PAHs, HCHs, DDTs AND CHLOROPHENOLS IN SEWAGE SLUDGE FROM DELHI

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Introduction

The sewage treatment plants (STPs) receive waste from residential, institutional, commercial and industrial sources with toxic organic pollutants (OPs) (Ju *et al.*, 2009; Clarke *et al.*, 2010). Sewage sludge is the residual solid (~40-80% organic materials) generated as a byproduct during wastewater treatment processes may be suitable as a fertilizer and soil conditioner. Pollutants have good sorption affinity towards the organic material in sewage sludge. So, sewage sludge can be considered as a composite matrix containing OPs, which risk its dumping and/or application on land as fertilizer.

The US EPA's 16 priority PAHs are released from pyrogenic and petrogenic sources having high sorption affinity for particles (ATSDR. 1995; Oleszczuk, 2006; Ju *et al.*, 2009; Poluszyńska *et al.*, 2017). DDT and HCH (OCPs) have been enlisted as POPs in the Stockholm Convention (ATSDR 2005, 2008; UNEP, 2017). The agricultural use of these compounds has been banned in most of the countries worldwide, including India. However, the Government of India restricted their use in vector control for the purpose of public health under the WHO guidelines (UNEP, 2017). Chlorophenols (CPs) are aromatic hydroxyl compounds constitute the group of phenolic compounds and mainly used as preservatives, disinfectants and in production of herbicides, fungicides, insecticides, pharmaceuticals and dyes (Michalowicz and Duda,2007) have been recognized as priority pollutants by the European Union (EU) and US EPA (EC, 2001; USEPA, 2017).

India being predominantly an agricultural country uses sewage sludge as an economically viable source of fertilizer. The most common practices of sludge disposal in the country are for land filling and in agricultural fields as soil fertilizer. The sewage generation during year 2015 was estimated to be 61754 million liters per day (MLD). The contamination of sewage sludge borne toxic OPs has not been explored in India. Therefore, it is imperative to assess the levels of toxic OPs in sewage sludge in order to understand their levels and assess their potential risk on the terrestrial environment and ecosystem in general. This paper deals with levels of 16 priority PAHs, OCPs and CPs in sewage sludge collected from sewage treatment plants (STPs) of Delhi, India.

Materials and Methods

Delhi (28.38°N and 77.13°E), the capital of India with ~ 17 million population and 1483 km^2 area lies on the banks of the river Yamuna, which experiences a hot and humid climate. There are two gasoline based and one coal based thermal power station operational in Delhi. Delhi Government has employed several pollution control measures such as phasing out/ban on old commercial/transport vehicles, diesel sulphur reduction, switched over coal based power plants to beneficiated coal and gasoline, closure/shifting of polluting industries, Delhi Metro and CNG as mandatory fuel in public transportation. Approximately, 3800 MLD (millions liter per day) of domestic and industrial sewage/wastewater is generated by the population of Delhi, for which adequate treatment facilities are not available to remove all the pollutants. Dry sludge (manure) is produced at various Sewage Treatment Plants of Delhi.

The selected STPs are located at East and South Delhi. These are mainly stationed in residential areas and are designed to treat wastewater of municipal origin. The activated sludge process is used for wastewater treatment in the STPs. The sludge samples in duplicates were collected, air dried, homogenized by grinding and 1mm size particles extracted for OCPs, PAHs and CPs.

Ultrasonic extraction with acetone-hexane (1:1 v/v) for OCPs and PAHs was done, extracts were cleaned with silica gel column and subjected to analysis by GC-ECD and HPLC, respectively. CPs were extracted with 0.1M NaOH in methanol using ultrasonic bath and liquid-liquid extraction at pH <2 with dichloromethane (Kumar *et al.*, 2014). The PAHs ([naphthalene (Npt), acenaphthene (ANe), acenaphthylene (ANy), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]-fluoranthene (BbF), benzo[k]fluoranthene (BkF), Benzo(a)pyrene (BaP), dibenzo[a,h]anthracene (DBA), indeno[1,2,3-cd]pyrene (Ind), and benzo[ghi]perylene (BghiP)]) were quantified by HPLC (Agilent 1100) equipped with UV Detector (UVD, λ=254 nm), on Supelcosil^{TM} LC-PAH column (25cm x 4.6 mm, 5 µm) using acetonitrile and water as mobile phase (Kumar *et al.*, 2015). OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH), DDTs (*p,p*-DDE, *o,p'*-DDT, *p,p'*-DDT,) were quantified using GC-ECD (Perkin Elmer, Clarus 500) on Elite-1 column (25 m x 0.20 mm with 0.33 µm). (Kumar *et al.*,2013). CPs [2-chlorophenol (2CP), 2,4-dichlorophenol (2,4DCP), 2,4,6-trichlorophenol (2,4,6TCP), pentachlorophenol (PCP)] were quantified by HPLC equipped with UVD (λ=280 nm) on *Ascentis* (Supelco) column (4.6 mm x 250 mm, 5 µm) using 0.15% *o*-phosphoric acid in methanol and 0.15% *o*-phosphoric acid water as mobile phase (Kumar *et al.,* 2014). Required quality control (QA/QC) analysis was performed including five level calibration, procedural blank, duplicate analysis and calibration verification and recovery studies. The average recoveries of PAHs were in the range of 105 to 109% (±5.4-9.8%), of OCPs in the range of 88 to 115% (±5.5-9.4%) and of CPs in the range of 75% to 95% (±3–6%). The LOD (S/N, >3) for OCPs, CPs, and PAHs were 0.01 ng mL^{-1}, 0.10 ngmL^{-1}, and 1.0 ng mL^{-1}, respectively.

Results and Discussion

The ∑16 PAHs ranged from 157 mg kg^{-1} to the 919 mg kg^{-1} with mean and median concentration levels of 520±124 mg kg^{-1} and 511 mg kg^{-1} respectively (Fig.1). The concentration of the 7 carcinogenic PAHs (∑7C-PAHs) ranged from 34-365 mg kg^{-1}. and constituted 28% of the total PAHs. The Fle and Any (3-ringed) along with Chr and Flt (4-ringed) were dominant PAHs. The observed variation could be attributed to anthropogenic activities arising from mixed sources of PAH contamination. Overall, the PAH profile followed the descending order of distribution as 3-ring PAHs (53.38%) > 4-ring PAHs (46.26%)> 5 ring PAHs (0.20%)> 6 ring PAHs (0.09%) > 2 ring PAH (Npt) (0.07%). The dominance of 3-4 ringed PAHs may be attributed to their semi-volatile and low vapour pressure characteristics which when associated with air particulate matter, readily deposit in the nearby areas and show resistance to degradation as well as air-surface exchange. Surface washings and run-off from contaminated sites may result in PAH load in the sewage sludge. In order to estimate the carcinogenic potency of the PAHs in sewage sludge, BaP toxic equivalent factors (TEFs) (Nisbet and Lagoy, 1992) have been used to derive the BaP toxic equivalent concentrations (BaP_{TEQ}). The BaP_{TEQ} for 16PAHs ranged from 0.64-4.9 mg BaP_{TEQ} kg^{-1}. The BaP_{TEQ} for ∑7C-PAHs ranged from 0.52-4.2 mg BaP_{TEQ} kg^{-1}, accounting for 84% of the total BaP_{TEQ} concentrations in the sewage sludge.

The composition profile and molecular ratios of various PAHs were used to identify the contamination sources of PAHs in sewage sludge. The observed pooled ratios of $\sum PAH_{LMW}$ and $\sum PAH_{HMW}$ suggest both pyrogenic and petrogenic sources for PAHs. The different isomeric ratios used for PAHs sources. The Phe/Ant ratio (1.51-12.58), indicating pyrogenic sources. The BaA/BaA+Chr (<0.2) and Flt/Flt+Pyr (<1) indicated combustion of petroleum. The IndP/IndP+BghiP ratio (<0.2-0.50) showing the petroleum sources such as combustion of fuels in vehicles and crude oil. BaP/BghiP ratio (0.05-0.78) indicating traffic as well as non-traffic sources. The STPs studied herein receive effluents from diverse point and non-point sources such as domestic, urban street runoff, automobile washings, business facilities, drainage water, wet and dry atmospheric deposition (dust/soot), etc. The effluents from such sources undergo homogenization upstream in the wastewater treatment plant and the organic contaminants in the final sludge are unlikely to retain the characteristics of the exact source from which they originate. This gives a varying fingerprint from “background concentration” as observed in the present study.

The concentration of ∑HCH and ∑DDT ranged between 797-23397 µg kg^{-1} and 84-398 µg kg^{-1}, respectively. The average concentration of the individual DDT and HCH isomers were presented in Fig.1. The average concentration of the individual DDT and HCH isomers were 3722±1436 µg kg^{-1}, 3483±2028 µg kg^{-1}, 415±153 µg kg^{-1}, 93±23 µg kg^{-1},103±29 µg kg^{-1}, 62±20 µg kg^{-1}, 73±20 µg kg^{-1}, respectively, for α-HCH, β-HCH, γ-HCH, δ-HCH, p,p’-DDE, o,p’-DDT and p,p’-DDT.

The compositional profile of HCH and DDT isomers are used to identify their contamination sources in the environment. In this study, α-HCH, β-HCH, γ-HCH and δ-HCH constituted 47%, 44%, 5% and 1% of the total HCH concentration, indicating metabolic degradation of the parent component of HCH. The α-HCH/γ-HCH ratio found in this study varied from 5-18, indicating prevalent technical HCH application in the current situation. Technical HCH was extensively used in the country till 1997. But after this, HCH has been banned in agriculture, with its use being restricted by Government of India only to public health programs as per guidelines of Stockholm Convention on POPs (UNEP, 2017). The observed higher ratio of α-HCH to γ-HCH may also be due to conversion of γ-HCH to α-HCH, because study area is located under the Tropic of Cancer with strong ultraviolet radiation and a biologically active environment suggesting the transformation from γ-HCH into α-HCH. Other studies with a significant correlation anticipated the use of technical HCH as well as lindane.

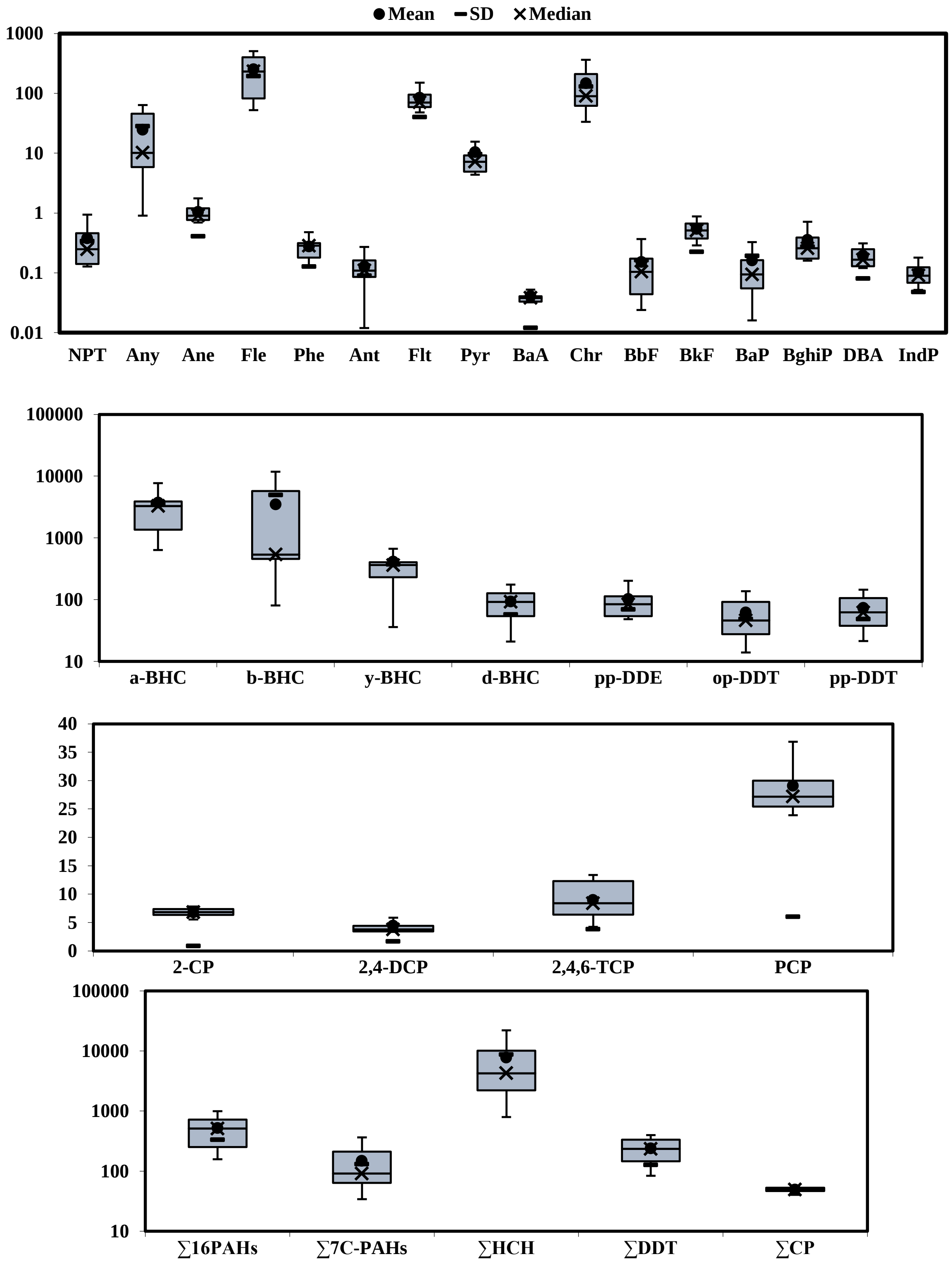

Fig.1. Box plot of individual and total PAHs, HCHs, DDTs and CPs in sewage sludge from Delhi (PAHs & CPs in mg/kg, HCH & DDT in µg/kg)

In the present study, the ratios of DDT/DDE were in the range of 0.54 to 4.61, indicating that both past and present inputs of DDT to the analysed sludge samples. In this study the low ratio of *o,p'*-DDT/*p,p'*-DDT (0.44 - 1.31) and the dominance of *p,p'*-DDT indicates a possible fresh *p,p'*-DDT input. After DDT application, much of the DDT might have been converted to *p,p'*-DDE. Thus the lower *o,p'*-DDT/*p,p'*-DDT ratio is possible due to the fresh input of the parent compounds.Government of India has withdrawn the use of DDT in agriculture, and its use has been restricted for Disease Vector Control purpose only (UNEP,2017).

The concentration of ∑CPs ranged between 40-57 mg kg^{-1} while the concentration of the individual compounds ranged from 5.5-7.8 mg kg^{-1}, 3.4-7.7 mg kg^{-1}, 4.2-13.4 mg kg^{-1}, 24-40 mg kg^{-1} for 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PeCP), respectively (Fig.1).

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