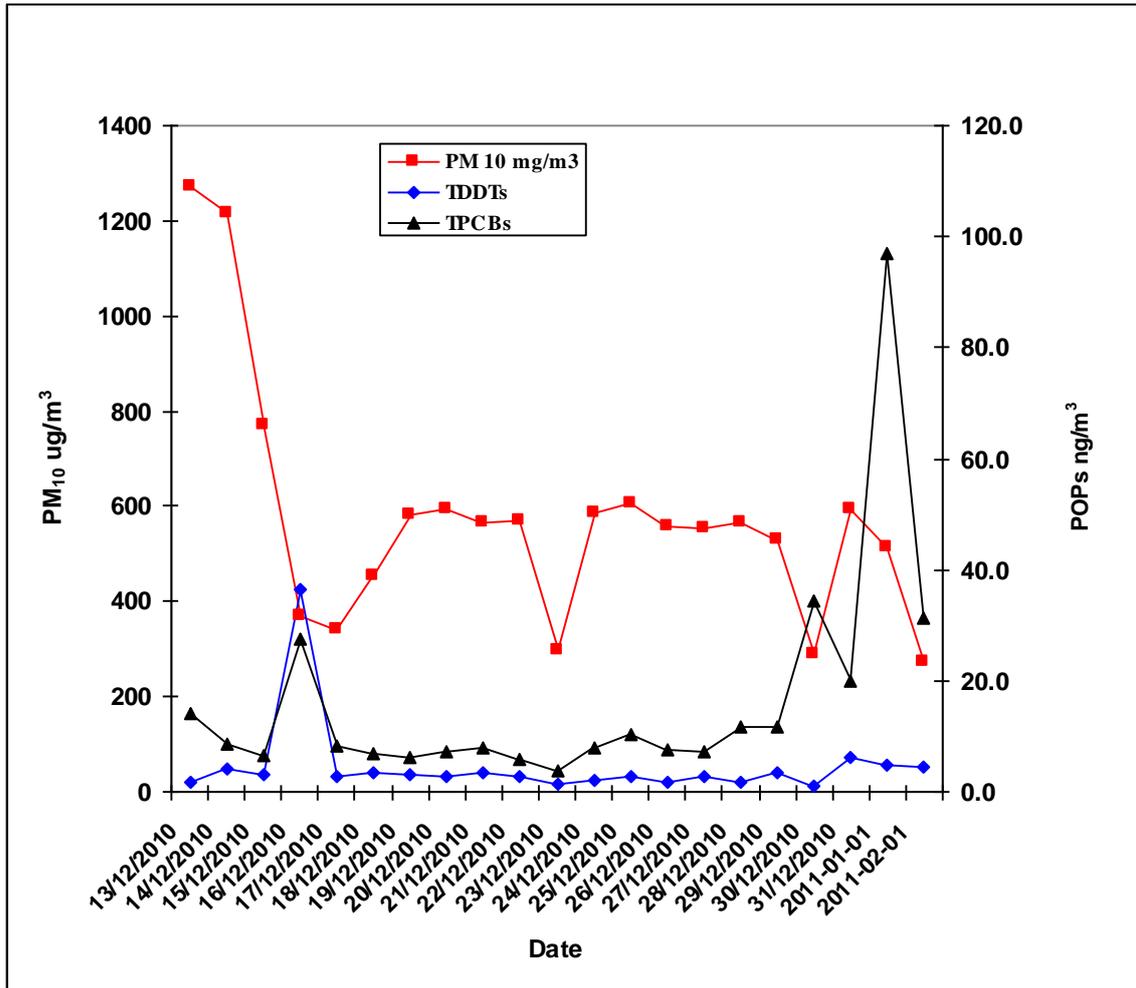


Figure 2a Daily concentrations of PM10 total DDTs and total PCBs in the ambient air of Riyadh during December- 2010- January 2011.

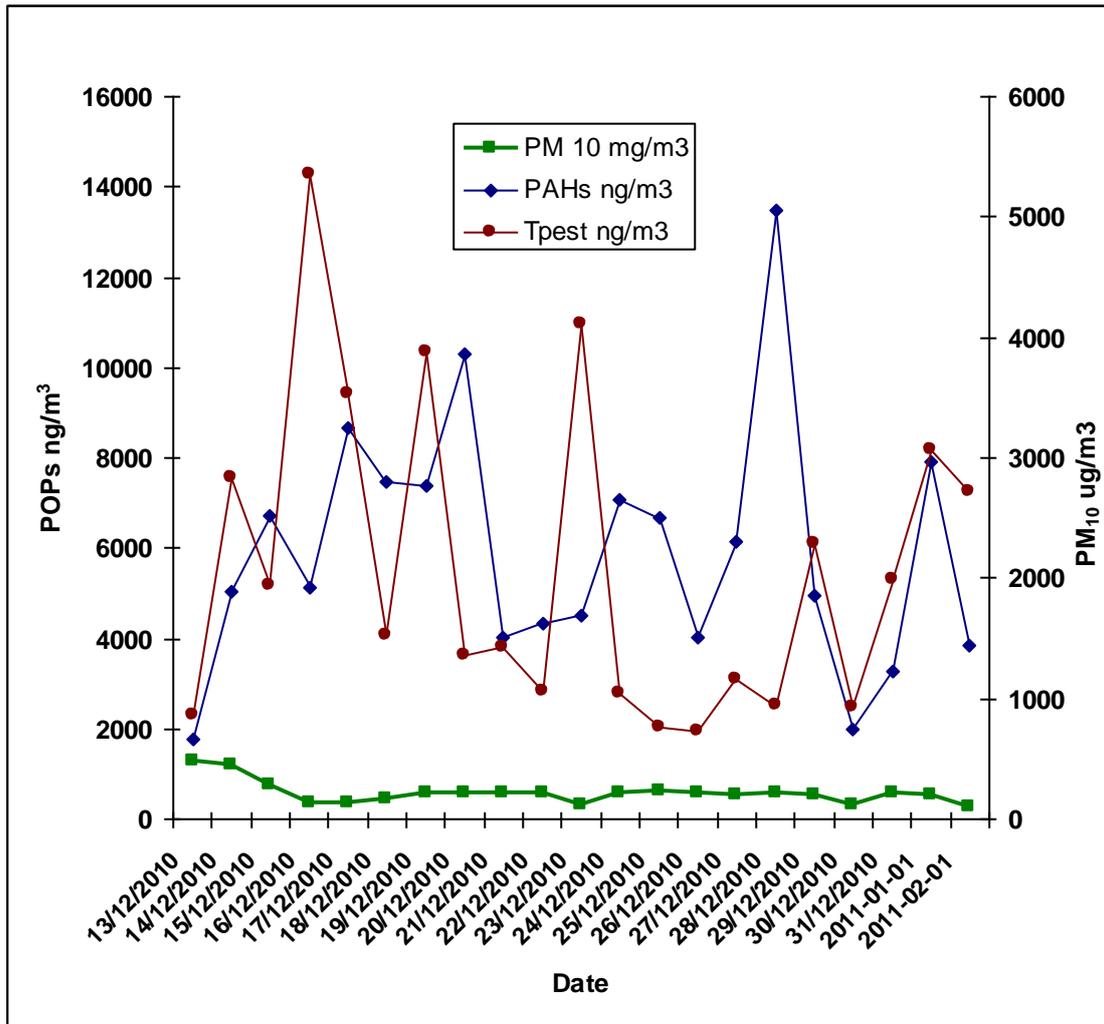


Figure 2b Daily concentrations of PM10 total PAHs and total pesticides in the ambient air of Riyadh during December- 2010- January 2011.

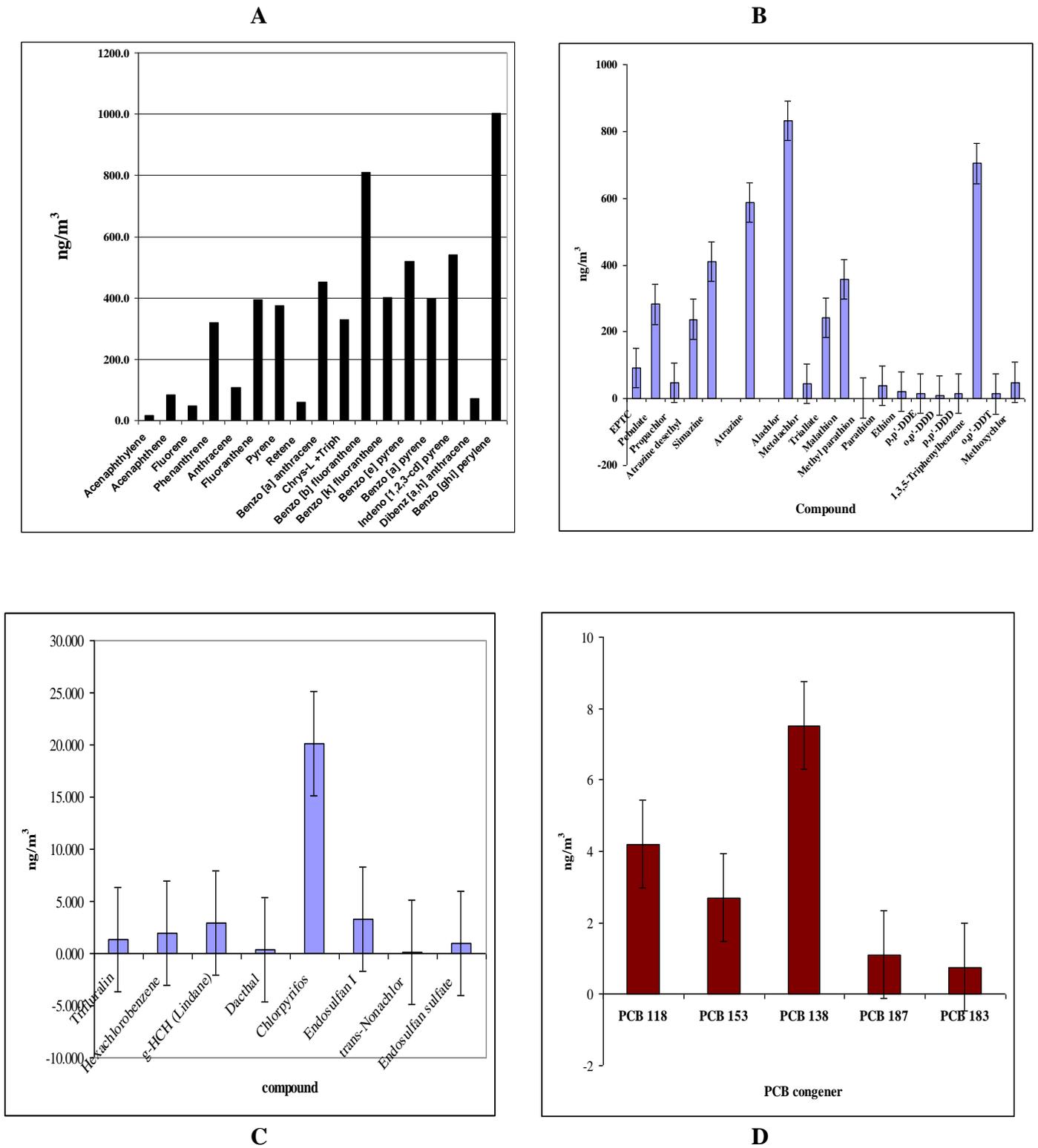


Figure 3 GC-MS average concentrations in PM10 ambient air of Riyadh city during December 2010 (A-PAHs, B- pesticides in EI-SIM, C- pesticides in CI-SIM, D- PCBs in CI-SIM mode)

Table 1 Sample general characteristics of particulate matter from ambient air of Riyadh

ID	Date	24 h time (min)	Net weight (mg)	Ambient concentration mg/m <sup>3</sup>	Temperature °C	Pressure (mbar)	Relative Humidity %	Wind Speed (m/s)	Wind Direction
HV-01	13/12/2010	1442	2199	1.27	15.2	946.5	35	4.1	N
HV-02	14/12/2010	1455	2122	1.22	12.3	952.2	37	3.1	N
HV-03	15/12/2010	1425	1316	0.77	12.6	950.3	42	1.0	SE
HV-04	16/12/2010	360	160	0.37	16.5	949.9	37	1.5	SE
HV-05	17/12/2010	1425	579	0.34	17.3	948.0	26	1.5	SE
HV-06	18/12/2010	1440	782	0.45	14.5	947.6	31	1.0	S
HV-07	19/12/2010	1440	1003	0.58	18.9	947.8	32	0.5	NNE
HV-08	20/12/2010	1462	1039	0.59	08.1	950.8	39	1.5	E
HV-09	21/12/2010	1420	966	0.57	07.8	952.2	47	1.5	NNE
HV-10	22/12/2010	1451	990	0.57	13.6	950.2	43	2.1	NNW
HV-11	23/12/2010	1557	553.7	0.30	13.1	947.4	43	1.5	NNW
HV-12	24/12/2010	1294	912	0.59	13.0	947.0	42	1.0	NE
HV-13	25/12/2010	1500	1092	0.61	14.2	947.3	43	1.0	E
HV-14	26/12/2010	1400	935	0.56	13.6	942.9	45	1.5	NE
HV-15	27/12/2010	1427	946	0.55	11.6	949.1	37	1.5	NW
HV-16	28/12/2010	1440	980	0.57	09.5	949.6	39	1.0	W
HV-17	29/12/2010	1414	895	0.53	10.7	950.1	36	1.5	SE
HV-18	30/12/2010	1430	498	0.29	14.1	948.1	41	4.6	SE
HV-19	31/12/2010	1450	1031	0.59	16.6	945.9	40	3.6	SSE
HV-20	01/01/2001	1405	868	0.51	13.1	948.8	57	1.5	N
HV-21	02/01/2011	1455	475	0.27	12.8	948.8	51	1.0	E

\*Note: Data were taken from the office of the Presidency for Meteorology and Environment in King Khalid International Airport, Riyadh, Saudi Arabia

Table 2 Analytical characteristic of PAHs determined by GC-MS-EI and CI in SIM mode

Parameter	Mean <sup>1</sup> ng/m <sup>3</sup>	± Stdev <sup>2</sup>	Min <sup>3</sup> ng/m <sup>3</sup>	Max <sup>4</sup> ng/m <sup>3</sup>	Ret. Time <sup>5</sup> min	Q-Ion <sup>6</sup> m/z	LOD <sup>7</sup> ng/ml	LOQ <sup>8</sup> ng/ml	Mean % Rec <sup>9</sup>
<b>PAHs EI-SIM</b>									
Acenaphthylene	18	8	4	40	16.61	152.1	2	7	42
Acenaphthene	84	72	24	296	17.29	154.1	1	3	42
Fluorene	47	41	14	178	19.39	166.1	1	3	42
Phenanthrene	321	197	109	765	23.15	178.1	3	10	56
Anthracene	107	115	21	432	23.19	178.1	1	3	56
Fluoranthene	395	221	134	991	27.88	202.1	1	3	79
Pyrene	376	160	87	774	28.72	202.1	3	10	79
Retene	59	31	29	149	30.18	219.1	1	3	79
Benz[a]anthracene	451	259	30	1224	33.57	228.1	1	1	70
Chrysene + Triphenylene	330	196	39	811	33.66	228.1	1	1	70
Benzo[b]fluoranthene	810	365	125	1602	37.56	252.1	1	1	70
Benzo[k]fluoranthene	402	446	28	1682	37.66	252.1	1	1	70
Benzo[e]pyrene	521	251	71	1060	38.45	252.1	1	3	70
Benzo[a]pyrene	400	248	32	945	38.62	252.1	1	3	78
Indeno[1,2,3-cd]pyrene	542	243	71	1017	42.17	276.1	1	3	80
Dibenz[a,h]anthracene	72	58	10	202	42.32	278.1	2	7	80
Benzo[g,h,i]perylene	1003	597	92	2281	43.02	276.1	1	1	80
<b>Pesticides EI-SIM</b>									
EPTC	91	49	0	190	14.38	128.1	1	3	69
Pebulate	282	163	108	911	16.72	128.1	1	3	69
Propachlor	47	122	0	437	19.6	120.1	2	7	69
Atrazine desethyl	238	502	0	2227	21.07	172	1	3	69
Simazine	409	1410	0	6447	22.41	201.1	2	7	69
Atrazine	587	809	0	3225	22.31	200.1	1	3	69
Alachlor	833	2202	0	10398	25.15	188.1	2	7	69
Metolachlor	44	48	-1	189	26.07	162.1	1	3	69

Triallate	242	349	0	1366	23.78	268	2	7	69
Malathion	358	417	0	1603	26.16	173.1	3	10	69
Methyl parathion	2	5	0	16	24.46	263	3	10	69
Parathion	39	34	20	171	26.7	291	3	10	69
Ethion	22	25	3	93	30.79	231	2	7	69
p,p'-DDE	15	25	0	123	29.58	317.9	1	3	69
o,p'-DDD	11	10	0	37	29.87	235	2	7	69
p,p'-DDD	15	31	2	147	30.86	235	2	7	69
1,3,5-Triphenylbenzene	704	388	69	1620	39.51	306	2	7	69
o,p'-DDT	14	27	2	131	30.86	235	2	7	69
Methoxychlor	49	84	4	347	33.89	227.1	2	7	69
<b>Pesticides CI-SIM</b>									
Trifluralin	1	1	0	3	14.23	335.1	1.0	1.0	77
Hexachlorobenzene	2	2	1	12	15.06	283.8	0.3	0.3	77
g-HCH (Lindane)	3	2	0	5	16.53	71	1.0	1.0	77
Dacthal	0	0	0	1	21.98	332	0.5	0.5	77
Chlorpyrifos	20	24	7	122	21.8	313	1.0	1.0	77
Endosulfan I	3	8	0	36	25.31	403.9	1.0	1.0	77
trans-Nonachlor	0	0	0	1	25.47	443.9	0.5	0.5	77
Endosulfan sulfate	1	0	0	2	29.82	385.9	0.5	0.5	77
<b>PCBs CI-SIM</b>									
PCB 118	4	11	0	51	28.02	325.9	0.5	0.5	77
PCB 153	3	2	1	9	29.01	359.9	0.3	0.3	77
PCB 138	8	6	2	27	30.18	359.9	3.0	3.0	77
PCB 187	1	1	0	5	30.85	393.9	0.5	0.5	77
PCB 183	1	1	0	4	31.1	393.9	0.3	0.3	77

1 Mean concentration ng/m<sup>3</sup> (n = 21)

2 ± standard deviation ng/m<sup>3</sup> (n = 21)

3 Minimum concentration ng/m<sup>3</sup> (n = 21)

4 Maximum concentration ng/m<sup>3</sup> (n = 21)

5 Retention time in minute

6 Method limit of detection ng/ml

7 Method limit of quantification ng/ml

8 Mean % recovery based on isotopically labeled compounds