

Full Length Research Paper

The level of persistent, bioaccumulative, and toxic (PBT) organic micropollutants contamination of Lagos soils

Alani Rose*, Olayinka Kehinde and Alo Babajide

Department of Chemistry, University of Lagos, Akoka, Lagos, Nigeria.

Accepted 28 January, 2013

Lagos is a highly urbanized coastal city, with several water channels linking the Lagos lagoon, a major source of seafoods to the people of Lagos and its environs. Contamination of Lagos soil with persistent bioaccumulative and toxic organic micropollutants (PBTs) would not only affect the non-target species residing in the soil, but also a concern that the chemicals could find their way into the lagoon via soil run-off and leaching. Soil samples were collected from three busy areas of Lagos and analyzed for polychlorinated biphenyls (PCBs), organochlorine pesticides (OCS), and polycyclic aromatic hydrocarbons (PAHs). Gas chromatography with mass selective detector (GC/MSD) was used for the analyses. Iddo had the highest percent (%) organic carbon content of 39.39% with highest total PAHs of 2,706.93 ng/g. The highest total PCBs of 23.63 ng/g was found in Apapa. PCB 74 was the only PCB found in all the soils and ranged between 3.55 and 23.64 ng/g at two locations in Apapa. PBTs found in highest concentrations were naphthalene (1,625.10 ng/g) at Iddo, p,p'DDE (117.98 ng/g) at Okobaba, and PCB 74 (23.63 ng/g) at Apapa 1. The levels of PBTs in Lagos soils are hereby presented.

Key words: Soil, (PBTs), (GC/MSD), organic carbon, Lagos.

INTRODUCTION

The issues of persistent bioaccumulative and toxic organic micropollutants (PBTs) such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCs), and polycyclic aromatic hydrocarbons (PAHs), and chemicals management have become serious issues in Nigeria. This is due to the fact that, attention has not been paid to the inventory of chemicals and chemical wastes in the country until of recent, though the use of chemicals in Nigeria for agriculture, health and other economic activities is high. Activities that introduce high concentrations of these PBTs into the environment are taking place uncontrolled. PBT chemicals do not readily breakdown in the environment and are not easily meta-

bolized; however, these may accumulate in ecological food chains through consumption or uptake and may cause many health hazards to the environment and humans (Ashutosh et al., 2012). Both government and citizens have limited awareness of the consequences of living under the present environmental situation; comprehensive data on PBTs are presently not available; and no legislations are presently in place to control such acts.

The production of PCBs has been banned globally, but significant quantities of these chemicals may still be available, especially in developing countries like Nigeria where the importation of used old goods of all sorts is still in progress. Old computers, electronics, electrical and home appliances, among other goods are being brought into Nigeria on daily basis. Electronic wastes are openly burnt and dumped at uncontrolled locations all over the country, especially in Lagos which is the most highly

*Corresponding author. E-mail: ralani@unilag.edu.ng. Tel: 2348025213236.

populated city in Nigeria, presently harboring not less than 15% of the total population (140 million) and about 80 to 85% of the industries in Nigeria. Several health effects are associated with PCB contamination (WHO, 1992).

Presently OCs are still in use for the control of vectors of diseases, including malarial mosquitoes and the ectoparasites that transmit typhus in Nigeria. Also, dichlorodiphenyltrichloroethane (DDT) is used for the control of agricultural and forest pests and so OCs are expected in the Lagos environment. There is a high tendency of these OCs being circulated by air masses as well as washed into the lagoon during rainy season and via the drainage systems. OCs has been identified as endocrine disrupting substances, which makes the exposure to these substances quite unsafe.

The concern about PAHs is that some of the compounds are toxic, mutagenic, or are known or suspected carcinogens.

Apart from being washed into the lagoon via runoffs and leaching, plants and animals can take up these PBTs directly from the contaminated soils. In the investigation of the uptake of trace elements and PAHs by vegetables grown in soils contaminated by trace elements and PAHs (Larsen et al., 2002), higher concentrations of these contaminants were found in vegetables grown in contaminated soils than those grown on uncontaminated soils. Another study by Edwards (1988) revealed that plants take up these pollutants through various pathways, including root uptake and atmospheric deposition from gaseous or particulate forms. Human health is therefore endangered by the consumption of vegetables grown on soils contaminated by PBTs. Consumption of PBT-contaminated foods is the most significant route of exposure to PBTs for the general human (Leeuwen and Vermeire, 2007).

According to Sezgin et al. (2003), soil pollution may threaten human health not only through its effect on the hygiene quality of food and drinking water, but also through its effect on air quality, for example, enriched pollutant contents in airborne particles originating from soil.

Presently, monitoring and toxicity data on PBTs in Nigerian soils are not available, and so the extent of pollution in the country in general and Lagos in particular is unknown.

The International persistent organic pollutants (POPs) elimination project (IPEP), in its awareness-raising on socio-economic effects of POPs in Nigeria in May, 2006, stressed the need to take an inventory of all the sources of POPs in the Nigeria, and also to generate a database on the current environmental levels of POPs in the country.

Considering the type of activities that take place in Lagos and the ever fast growing population of the city, it was deemed necessary to carry out this study. Survey of pollutants contents is a key to effective management of soil quality (Weiss et al., 1994). This work therefore aimed at

providing a baseline information on PBTs by monitoring the level of PBTs (PCBs and OCs) and PAHs in Lagos soils and evaluating the soil environmental quality in terms of these pollutants in Nigeria.

MATERIALS AND METHODS

Sampling and sample preparation

Soil samples were collected from two locations (Iddo and Okobaba) close to the lagoon in December, 2006. The samples were air-dried in aluminium wrapped trays for about a week, sieved through a 2 mm mesh screen, and packed in 100 ml amber glass bottles with aluminium sealed caps prior to extraction. Sample preparation and analysis was carried out according to Lazar et al. (1992). Moisture and organic carbon contents of the soil samples were determined.

Soil extraction by soxhlet method

Soil samples were extracted by soxhlet method (USEPA, 1996). Samples were extracted in groups of six, one of which was the blank containing 50 g of anhydrous sodium sulphate. 10 g anhydrous sodium sulphate (previously muffled at 450°C overnight) was added to a cleaned glass thimble. 5 g of air-dried soil sample was weighed into a labeled mortar and 50 g sodium sulphate added and ground until a free flow was attained.

A wide-mouthed glass funnel (funnel was well rinsed between samples) was used to transfer sample to the thimble containing the 10 g anhydrous sodium sulphate. The mortar was cleaned with 10 g of sodium sulphate. This was repeated with another 10 g sodium sulphate, and both added to the thimble. The label on the mortar was transferred to the thimble and the sample spiked with a known volume (100 µl that is, 200 ng/ml) of surrogate spiking solution, a mixture of three ¹³C-labelled PCBs (¹³C-PCB 52, ¹³C-PCB 153 and ¹³C-PCB 37), prior to soxhlet extraction. The standard reference material (SRM) also passed through the same process alongside the samples.

Soxhlet extraction was carried out with 300 ml of acetone: hexane (1:1) for 16 to 24 h. The soxhlet apparatus turned off and the samples allowed to cool for 4 h. Using rotary evaporator, the cooled samples were either concentrated to about 50 ml for back extraction or to about 2 ml for florisil clean up.

Back extraction of soil extracts

Samples with moisture content above 2% were concentrated to about 50 ml in a round bottomed flask and added to separating funnel with 200 ml of Millipore water for back extraction in order to remove the water before florisil cleanup. The flask was rinsed with 50 ml of hexane and added to the separatory funnel and shaken, releasing the pressure at intervals. The water was poured off into a beaker and reserved, while the hexane fraction was drained into same round-bottom flask that originally contained the sample. The tap of the separatory funnel was closed and the water placed into the funnel again. 25 ml of hexane was added and shaken. This was repeated and the hexane fractions combined.

Sodium sulphate extraction was then carried out. 25 ml of 50:50 dichloromethane (DCM): hexane was added to large sodium sulphate columns. Glass wool was added to each column. 30 g of sodium sulphate was also added to each column. The sample was then added to the column and the valve opened for the extract to drip at the rate of 3 drips/s. The round-bottom flask was rinsed 3 times using a total volume of 25 ml of 50:50 DCM: hexane. When the level of liquid in the column was just above the sodium sulphate

surface, 250 ml of 50:50 DCM: hexane was added and eluted. The extract was concentrated to about 2 ml, ready for florisil cleanup.

Sample analysis

Sample extracts obtained after florisil cleanup were combined and rotoevaporated to 1 ml and analyzed for PAHs, PCBs and OCs by gas chromatography (GC). Analysis was run on a Hewlett-Packard (Avondale, PA) Model 5890/5970 Gas chromatography with mass selective detector (GC/MSD) (quadrupole mass analyzer, 70eV) equipped with a Hewlett-Packard 7673A autosampler and a 30 m × 0.25 mm. I.D. × 0.10 μm DB-5 film thickness column. 1 μl sample was injected using a splitless injection mode at 250°C injection temperature and GC/MSD interface temperature of 280°C. A mixture of three ¹³C-labelled PCBs (¹³C-PCB 52, ¹³C-PCB 153 and ¹³C-PCB 37) was used as surrogate standard. The PAHs, PCBs, and OCs were identified and quantified by comparison of retention times and spectra of internal standards. The detection limit ranged between 0.02 to 0.06 ng/g for OCs, between 0.03 to 0.11 ng/g for PCBs, and 0.02 ng/g for PAHs. Contaminants that were not detected were replaced with the detection limit value. Soil samples were analyzed for 16 PAHs, 209 PCBs, and 16 OCs and the results were expressed on dry weight basis.

Quality assurance/quality control

Quality assurance and quality control measures were carried out. The problem of interferences was extensively addressed. Instrument control, calibration, and stability were checked on regular bases and during each run. For PAHs, 6 levels of concentration were run for the calibration standard to determine the instrument linear range. The linear ranges for PCBs and OCs were also calibrated and confirmed to be accurate (that is, above 0.99 for each of the analytes before the GC/MSD was run). The instrument detection limit (IDL) was also determined for each analyte. For the method quality control, the samples were run in batches. Each batch (of not more than 12) consisted of a blank, SRM, and the samples. The blank helped to ensure that contaminants, even the target analytes, were not introduced into the samples due to poor laboratory practices. NIST SRM 1944 which provided certified values for some OCs, PCBs and PAHs was used. This was for the purpose of determining the accuracy of the method. Duplicate of a sample was also used to determine the precision of the method. The SRM ensured that the samples were processed correctly and that the GC was detecting the analytes consistently overtime. All the samples in each batch were spiked with surrogate spiking standard. This helped in the determination of the percent (%) recovery. The problem of interference, apart from being checked in the blank, was also addressed by proper cleaning of glassware (there were methods for this and over 60% of the solvents used were for glassware cleaning), florisil cleanup of the extracts, gel permeation chromatography (GPC) cleanup, and the treatment of soil extracts with activated copper (prepared accordingly) for sulphur cleanup.

Percent moisture content determination

Aluminum boats were weighed and dried for 24 h and about 1 g of each air-dried soil, already homogenized in a mortar, was placed in the boat and weighed. The weighed boats with samples were placed in an oven and dried at 110°C for 24 h (overnight). After cooling they were weighed and their weights recorded. The moisture content was used for correction of the dried weight of sample actually taken for analysis.

Percent organic carbon content determination

Porcelain boats were labeled and dried in an oven at the temperature of 110°C for 24 h and kept in the desiccator. These boats were weighed and 1 g of each air-dried soil sample, already homogenized in a mortar, was placed in the labeled porcelain boat, and weighed. The boats with samples were placed in a furnace and muffled at 450°C for 24 h (overnight). The boats were removed from the furnace and placed in a desiccator and allowed to cool. They were weighed and the percent organic carbon was calculated.

RESULTS AND DISCUSSION

Soil properties

The properties investigated in the soil samples are shown in Table 1. The organic carbon contents ranged between 0.47% at Apapa 1 to 39.39% at Iddo. Organic carbon content at Okobaba was equally high (24.95%) compared to those at Apapa locations. Moisture contents ranged between 2.07 and 6.49%, with Apapa 1 having the highest moisture content of 6.49%, while Iddo and Okobaba had close values of 4.22 and 4.92%, respectively.

PAHs

The concentrations of individual PAHs determined in the soil samples are shown in Table 2. Sum PAHs, which comprise 16 Environmental Protection Agency (EPA) priority PAHs, ranged between 30.92 to 2,706.93 ng/g. The highest PAH level was found in Iddo soil which showed the influence of high municipal activities (industrial, agricultural, municipal and domestic waste burning and disposal, and several other activities). At Iddo, only Anthracene, Benzo(k)fluoranthene, Benzo(b)fluoranthene, and Benzo(g,h,i)perylene were below the Dutch values for unpolluted soil. The values at Apapa were all below the Dutch values for unpolluted soil (Table 2), except for Phenanthrene, Fluoranthene and Chrysene at Apapa 2. Benzo(a)pyrene, a known carcinogen which has sufficient evidence of carcinogenicity in experimental animals according to the estimation of the International Agency for Research on Cancer (Manoli et al., 2000), was identified in all soil samples. BaP concentration in Okobaba soil (59.59 ng/g) was found to be above the target level of 25 ng/g (Table 2) set by Dutch government.

The PAH levels in Lagos soils, at some locations such as Iddo (Table 2), competes greatly with the levels found by Zohair et al. (2006) in soils from organic farms in England ranging from 590 ± 43 to 2301 ± 146 ng/g (Table 3). Based on reported background, PAHs concentrations of 2 to 22 ng/g in Bulgaria by Atanassov et al., (2001) and suggested level of endogenous total PAHs concentrations of 1 to 10 ng/g in soils (Edwards, 1983), it

Table 1. Analysis of moisture and organic carbon contents of soil samples from Lagos in December, 2006.

Soil property	Sample locations				
	Iddo	Okobaba	Apapa 1	Apapa 2	Apapa 3
Percent moisture	4.22	4.92	2.07	6.49	2.36
Percent organic carbon	39.39	24.95	0.47	4.97	0.92

Table 2. PAH concentrations in soil samples from different locations in Lagos, Nigeria in December, 2006, and Dutch target values for unpolluted soil (VROM, 1994).

Soil PAHs (ng/g)	Apapa 1	Apapa 2	Apapa 3	Okobaba	Iddo	Dutch target value
LMW PAHs						
NA	ND	1.54	11.20	355.03	1625.10	
AL	0.54	0.59	ND	ND	35.52	
AE	ND	1.11	10.61	ND	45.43	
FL	0.41	1.56	10.85	17.31	60.97	
PHE	1.21	9.79	56.31	225.80	497.34	45
AN	2.69	4.34	6.71	18.66	ND	50
HMW PAHs						
FLT	1.46	16.41	65.53	96.79	144.81	20
PY	4.59	24.18	61.14	79.47	149.64	
B(a)A	0.59	7.68	18.89	32.74	23.42	20
Chrysene	5.30	7.69	20.12	76.76	75.49	20
B(b)F	1.77	10.42	20.93	47.79	21.02	
B(k)F	1.08	6.74	14.63	37.29	16.56	25
B(a)P	7.39	13.70	9.02	59.59	3.70	25
IP	1.49	5.59	10.80	39.97	ND	25
D(ah)A	ND	ND	1.87	5.39	ND	
B(ghi)P	2.42	ND	13.41	32.84	7.93	20

ND, No detection.

Table 3. Comparing PAH contents of Lagos soils with literature data.

Soil	Concentration (ng/g)	References
Lagos	0.41 - 1625.10	Reported in this research
England farmland	590 - 2301	Zohair et al. (2006)
Bulgaria	2 - 22	Atanassov et al. (2001)
Italy	89.5 - 4488	Morillo et al. (2007)
Italy	100 - 1000	Minissi et al. (1998)
Czech Republic	1000	Sanka (2001)
Japan	80 - 1640	Škrbić et al. (2005)

could be concluded that Lagos soils are contaminated above the natural and background level as majority of the values range above 10 ng/g (Table 2).

PAH concentrations in Lagos soils at Apapa 3, Okobaba and Iddo ranging from 56.31 to 1625.10 ng/g, compare greatly with the range of background PAHs levels between 89.5 to 4488 ng/g in soils in Italy as

reported by Morillo et al. (2007), 100 to 1000 ng/g as reported by Minissi et al. (1998), 1000 ng/g in Czech Republic as reported by Sanka (2001), and 370 to 770 ng/g for Krakow in Poland, 800 to 1,300 ng/g and 80 to 1,640 ng/g in Japan as reported by Škrbić et al. (2005).

Individual PAH concentrations (including BaP concentration of 59.59 ng/g) at Okobaba were all above

Table 4. PCB concentrations in soil samples from different locations in Lagos in December, 2006.

Soil PCB (ng/g)	Apapa 1	Apapa 2	Apapa 3	Okobaba	Iddo
PCB18	ND	ND	ND	0.39	0.72
PCB16/32	ND	ND	ND	0.17	0.20
PCB31/28	ND	ND	ND	0.76	ND
PCB33/20	ND	ND	ND	0.15	ND
PCB52	ND	ND	0.36	ND	ND
PCB49	ND	ND	0.65	ND	0.64
PCB47/48	ND	ND	0.37	ND	ND
PCB40	ND	2.31	ND	ND	ND
PCB74	9.29	23.64	3.55	9.54	5.01
PCB95	ND	ND	0.39	0.35	0.16
PCB101	ND	ND	0.27	ND	0.24
PCB99	ND	ND	0.39	ND	ND
PCB110	ND	ND	ND	0.41	ND
PCB105	ND	ND	0.85	4.04	ND
PCB136	ND	ND	ND	ND	0.10
PCB149	ND	0.21	0.33	0.59	0.33
PCB153	ND	0.12	0.61	0.92	0.48
PCB138	ND	ND	0.24	0.77	0.43
PCB187/182	ND	ND	0.30	ND	0.24
PCB183	ND	ND	ND	ND	0.07
PCB185	ND	ND	ND	ND	1.16
PCB174	ND	ND	ND	ND	0.26
PCB177	ND	ND	ND	ND	0.11
PCB171	ND	ND	ND	ND	0.46
PCB180	ND	ND	0.60	ND	0.45
PCB201	ND	ND	0.23	ND	ND
PCB196/203	ND	ND	0.23	ND	ND

ND, No detection.

the target values set by Dutch government for unpolluted soil for almost all studied cases except for Anthracene. PAHs were found at levels. At Apapa, few PAHs were found to be higher in concentrations than the Dutch government target values. The PAHs that were not detected at some locations include Naphthalene, Acenaphthylene, Acenaphthene, Anthracene, Dibenzo(ah)anthracene, Indeno(1,2,3,cd)pyrene and Benzo(ghi)perylene. PAHs found in high concentrations include Naphthalene, Phenanthrene, Fluoranthene, Pyrene, Chrysene, and Benzo(a)pyrene. The most contaminated locations with PAHs were Iddo (a very busy, highly populated residential, commercial and industrial area of Lagos) and Okobaba, while the least contaminated was Apapa 1.

PCBs

Soil samples were analyzed for 72 PCBs but only 27 PCBs were found as shown in Table 4. The PCB

concentrations in Lagos soils which ranged from 0.07 ng/g of PCB183 in Iddo soil to 9.54 ng/g of PCB 74 in Okobaba compared well with the concentrations of PCBs in soils from organic farms in England which ranged from 3.56 ± 0.73 to 9.61 ± 1.98 ng/g as reported by Zohair et al. (2006), except for 23.64 ng/g of PCB74 in Apapa 2 soil. Background PCB concentrations in various types of soil in Poland which ranged between 2.3 to 38 ng/g (Falandysz et al., 1997), and 1 ng/g in Bulgaria (Atanassov et al., 2001) were very similar to the values obtained in Lagos soils.

As shown in Table 5, PCB concentrations were similar in many countries with exception of slightly higher values (0 to 134 ng/g) in Romania, and more pronounced in Katowice town in Poland (67 to 870 ng/g) reported by Škrbić et al. (2005). The most abundant PCB, which was also present in all the soils, was PCB74 and was found in Apapa 2. Generally, Apapa area of Lagos is a highly populated residential and industrial area where oil related activities concentrate. More PCB congeners were found in Iddo, Apapa 3 and Okobaba, though in low

Table 5. Comparing PCB contents of Lagos soils with literature data.

Soil	Concentration (ng/g)	References
Lagos	0.07 - 23.64	Reported in this research
England farmland	3.56 - 9.61	Zohair et al. (2006)
Bulgaria	1.00	Atanassov et al. (2001)
Poland	2.3 - 38	Falandysz et al. (1997)
Poland	67 - 870	Škrbić et al. (2005)

Table 6. OC concentrations in soil samples from different locations in Lagos in December, 2006.

Soil OCs (ng/g)	Apapa 1	Apapa 2	Apapa 3	Iddo	Okobaba
1245-TCB	ND	ND	ND	1.09	2.18
1234-TCB	ND	ND	ND	0.90	1.23
QCB	ND	ND	ND	1.07	1.40
HCB	ND	ND	ND	1.60	0.48
a-BHC	ND	ND	ND	4.15	1.01
b-HCH	ND	ND	ND	10.05	ND
d-HCH	ND	ND	ND	ND	ND
g-HCH	4.62	ND	ND	ND	ND
Trans-chlordane	0.28	ND	ND	ND	ND
Cis-chlordane	0.29	ND	ND	ND	ND
Trans-nonachlor	0.48	ND	ND	ND	ND
p,p'DDE	4.66	ND	ND	2.33	117.98
p,p'-DDD	ND	ND	ND	0.98	63.61
Cis-nonachlor	0.13	ND	ND	ND	ND
p,p'-DDT	ND	ND	ND	29.56	33.22
Mirex	ND	0.60	ND	ND	ND

concentrations. In Apapa 1, only PCB74 (9.29 ng/g) was found.

OCs

Lagos soil samples were investigated for OCs based on the standard mixture of 16 OCs and 15 of them were found as shown in Table 6. No OC was found in Apapa 3 soil, also d-HCH was not found in any of the soil samples evaluated. The concentrations of OCs in Lagos soils which ranged from 0.13 to 117.98 ng/g were in some cases below and in some cases within the range (52.2 ± 4.9 to 478 ± 111 ng/g) obtained in soils from organic farms in England by Zohair et al. (2006). Among the OCs, p,p'-DDE, p,p'-DDD and p,p'-DDT predominated with concentrations of 118.00, 63.61, and 33.22 ng/g, respectively in Lagos soils. Apart from the DDTs, β -HCH predominated with the concentration of 10.05 ng/g. This strongly agreed with the report by Zhang et al. (2005) that among the OCs and their homologues or isomers analyzed in Hong Kong soils, β -HCH and p,p'-DDE were the two predominant substances according to the

concentrations and detectable ratios, though the concentrations in Lagos soils were higher than the values (6.12 and 0.41 ng/g for β -HCH and p,p'-DDE, respectively) in soils from that report.

Two HCH isomers were found in Lagos soils. Gamma-HCH (lindane) was found in only the samples from Apapa 1 (4.62 ng/g), while β -HCH (10.05 ng/g) was found also in one sample from Okobaba (a slum settlement at the shore of the lagoon). The use of OCs for insect vectors and pest control is expected to be relatively high around this location. Also, the HCHs are very useful for the treatment of timber against wood boring insects (Walker, 2009). This was also a likely source of OCs at Okobaba where wood business is the major business of the inhabitants. High concentration of gamma-HCH at this location could therefore be attributed to the pattern of use, which is one of the factors that influence OC distribution, according to Mackay et al. (1997).

Lindane in Lagos soil was present within the level (1.54 to 5.60 ng/g) observed by Manz et al. (2001) in agricultural soils in central Germany, and much higher than the level (0.9 ng/g) reported by Holoubek et al. (1999) for Slovak Republic. Concentration for p,p'-DDT in

Table 7. Comparing OC contents of Lagos soils with literature data.

Soil	Concentration (ng/g)	References
Lagos	0.13 - 117.98	Reported in this research
Lagos	4.62 (Lindane)	Reported in this research
Central Germany	1.54 - 5.60 (Lindane)	Manz et al. (2001)
Lagos	29.56 - 33.22 (p,p'DDT)	Reported in this research
Czech Republic	1.0 - 1.05.1 (p,p'DDT)	Holoubek et al. (1999)
England farms	52.2 - 478	Zohair et al. (2006)
Slovak Republic	0.9	Holoubek et al. (1999)
Bulgaria	2.83 - 423.60	Shegunova et al. (2001)

Table 8. Sum PBTs (ng/g dry weight sample) in soils from different locations.

Location	PAHs (ng/g)	PCBs (ng/g)	OCs (ng/g)	Percent organic carbon
Iddo	2706.93	11.02	51.73	39.39
Okobaba	1125.00	18.08	221.11	24.95
Apapa	30.92	9.29	10.47	0.47
Apapa 1	111.30	26.27	0.59	4.97
Apapa 2	332.00	9.35	0.00	0.92

Lagos soils were above the range (1.0 to 5.1 ng/g) reported in some European countries by Holoubek et al. (1999) for Czech Republic and 0.26 to 17.86 ng/g by Škrbić et al. (2005) for Novi Sad (Table 7). Our result was found within the range (2.83 to 423.60 ng/g) reported by Shegunova et al. (2001) for Bulgaria. Concentration for p,p'-DDE was the highest (117.98 ng/g) in Lagos soil at Iddo, a location with very high municipal and agricultural activities. At location A (Iddo), p,p'DDT was the highest in concentration (29.56 ng/g), followed by b-HCH (10.05 ng/g). At B3 (Okobaba), the DDTs were very high in concentration (p,p'DDE, 117.98 ng/g; p,p'DDD, 63.61; and p,p'DDT, 33.22 ng/g) compared to other OCs (ranging between 0.48 ng/g of HCB to 2.18 ng/g of 1245-TCB). Okobaba sample site is actually a slum settlement by the lagoon front, where mosquito breeding rate could be very high. The key factor responsible for p,p'DDT concentration is the pattern of use (Mackay et al., 1997). DDT containing pesticides appeared to be used more for mosquito control in Okobaba area than in Iddo.

Sum PBTs

The results from this study showed that PBT contamination of Lagos soils vary with locations. Table 8 showed that PAHs were the most abundant of the contaminants assessed in Lagos soils, with Iddo soil having the highest sum PAHs of 2706.93 ng/g. Of all the locations assessed in this study, Iddo is the one with highest municipal activities. This result therefore agrees with the report by Van metre et al. (2000), that the largest

concentrations of PAHs generally are found in urbanized areas, where the potential sources include atmospheric deposition, surface runoff, municipal wastes, sewage effluents, industrial effluents, and spills and leakage of fossil fuels. It was also noticed that Iddo soil also had the highest percent organic carbon of 39.39%.

Sum PAHs content in some locations in Lagos (Iddo and Okobaba) were above (2706.93 to 1125.00 ng/g), and in some cases (Apapa soils) lower (30.92 to 332.00 ng/g) than the values of the ones determined for the agricultural soils of Czech Republic (693 to 1,067 ng/g) by Škrbić et al. (2005), and Slovakia (204 to 1,093 ng/g) by Linkeš et al. (1997).

Sum PAHs of 1,125.00 ng/g was found at Okobaba, and this reflected the influence of the incessant burning of saw dust and domestic wastes that take place at this location. Sum PAHs at Iddo was 8 to 90-fold higher than the values at Apapa locations, which are mainly influenced by oil related activities. Also, sum PAHs at Okobaba was 3 to 24-fold higher than those of Apapa locations. Sum PAH determined in Lagos soils were much lower than the intervention value for soil sanitation (40,000 ng PAHs/g) used by the Dutch government (VROM, 1994; Van Brummelen et al., 1996).

Sum PCBs (27 PCBs found) determined in Lagos soil which ranged from 9.29 to 26.27 ng/g were far above (from 30 to 114 times) the range of values (0.36 and 0.23 ng/g) obtained in Novi Sad as reported by Sanka (2001), when compared.

Considering that the limit value for the sum OCs is 0.1 mg/kg (100 ng/g), according to Slovenian regulation (Zupan et al., 2001), the contents of the ones determined

Table 9. Relationship between PAHs at different locations.

ANOVA						
Source of variation	SS	df	MS	F	P-value	F _{critical}
Between groups	393630.4	4	98407.59	2.510638	0.05034	2.515318
Within groups	2508560	64	39196.25			
Total	2902190	68				

Table 10. Relationship between individual PAHs.

ANOVA						
Source of variation	SS	df	MS	F	P-value	F _{critical}
Between groups	908890.5	15	60592.7	1.611104	0.102215	1.859477
Within groups	1993300	53	37609.43			
Total	2902190	68				

at most of the investigated sites in Lagos (except Okobaba) did not exceeded the value of 0.1 mg/kg and therefore they could not be a threat to the environment at these locations. At Okobaba, sum OCs was 221.11 ng/g, which doubled the limit value, and so, there is a serious threat of OCs at Okobaba in Lagos.

Sum PAHs was least at Apapa 1 (30.92 ng/g) and the percent organic carbon content was also least at this location (0.47%). As indicated in Table 1 and Figure 1, positive correlation between percent organic carbon contents and contaminant concentration was mostly reflected in the PAHs. This agreed with the report by Smith et al. (1988) that PAHs and other nonpolar organic compounds are strongly associated with the organic fraction.

When organic carbon normalization was carried out on the soil data, the variation in contaminant levels at different locations changed greatly. As shown in Figures 2 and 3, Iddo which had the highest PAH concentration leveled up with the other locations, while Apapa 3 which had low PAH concentration (Figure 2) became the most contaminated with PAHs (Figure 3). Other PBTs also leveled up on organic carbon normalization, especially at Apapa 1 location. With organic carbon normalization, Apapa 2 was seen as the most contaminated location with PAHs and PCBs, while Okobaba remained the most contaminated location with OCs.

Statistical analysis of soil PBTs using one way analysis of variance (ANOVA)

One way ANOVA was used to statistically correlate the PBTs (PAHs, PCBs, and OCs) in Lagos soils at various locations. The P-values (significant) showed how significantly different the factors in each group were. Statistically significant correlations were defined as those

with P-values less than or equal to 0.05, (Harwell et al., 2003).

PAHs

Table 9 shows that $F_{\text{calculated}}$ (0.05, 4, and 64) was 2.5106 and was less than the F_{critical} of 2.5153. Therefore, 'null hypothesis' was accepted and this indicated that there was no statistical significant difference in the PAH concentrations with respect to sample locations. The P-value of 0.0503 being higher than 0.05 also indicated that there was no statistical significant difference in the PAH concentrations. Descriptive statistics showed that Iddo had the highest mean PAH concentration of 208.22 ng/g. This showed that more PAHs were generated at Iddo, and that Iddo was closer to PAH source points than other locations. Iddo also had the highest variance of 198507.10, while the values for other locations ranged from 4.50 (Apapa 1) to 9214.64 (Okobaba). This was likely due to different loadings as a result of diverse activities that generated the PAHs at different locations.

Table 10 shows that $F_{\text{calculated}}$ (0.05, 15, and 53) was 1.611104 and was less than the F_{critical} of 1.859477. Therefore, 'null hypothesis' was accepted and this indicated that there was no statistical significant difference between individual PAHs. The P-value 0.102215 being higher than 0.05 also indicated that there was no statistical significant difference between individual PAHs. Descriptive statistics showed that Naphthalene, the most water soluble and mobile PAH in various sample location, had the highest mean PAH concentration of 498.22 ng/g.

Naphthalene also had the highest variance of 591414.30, while the values for others ranged from 6.20 (D(ah)A) to 44159.89 (Phenanthrene). This is as a result of the difference in the physicochemical properties of

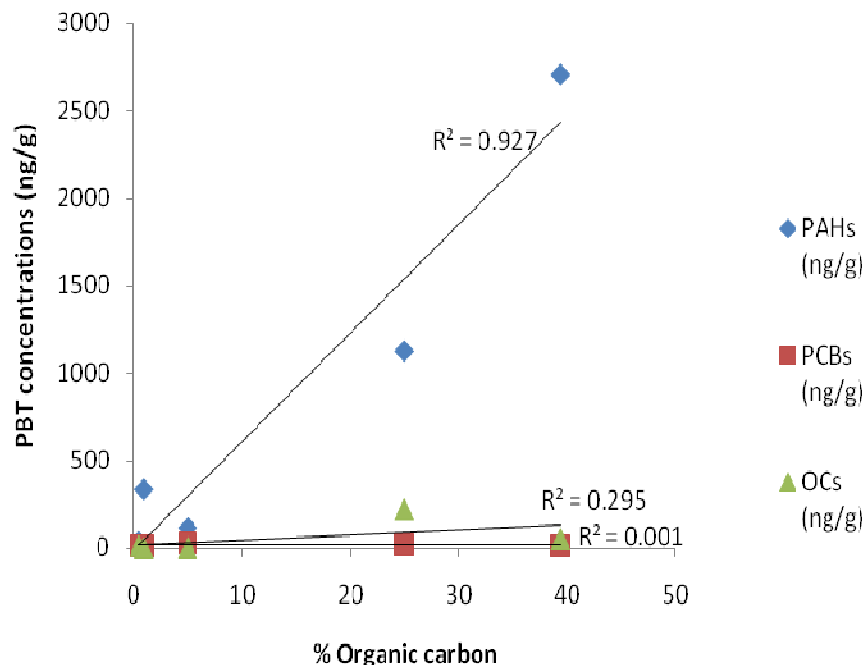


Figure 1. Correlation of organic carbon with PBTs in Lagos soils.

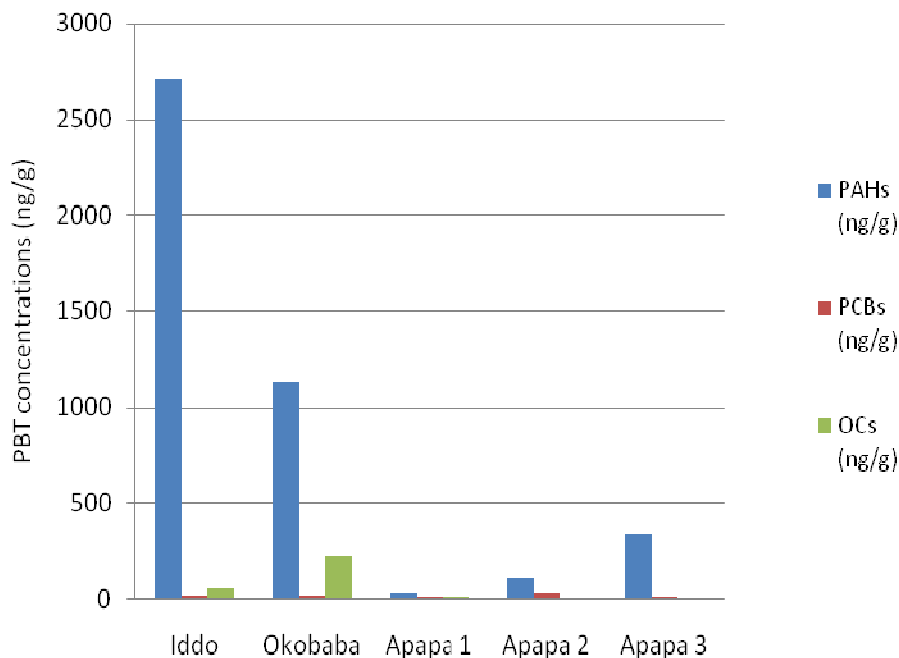


Figure 2. PBT concentrations (ng/g samples) at different locations.

different PAHs. Naphthalene is widely distributed in the environment, occurring as natural constituents of the fossil fuels and their anthropogenic pyrolysis products (Kanaly and Harayama, 2000). This report also agreed with that of Oosterbaan and Jamet (1998). According to

Oosterbaan and Jamet (1998), who investigated the pollution of the groundwater at the former gas work and coking plants sites, PAH contamination is primarily composed of Naphthalene, that is, Naphthalene was presented about 50% of the total PAH concentration in

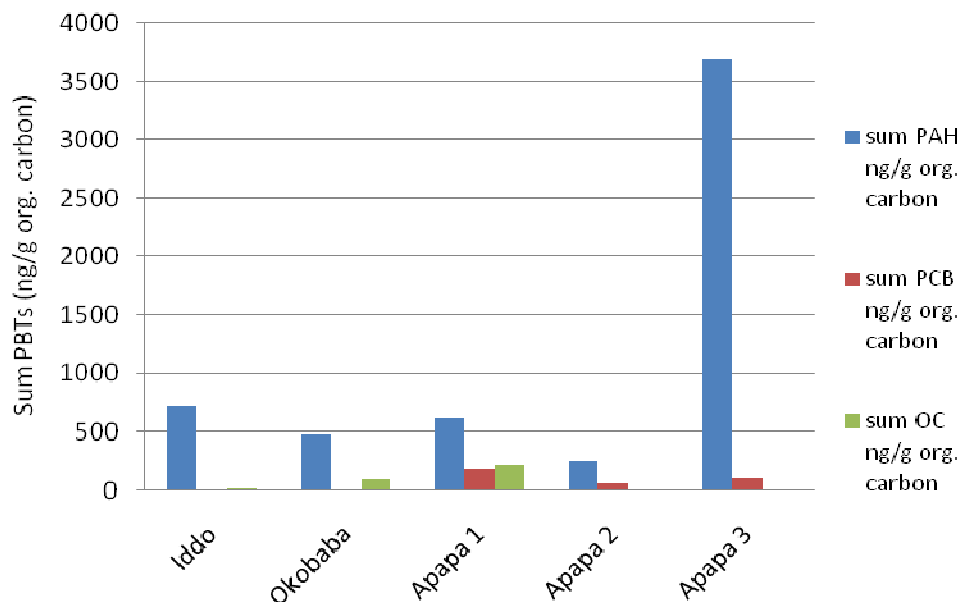


Figure 3. PBT concentrations on normalization with organic carbon at different locations.

Table 11. Relationship between PCBs at different locations.

ANOVA						
Source of variation	SS	df	MS	F	P-value	F _{critical}
Between groups	8.023871	4	2.005968	0.344953	0.847136	2.44135
Within groups	755.9748	130	5.815191			
Total	763.9987	134				

Table 12. Relationship between individual PCBs.

ANOVA						
Source of variation	SS	df	MS	F	P-value	F _{critical}
Between groups	489.3007	26	18.81926	7.398959	2.74E-14	1.598423
Within groups	274.6981	108	2.5435			
Total	763.9987	134				

the groundwater samples. Naphthalene exposure causes skin damage, respiratory damage, anemia, nausea, vomiting, diarrhea, blood in urine and cataract etc in human (ATSDR, 1990).

PCBs

Table 11 shows that $F_{\text{calculated}}$ (0.05, 4, and 130) was 0.344953 and was less than the F_{critical} of 2.44135. Therefore, 'null hypothesis' was accepted and this indicated that there was no statistical significant difference in the PCB concentrations with respect to sample locations. The P-value of 0.8471 being higher

than 0.05 also indicated that there was no statistical significant difference in the PCB concentrations.

Descriptive statistics showed that Apapa 2 had the highest mean PCB concentration of 0.97 ng/g. This showed that PCB concentrations in Lagos soils were generally low except at Apapa 2. Apapa 2 also had the highest variance of 20.71, while the values for other locations ranged from 0.469921 (Apapa 3) to 3.770187 (Okobaba). This indicated that there was a high use of PCB containing products in Apapa 2 compared to other locations.

Table 12 shows that $F_{\text{calculated}}$ (0.05, 26, and 108) was 7.398959 and was greater than the F_{critical} of 1.598423. Therefore, 'alternative' hypothesis was accepted and this

Table 13. Relationship between OCs at different locations.

ANOVA						
Source of variation	SS	df	MS	F	P-value	F _{critical}
Between groups	2370.375	4	592.5938	2.486568	0.051192	2.502656
Within groups	16682.26	70	238.318			
Total	19052.63	74				

Table 14. Relationship between individual OCs.

ANOVA						
Source of variation	SS	df	MS	F	P-value	F _{critical}
Between groups	3706.632	14	264.7594	1.03516	0.432761	1.860242
Within groups	15346	60	255.7667			
Total	19052.63	74				

Table 15. Relationship between different PBTs in Lagos soils.

ANOVA						
Source of variation	SS	df	MS	F	P-value	F _{critical}
Between groups	11539.75	2	5769.875	2.279985	0.144787	3.885294
Within groups	30367.96	12	2530.664			
Total	41907.71	14				

indicated that there was statistical significant difference between individual PCBs. The P-value of 2.74E-14 being lower than 0.05 also indicated that there was statistical significant difference between individual PCBs.

Descriptive statistics showed that PCB74, a lower chlorinated PCB (2-4 chlorine substitutions), had the highest mean PCB concentration of 10.20 ng/g. PCB74 also had the highest variance of 63.27, while the values for others ranged from 0.0010 (PCB183) to 3.0696 (PCB105).

OCs

Table 13 shows that $F_{\text{calculated}}$ (0.05, 4, and 70) was 2.486568 and was less than the F_{critical} of 2.502656. Therefore, 'null hypothesis' was accepted and this indicated that there was no statistical significant difference in the OC concentrations with respect to sample locations. The P-value of 0.0512 being higher than 0.05 also indicated that there was no statistical significant difference in the OC concentrations. This result suggests a fairly constant source of OCs existed. Descriptive statistics showed that Iddo had the highest mean OC concentration of 14.74 ng/g. This could therefore be attributed to the pattern of use, which is one

of the factors that influence OC distribution, according to Mackay et al. (1997). Iddo also had the highest variance of 1130.00, while the values for other locations ranged from 0.00 (Apapa 3) to 58.97915 (Okobaba).

Table 14 shows that $F_{\text{calculated}}$ (0.05, 4, and 64) was 1.03516 and was less than the F_{critical} of 1.860242. Therefore, 'null hypothesis' was accepted and this indicated that there was no statistical significant difference in the OC concentrations with respect to sample locations. The P-value of 0.4328 being higher than 0.05 also indicated that there was no statistical significant difference between the concentrations of individual OCs. This result suggests a fairly constant source of OCs.

Descriptive statistics showed that p,p'DDE had the highest mean concentration of 24.99 ng/g. This agreed with the report that p,p'DDE was found to be more stable and persistent (refractory) than either p,p'DDT or p,p'DDD and underwent strong biomagnifications with transfer along food chain (Walker, 2009). P,p'DDE also had the highest variance of 2705.863, while others ranged from 0.003418 (cis-nonachlor) to 803.3004 (p,p'DDD). It was observed that all members of the DDT group (p,p'DDE, p,p'DDD and p,p'DDT) had variance values (297.223, 803.3004 and 2705.863, respectively) than other OCs.

PBTs

Table 15 shows that $F_{\text{calculated}}$ (0.05, 4, and 64) was 2.279985 and was less than the F_{critical} of 3.88529. Therefore, 'null hypothesis' was accepted and this indicated that there was no statistical significant difference in the PBT concentrations with respect to sample locations. This result suggests that a fairly constant source of PBTs exist. The P-value of 0.144787 being higher than 0.05 also indicated that there was no statistical significant difference in the PBT concentrations.

Descriptive statistics showed that PAHs had the highest mean concentration of 64.22 ng/g. This showed that PAHs were the most abundant PBTs in Lagos soils. PAHs also had the highest variance of 7440.104, while PCBs and OCs had variance values of 15.62672 and 136.26, respectively. This was likely due to different loadings as a result of diverse activities that generated the PAHs at different locations.

Conclusion

Iddo soil had the highest concentrations of PAHs and OCs, while PCBs were highest in Apapa 2 soil. Soil assessment based on background PAHs level of soil in some countries like Italy, Czech Republic, England, Japan, and Poland, revealed that Lagos has been contaminated. Also, based on the values of identified PAHs components it could be concluded that they were above the suggested level of endogenous total PAHs concentrations in soils, and also above the target values set by Dutch government in almost all studied cases, including BaP. Comparison of the obtained PCBs contents with literature data from England, Poland, Bulgaria and Novi Sad revealed that PCB levels in soil samples from some locations in Lagos presented major environmental risks. Comparing OCs contents from literature data from England, Poland, Czech Republic, Slovak Republic, Bulgaria, Germany, Hong Kong and Novi Sad, it is observed that Lagos soils are polluted with OCs. Since the OCs at Okobaba doubled the limit value according to Slovenian regulation, it could be concluded that there is a serious threat of OCs at some locations in Lagos.

REFERENCES

- Ashutosh B, Madhuri KL, Koushalya D, Ashok M, Ravindra NS (2012). Degradation of Naphthalene by a novel strain *Bacillus licheniformis* BMIT5ii (MTCC 9446). Ashutosh Bahuguna et al. J. Pharm. Res. 5(3):1600-1604. ISSN: 0974-6943.
- Atanassov I, Terytze K, Atanassov A (2001). Background values for heavy metals, PAHs and PCBs in the soil of Bulgaria. In Assessment of the Quality of Contaminated Soils and Sites in Central and Eastern European Countries (CEEC) and New Independent States (NIS), Proceeding of International Workshop, Sofia, Bulgaria, 30 September-3 October; Terytze K, Atanassov I Eds. pp. 83-108.
- ATSDR (Agency for Toxic Substances and Disease Registry) (1990). Toxicological Profile for Naphthalene and 2-Methylnaphthalene. Prepared by Life Systems, Inc., under Subcontract to Clement Associates, Inc., for ATSDR, U.S. Public Health Service under Contract No. 205-88-0608, ATSDR/TP-90-18.
- Edwards NT (1988). Assimilation and metabolism of polycyclic aromatic hydrocarbons by vegetation-An approach to this controversial issue and suggestions for future research. In M. Cook and A. J. Dennis (ed.) polycyclic aromatic hydrocarbons: A decade of progress 10th Int. Symp. Battile Press. Columbus, OH. pp. 211-299.
- Edwards NTJ (1983). Polycyclic aromatic hydrocarbons (PAHs) in the terrestrial environment – A review. J. Environ. Qual. 12:427-441.
- Falandysz J, Kawano M, Wakimoto T (1997). Polichlorinated biphenyls (PCBs) contamination of soil in a former army base in Poland. Organohalen Compd. 42:172-177.
- Holoubek I, Kocan A, Holoubkova I, Kohoutek J, Falandysz J (1999). Persistent, bioaccumulative and toxic chemicals in central and eastern European countries - State-of-the-art report. Sci. Pollut. Res. 6:183.
- Kanally RA, Harayama S (2000). Biodegradation of the high molecular weight polycyclic aromatic hydrocarbons by bacteria. J. Bacteriol. 182(8):2059-2067.
- Larsen EH, Samse-Petersen L, Larsen PB, Bruun P (2002). Uptake of Trace Elements and PAHs by Fruit and Vegetables from Contaminated Soils. Environ. Sci. Technol. 36:14.
- Lazar R, Edwards RC, Metcalfe CD, Metcalfe T, Gobas FAPC, Haffner GD (1992). A simple, novel method for the quantitative Analysis of coplanar (non-ortho substituted) polychlorinated biphenyls in environmental samples. Chemosphere 25:493-504.
- Leeuwen V, Vermeire S (2007). Risk assessment of chemicals, An Introduction. Netherlands, Springer pp. 1-621.
- Linkeš V, Kobza J, Švec M, Ilka P, Pavlenda P, Barančikova G, Matušková L (1997). Soil Monitoring of Slovak Republic, Present State of Monitored Soil Properties. The Results of Partial Monitoring System-Soil as a Part of Environment Monitoring of Slovak Republic for the Period 1992/1996. Soil Fertility Research Institute (VUPU): Bratislava, Slovak Republic. P. 73.
- Mackay D, Shiu WY, Ma KC (1997). Illustrated Handbook of Physical Chemical Properties and Environmental Fate for Organic Chemicals, Vol. V. Pesticide Chemicals. Lewis Publishers/CRC Press, New York.
- Manoli E, Samara C, Konstantinou I, Albanis T (2000). Polycyclic aromatic hydrocarbons in the bulk precipitation and surface waters of Northern Greece. Chemosphere 41:1845-1855.
- Manz M, Wenzel KD, Dietze U, Schuurmann G (2001). Persistent organic pollutants in agricultural soils of central Germany. Sci. Total Environ. 277:187-198.
- Minissi S, Caccese D, Passafiume F, Grella A, Ciccotti E, Rizzoni M (1998). Mutagenicity (micronuclear test in *Vicia faba* root tips), polycyclic aromatic hydrocarbons and heavy metal content of sediment collected in Tiber river and its tributaries within the urban area of Rome. Mutat. Res. 420:77-84.
- Morillo GE, Romero AS, Maqueda PC, Madrid L, Ajmone-Marsan F, Grcman H, Davidson CM, Hursthouse AS, Villaverde CJ (2007). Soil pollution by PAHs in urban soils: A comparison of three European cities. J. Environ. Monit. 9:1001.
- Oosterbaan J, Jamet P (1998). Characterization of PAH on former gaswork and coking plants by exploratory statistics, Proceeding of papers of 4th International Symposium and Exhibition on Environment in Central and Eastern Europe (CD), #313, Warsaw. pp. 1-7.
- Sanka M (2001). Program of soil monitoring and register of contaminated sites in the Czech Republic: Their role as database sources in state administration and for setting the limit values in soil. In Assessment of the Quality of Contaminated Soils and Sites in Central and Eastern European Countries (CEEC) and New Independent States (NIS), Proceeding of International Workshop, Sofia, Bulgaria, Terytze, K.; Atanassov, I., Eds. pp. 33-36.
- Sezgin N, Kurtulus H, Demir G, Nemlioglu S, Bayat C (2003). Determination of heavy metal concentrations in street dust in Istanbul E-5 highway. Environ. Int. 29:979-985.
- Shegunova P, Terytze K, Atanassov I (2001). Priority organic pollutants in soils of Bulgaria. In Assessment of the Quality of Contaminated Soils and Sites in Central and Eastern European Countries (CEEC)

- and New Independent States (NIS), Proceeding of International Workshop, Sofia, Bulgaria, 30 September-3 October; Terytze, K.; Atanassov, I., Eds. pp. 202-209.
- Škrbić B, Cvejanov J, Djurišić-Mladenović N (2005). Some Toxic Substances in Surface Soil in Novi Sad Area. Faculty of Technology, Bulevar cara Lazara 1, 21000 Novi Sad Serbia pp. 1-10.
- Smith JA, Witkowski PJ, Fusillo TV (1988). Manmade organic compounds in the surface waters of the United States-A review of current understanding: U.S. Geol. Surv. Circ. 1007:92.
- Van Brummelen TC, Verweij SA, Van Gestel CAM (1996). Enrichment of polycyclic aromatic hydrocarbons in forest soils near a blast furnace plant. *Chemosphere* 32:293-314.
- Van metre PC, Manler BJ, Furlong ET (2000). Urban Sprawl Leaves its PAH Signature. *Environ. Sci. Technol.* 34:4064-4070.
- VROM (1994). Environmental Quality Objectives in the Netherlands. Ministry of Housing. Spat. Plan. Environ. P. 465.
- Walker CH (2009). Organic Pollutants. An Ecotoxicological Perspective., New York., CRC press: pp. 1-414
- Weiss P, Riss A, Gschmeidler E, Schentz H (1994). Investigation of heavy metal, PAH, PCB patterns and PCDD/F profiles of soil samples from an industrial urban area (Linz, upper Austria) with multivariate statistical methods. *Chemosphere* 29:2223-2236.
- WHO (World Health Organisation) (1992). Environmental Health Criteria 140; Polychlorinated biphenyls and terphenyls (Second Edition). No. 68.
- Zhang HB, Luo YM, Zhao QG, Wong MH, Zhang GL (2005). Residues of organochlorine pesticides in Hong Kong soils. *Chemosphere* 63:633-641.
- Zohair A, Salim AB, Soyibo AA, Beck AJ (2006). Residues of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides in organically-farmed vegetables. *Chemosphere* 63(4):541-553.
- Zupan M, Turk I, Lobnik F (2001). Soil pollution assessment in Slovenia. In Terytze, K., Atanassov, I. (Eds.), Proceedings of International Workshop "Assessment of the Quality of Contaminated Soils and Sites in Central and Eastern European Countries (CEEC) and New Independent States (NIS)", Sofia, Bulgaria. pp. 79-82.