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DISTRIBUTION AND POSSIBLE SOURCE IDENTIFICATION OF POTENTIALLY TOXIC ORGANIC SUBSTANCES (PTOS) IN SEWAGE SLUDGE OF DELHI

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ABSTRACT
In this study, sewage sludge from 6 sewage treatment plants in Delhi were characterized for 27 potentially toxic organic substances (PTOS). Out of these, 16 EPA-priority Polycyclic Aromatic Hydrocarbons (PAHs) were found present at the highest level, ranging from 157-991 mg kg^{-1} with an average of 521±124 mg kg^{-1}. Out of these, 7 carcinogenic PAHs accounted for 28% of the total PAH content in the sewage sludge. The organochlorine pesticides (DDT and HCH isomers) were present in the range 880-23564 µg kg^{-1} withan average of 7952±3519µg kg^{-1} while chlorophenols varied from 40-67 mg kg^{-1} with an average concentration of 49±2.4 mg kg^{-1}. The diagnostic concentration ratios used for source identification of PAHs suggested their mixed origin comprising pyrogenic and petrogenic activities responsible for the hydrocarbons in the sewage sludge. DDT prevalence could be linked to the ongoing and past usage of DDT in vector control activities but not from diclofol. Benzo(a)pyrene toxic equivalent (BaP$_{TEQ}$), a relative carcinogenic potential of the PAHs to BaP was estimated and presented.

Keywords: *Potentially Toxic Organic Substances (PTOS); Polycyclic Aromatic Hydrocarbons (PAHs); Organochlorine Pesticides; Chlorophenols (CPs); Sewage Sludge*

INTRODUCTION
Sewage sludge is the residual solid generated as a byproduct during wastewater treatment processes. It contains 40-80% organic material dry weight basis which makes it suitable as a soil fertilizer and soil conditioner. However, the sewage treatment plants (STPs) receive potential input of contamination from wide range of sources such as residential, institutional, commercial and industrial establishments. Waste streams from such sources contain toxic organic contaminants which have goodsorption affinity towards the solid sludge material owing to their high octanol water partition coefficient (Log K$_{ow}$). The characteristic representatives of such toxic organic contaminants (OCs) reported to be present in sewage sludge are polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), chlorophenols (CPs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and brominated flame retardants such as polybrominated diphenyl ethers (PBDEs) (Ju *et al.,* 2009; Clarke *et al.,* 2010; Khadar *et al.,* 2010). Hence, sewage sludge can be considered as a composite matrix containing a wide array of organic micro-pollutants, which risk its dumping and/or indeterminate application on land as fertilizer.
PAHs are a large group of stable aromatic compounds having low water solubility, high sorption affinity for particles and less volatility with increasing molecular weight (Ju *et al.,* 2009). These compounds are known to adsorb onto the sludge and are removed from wastewater over 90% during wastewater treatment processes (Oleszczuk, 2006). In fact, PAHs constitute the most common group of organic pollutants present at significant levels in sewage sludge (Poluszyńska *et al.,* 2017). The major source for release of PAHs into the environment include incomplete combustion of hydrocarbons such as coal, petroleum products, wood, grasses, biomass, and wastes of municipal and industrial origin.
The United States Environmental Protection Agency (US EPA) has recognized 16 PAHs as "priority pollutants" due to their toxic, carcinogenic and mutagenic characteristics. The International Agency for Research on Cancer (IARC) has evaluated the carcinogenic risk of PAHs and classified these as carcinogenic (Group 1), possibly carcinogenic (Group 2A) and probably carcinogenic (Group 2B) to humans (Poluszyńska *et al.,* 2017; IARC, 2005).

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DDT and HCH have been enlisted as Persistent Organic Pollutants (POPs) in the Stockholm Convention (UNEP, 2017). They are highly resistant to degradation, bio-accumulative and possess long-range environmental transport ability. OCPs are known to cause a wide range of chronic and acute toxicity including endocrine disruption, neurological damage, reproductive disorders, immune suppression, and birth defects (Wang *et al.,* 2007). The agricultural use of these compounds has been banned in most of the countries worldwide, including India. However, the Government of India allows their restricted use in vector control by indoor residual spraying (IRS) for the purpose of safeguarding public health under the guidelines of the World Health Organization (WHO) (UNEP, 2017). As a result, DDTs and HCHs have been frequently detected in soil and sludge samples (Wang *et al.,* 2007; Ju *et al.,* 2009; Clarke *et al.,* 2010; Kumar *et al.,* 2013).

Chlorophenols are aromatic hydroxyl compounds having chlorine atom (1-5) attached to the phenolic ring. They constitute the largest group of phenolic compounds and are mainly used as preservatives in wood, paint, paper and pulp, leather industries and as disinfectants in households (Michalowicz and Duda, 2007). In addition, they are also used as herbicides, fungicides, insecticides and as intermediates in production of pharmaceuticals and dyes (Michalowicz and Duda, 2007). Chlorophenols are known to be toxic, estrogenic, mutagenic, carcinogenic, anti-androgenic and a vasodilator in humans. They 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 land filling and in agricultural fields as soil fertilizer. The sewage generation during the year 2015 was estimated to be 61754 million liters per day (MLD). The contamination of sewage sludge borne toxic OCs has not been explored in India. Therefore, it is imperative to assess the levels of toxic OCs in sewage sludge in order to understand their levels and assess their potential risk on the terrestrial environment and ecosystem in general.

In this paper, we report the levels of polycyclic aromatic hydrocarbons, chlorophenols and organochlorine pesticides, hereafter referred to as potentially toxic organic substances (PTOS), in sewage sludge collected from sewage treatment plants (STPs) of Delhi, India.

MATERIALS AND METHODS
Study Area and Sampling
Delhi, the capital of India lies in the geographical coordinates of 28.38°N and 77.13°E in the banks of the river Yamuna. It houses a population of approximately 17 million within an area of 1483 km², out of which 68% is urbanized. The climate of Delhi is generally hot and humid with atmospheric temperature soaring upto 40-45°C during summer (early April to mid-October, including monsoon season from July to September) and falling to 4-5°C during winter months (November to January). The transportation is dominantly road based in Delhi with 8.84 million registered vehicles (private vehicles, 8.48 million; commercial vehicles, 0.36 million). There are two gasoline based (Indraprastha Gas Turbine, IGT) and the Pragati Power plants) and one coal based thermal power station operational in Delhi (Delhi Government, 2015). There are numbers of designated industrial areas with various activities. 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.

At present, around 830 MGD (million gallons per day) of drinking water is being supplied to population of Delhi. Approximately, 3800 MLD (millions liter per day) of domestic and industrial sewage/waste water is generated in Delhi, for which adequate treatment facilities are not available to remove all the pollutants (ENVIS, 2013). The sewage generated @ 80% of total potable water consumption is estimated about 680 MGD. Dry sludge (manure) is produced at various Sewage Treatment Plants of Delhi. This manure being rich in nutrients i.e. nitrogen, phosphorous, potassium and other valuable organic matter, is available for use in agriculture (Delhi Government, 2017). The selected STPs in this study i.e. K-1 and OKH-2 - OKH-6 located in east and south Delhi, respectively. These are mainly stationed in

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residential areas and are designed to treat wastewater of municipal origin. However, there are a number of designated industrial units in nearby vicinity of the selected STPs.

Sample Preparation

The collected sludge samples were air dried in clean and dark environment in the laboratory. The dried samples were homogenized by grinding and sieving through 1mm sieve and stored in amber colored glass bottles in dark at 4±2 °C for further processing. Extraction procedure for OCPs, PAH compounds and CPs were followed separately.

For OCPs and PAHs, the dried sludge samples were extracted with a mixture of acetone-hexane (1:1 v/v) in ultrasonic water bath and the extract was concentrated using a rotary evaporator (Eyela, Tokyo, Japan) to 2 mL. Concentrated extracts were divided into two aliquots of 1 mL each, to process separately for analysis of PAHs and OCPs following the USEPA protocol in method 3630C.

In case of chlorophenols, 5-10 g of dried sludge sample was taken for extraction with solvent mixture of 0.1M NaOH in methanol (75 ml) using ultrasonic bath for 30 min and transferred to separatory funnel for extraction at pH <2 with 50 ml of dichloromethane (Kumar *et al.,* 2014). The organic phase was concentrated to near 5 ml and solvent exchanged to methanol. The final volume was reduced to 1.0 ml under a gentle stream of nitrogen gas using Turbo Vap (Caliper, USA) and Minivap (Supelco, USA).

Instrumental Analysis

The PAHs were quantified using HPLC system (Agilent 1100 Series, Waldbronn, Germany) equipped with UV Diode Array Detector (DAD, λ=254 nm), auto sampler, quaternary pump and degasser. Separation was conducted on a Supelcosil^{TM} LC-PAH analytical column (25cm x 4.6 mm, 5 µm) attached with guard column (Eclipse XDB-C8 (4.6 × 12.5 mm, 5 µm)). Gradient grade acetonitrile (60 %) and water (40 %) was used as mobile phase with linear flow (1.0 mLmin^{-1}) in 42 min to 100% acetonitrile (Kumar *et al.,* 2015).

For separation and quantification of OCPs, gas chromatograph (Perkin Elmer, Clarus 500, USA) attached with auto sampler and equipped with an electron capture detector (ECD, ^{63}Ni) was used. The carrier gas used was nitrogen gas (purified laboratory grade) having a flow rate of 1.0 mL min^{-1}. The separation of pesticide isomers was carried on Elite-1 fused silica capillary column having particulars 25 m x 0.20 mm with 0.33 µm particle size. The column oven temperature conditions were optimized starting from 170 ^{o}C and increased to 220 ^{o}C at ramp rate of 7 ^{o}C min$^{-1.}$ The temperature was further increased to 250 ^{o}C at 5 ^{o}C min^{-1} and held for 6.86 min. The injector and detector temperatures were maintained at 250 ^{o}C and 350 ^{o}C, respectively (Kumar *et al.,* 2013).

Chlorophenols were quantified by high performance liquid chromatograph (HPLC) (Series 1100, Agilent Technology Inc., Santa Clara, CA, USA), equipped with a vacuum degasser (Agilent, G1379A), quaternary pump (Agilent, G1311A), diode array detector (Agilent, G1315B) and an auto sampler (Agilent, G1329B). A sample aliquot of 10 µL volume was injected for chromatographic analysis on a C18 reverse phase column (4.6 mm x 250 mm, 5 µm particle) (Ascentis®, Supelco, USA) maintained at 25±1°C.A guard column (4.6 mm x 12.5 mm, 5 µm particle) attached before the analytical column was used to prevent any contamination into the analytical column. The mobile phase used for separation of the CPs was a mixture of methanol (with 0.15% *o*-phosphoric acid) and water (with 0.15% *o*-phosphoric acid) at a linear flow of 20% methanol and 80% water at 0.7 mLmin^{-1} to 95% methanol in 30 min (Kumar *et al.,* 2014). The peaks were identified at 280 nm using diode array detector.

Analytical Quality Control

Comparison of peak areas with external standards was done and five level calibration curves of the standards were used to quantify the concentrations of target compounds. A procedural blank consisting of all chemicals and solvents was run to check for interferences and cross contamination. Quality assurance quality control (QA/QC) analysis was performed with the inclusion of analysis of procedural blanks (analytes concentrations were <MDL 'method detection limit'), random duplicate samples (standard deviation <10%), random calibration verification (standard deviation <10%) and five level calibration curves with the r^2 value of 0.999. The presented data are the average of duplicate analysis of each sample. Due to non-availability of certified reference material, recovery study was undertaken by analysis of

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fortified samples with the addition of known quantity of standards. The spiked and non-spiked samples were processed separately in duplicate as real samples, and values obtained in spiked and non-spiked samples were systematically compared. The average recoveries of PAHs were in the range of 105 to 109% ($\pm$5.4-9.8%), of OCPs in the range of 88 to 115% ($\pm$5.5-9.4%) and of CPs in the range of 75% to 95% ($\pm$3–6%). The limits of detection (LOD) were estimated using signal to noise ratio >3:1. The calculated LOD for OCPs, CPs, and PAHs were used as 0.01 ng mL^{-1}, 0.10 ng mL^{-1}, and 1.0 ng mL^{-1}, respectively. Concentrations above detection limit were taken for calculation and below MDL were taken as zero (0) in the calculations. Moisture content of samples was determined separately to report data on dry weight basis.

RESULTS AND DISCUSSION
Polycyclic Aromatic Hydrocarbons (PAHs)
Targeted 16 PAHs were detected in all the sludge samples which indicated the ubiquity of PAHs in the environment. The total ($\sum$16 PAHs) and individual concentrations of 16 PAHs have been presented in Table 1. The $\sum$16 PAHs ranged from 157 mg kg^{-1} (OKH-4) to 919mg kg^{-1} (K-1) with mean and median concentration levels of 520$\pm$124 mg kg^{-1} and 511 mg kg^{-1} respectively. Amongst the 16 PAHs, the most abundant PAH was observed to be fluorene (Fle) (48%; mean 252$\pm$79 mg kg^{-1}) followed by chrysene (Chr) (28 %; mean 147$\pm$53 mg kg^{-1}), fluoranthene (Flt) (16%; mean 84$\pm$16 mg kg^{-1}) and acenapthylene (ANy) (4.7 %; mean 25$\pm$12mg kg^{-1}). The rest of the compounds contributed only 3% of the total PAHs. The concentration of the 7 carcinogenic PAHs ($\sum$7PAH$_{car}$: BaA, Chr, BbF, BkF, BaP, DBA, Ind) ranged from 34-365 mg kg^{-1}. The $\sum$7PAH$_{car}$ constituted 28% of the total PAHs, similar to the Tunisian sludges (29%) (Khadar *et al.,* 2010) and close to the textile wastewater sludge in China (33%) (Ning *et al.,* 2014), but much lower than in the sludge samples derived from municipal wastewater treatment plants of Greece (62%) (Manoli and Samara, 1999) and China (88%) (Cai *et al.,* 2007). Benzo(a) Pyrene (BaP), the most potent carcinogenic PAH ranged from 0.02-0.53 mg kg^{-1} in the present study. The other countries have reported a higher concentration maxima for BaP in sewage sludge such as in Poland (<0.04-1.30 mg kg^{-1}) (Poluszyńska *et al.,* 2017); Korea (0.032-4.93 mg kg^{-1}) (Ju *et al.,* 2009).

The most dominant PAHs found in this study were Fle and Any (3-ringed compounds) along with Chr and Flt (4-ringed compounds). The location-wise PAH distribution profile observed in the studied STPs has been illustrated in Figure 1. It can be clearly seen that a homogenous pattern for PAHs occurred throughout, where 3-4 ringed PAHs dominated over other PAHs in all the samples. In case of sewage sludge from locations OKH-3 and OKH-4, 4-ringed PAHs were more dominant while in OKH-6, 3-ring PAHs accounted for most 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 (ANy, ANe, Fle, Phe, Ant) (53.38%) > 4-ring PAHs (Flt, Pyr, BaA, Chr) (46.26%) > 5 ring PAHs (BbF, BkF, BaP, DBA) (0.20%) > 6 ring PAHs (Ind, BghiP) (0.09%) > 2 ring PAH (Npt) (0.07%).

The higher accumulation of 3-4 ringed PAHs in the sewage sludge samples 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. On the other hand, 2-ringed naphthalene (Npt) has low particulate sorption affinity (log K_{ow}= 3.37), high water solubility (30 mg L^{-1}) and volatility, which makes it capable of greater mobility and selective partition onto the solid phase of the sewage sludge. HMW PAHs are known to have very low water solubility (<0.5 ng L^{-1}) and high sorption to the solid phase, which may again contribute to its low extraction tendency from the sludge material. Similar results have been reported in most of the studies where 3-4 ringed PAHs were found to be the most dominant PAH species while the relative abundance of 2 and 6 ringed PAHs were the lowest in sewage sludge (Baran and Oleszczuk, 2003; Ju *et al.,* 2009; Khadar *et al.,* 2010; Ning *et al.,* 2014). However, as an exception, Dai *et al.,* (2007) reported dominance of higher molecular weight (HMW) PAHs (5-6 ringed PAHs) in sewage sludge, which was responsible

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for 88-93% of the total PAH content. The authors have linked the observed dominance of HMW PAHs in the sewage sludge to input of wastewater from combustion sources in their study.

Table 1: Concentration of PAHs, OCPs and CPs in Sludge Samples Collected from STPs

Compounds	Concentration			
	Range	Mean±SE	Median	%∑
Polycyclic Aromatic Hydrocarbons (mg kg^{-1})				
Napthalene (Npt)	0.13-1	0.38±0.14	0.25	0.07
Acenapthylene (ANy)	0.90-64	25±12	10	4.7
Acenaphthene (ANe)	0.69-1.8	1±0.17	0.91	0.2
Fluorene (Fle)	52-506	252±79	232	48
Phenanthrene (Phe)	0.13-0.48	0.28±0.05	0.28	0.05
Anthracene (Ant)	0.01-0.27	0.13±0.04	0.11	0.02
Fluoranthene (Flt)	48-155	84±16	70	16
Pyrene (Pyr)	4-30	10±3.9	7.20	2
Benzo(a)anthracene (BaA)	0.03-0.06	0.04±0.005	0.04	0.01
Chrysene (Chr)	34-363	147±53	90	28
Benzo(b)fluoranthene (BbF)	0.02-0.46	0.15±0.07	0.10	0.03
Benzo(k)fluoranthene (BkF)	0.29-0.87	0.54±0.09	0.51	0.10
Benzo(a)pyrene (BaP)	0.02-0.53	0.16±0.08	0.09	0.03
Benzo (g,h,i)perylene (BghiP)	0.16-0.87	0.35±0.11	0.26	0.07
Dibenzo(a,h)anthracene (DBA)	0.12-0.31	0.19±0.03	0.17	0.04
Indeno(1,2,3-cd)pyrene (Ind)	0.05-0.18	0.10±0.02	0.09	0.02
∑16 PAHs	157-991	521±124	511	100
Organochlorine pesticides (µg kg^{-1})				
α-HCH	637-10303	3722±1436	3283	47
β-HCH	80-11799	3483±2028	538	44
γ-HCH	36-1120	415±153	364	5.2
δ-HCH	21-175	93±23	92	1.2
pp-DDE	48-233	103±29	85	1.3
op-DDT	14-137	62±20	46	0.78
pp-DDT	21-145	73±20	62	0.92
∑OCPs	880-23564	7952±3519	4493	100
Chorophenols (mg kg^{-1})				
2-Chlorophenol	5.5-7.8	6.8±0.34	6.8	14
2,4-Dichlorophenol	3.4-7.7	4.4±0.68	3.8	9
2,4,6-trichlorophenol	4.2-13.4	8.9±1.6	8.4	18
Pentachlorophenol	24-40	29±2.5	27	59
∑CPs	40-57	49±2.4	49	100

*SE =Std Error

PAH Source Identification

The composition profile of PAHs having varying number of aromatic rings and molecular indices (concentration ratios of various PAHs) has frequently been used to identify the contamination sources of PAHs in the environmental matrices (Yunker *et al.,* 2002). Low Molecular Weight (LMW) PAHs (number of rings<4) are known to be formed from low temperature combustion processes of wood, grass, paper, industrial oil, un-burnt residual fossil fuels, light duty vehicles and coal gasification (petrogenic sources) while high molecular weight (HMW) PAHs (number of rings≥4) originate from high temperature combustion in coal-fired industries, heavy oil combustion, coke oven and heavy-duty motor vehicular emission (pyrolytic sources) (Dai *et al.,* 2007). Hence, the $\sum_{LMW}/\sum_{HMW}$ ratio < 1 suggests

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pyrolytic origin of PAHs while a ratio > 1 indicates petrogenic sources of PAHs contamination (Wilcke, 2007). The observed pooled ratios of $\sum_{LMW}$ and $\sum_{HMW}$ ranged from 0.4-4.2 (mean 1.4), which suggest both pyrogenic and petrogenic sources for PAHs in the present study. The different isomeric ratios used for discriminating pyrogenic from petrogenic hydrocarbons were Phe/Ant, BaA/(BaA+Chr), Flt/(Flt+Pyr), BbF/BkF, Ind/(Ind+BghiP), BaP/BghiP. The average ratio values and their range (in parenthesis) were 3.87 (1.51-12.58), 0.0006 (0.001-0.012), 0.90 (0.8-0.96), 0.27(0.06-0.45), 0.42 (0.05-0.78) for Phe/Ant, BaA/BaA+Chr, Flt/Flt+Pyr, Ind/(Ind+BghiP), and BaP/BghiP, respectively. The LMW PAHs Phe/Ant ratio estimated in the present study varied from 1.51-12.58 with an average value of 3.87, indicating pyrogenic sources such as fuel combustion in the study area. However, both the four ring PAH ratios: BaA/BaA+Chr and Flt/Flt+Pyr), implied petrogenic source for the sewage sludge. The values of BaA/BaA+Chr and Flt/Flt+Pyr were consistently <0.2 and <1, respectively, for all the sludge samples. This indicated PAH contamination could result from combustion of petroleum sources such as gasoline and diesel engine. However, the high concentration of Chr in the present study excludes diesel or its soot as the main PAH source as diesel PAHs are largely composed of LMW PAHs and HMW PAHs are removed during refining (Burns *et al.,* 1997). For Ind/(Ind+BghiP) ratio, a value<0.2 indicates petroleum source; the ratio between 0.20-0.50 indicates liquid fossil fuel combustion while ratio value >0.5, indicates biomass combustion. In the present study, the Ind/Ind+BghiP ratio was <0.2-0.50, showing that the PAHs mainly resulted from petroleum sources such as combustion of fuels in vehicles and crude oil. Lastly, BaP/BghiP ratio was found to vary from 0.05-0.78, indicating traffic as well as non-traffic sources responsible for current PAH emission. Municipal wastewater treatment plants studied herein receive effluents from diverse point and non-point sources such as domestic heating, urban street runoff, automobile washings, small 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. Hence, the use of molecular diagnostic ratios may not be an appropriate representative of any particular PAH source in sewage sludge. In addition to this, Katsoyiannis *et al.,* (2007) pointed that the PAHs undergo attenuation processes during wastewater treatment, resulting in varying PAH concentration in the final sludge. Although, the use of concentration ratios may not be accurate in understanding PAH source in sewage sludge, it may enable one to adjudge source prevalence in the study area.
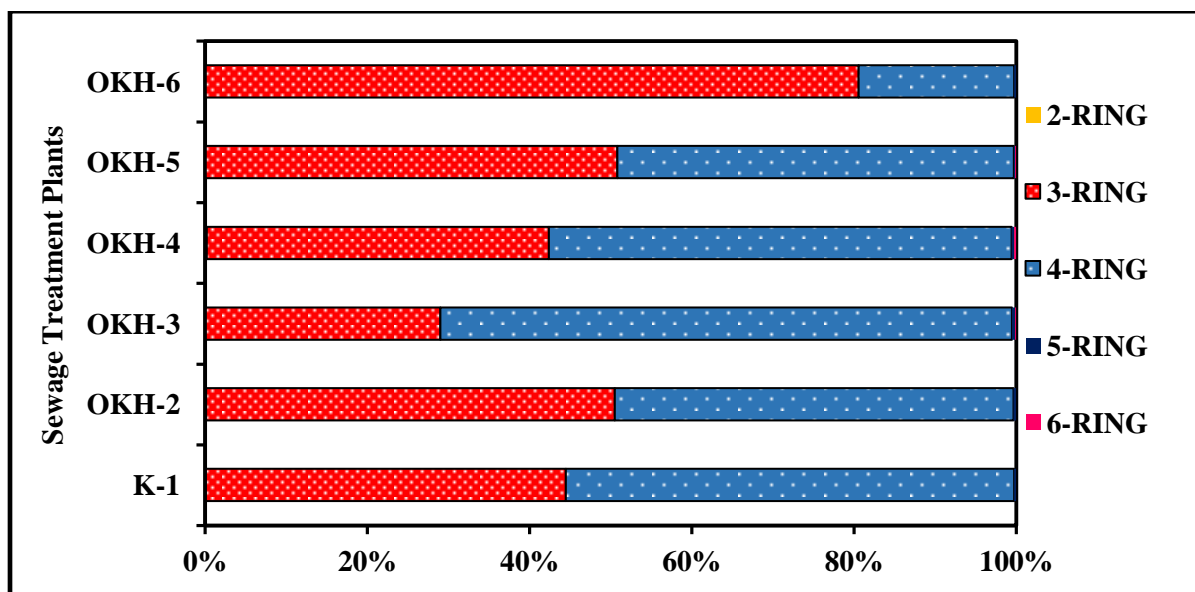

Figure 1: Abundance of PAHs Group Homolog in Sewage Sludge of Delhi

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Table 2: Toxicity Equivalency (BaP$_{TEQ}$) of Priority PAHs in Sewage Sludge

Compounds	Concentration(μg TEQ kg^{-1})			
	TEF	Range	Mean±SE	%$\sum$
Napthalene (Npt)	0.001	0.13-1	0.57±0.14	0.02
Acenapthylene (ANy)	0.001	0.90-64	25±11	1.07
Acenaphthene (ANe)	0.001	0.69-1.75	1.04±0.16	0.05
Fluorene (Fle)	0.001	52-506	252±79	11
Phenanthrene (Phe)	0.001	0.13-0.48	0.28±0.05	0.01
Anthracene (Ant)	0.01	0.12-2.7	1.3±0.36	0.06
Fluoranthene (Flt)	0.001	48-155	84±16	3.7
Pyrene (Pyr)	0.001	4.4-30	10±3.9	0.46
Benzo(a)anthracene (BaA)	0.1	3.2-6.4	4.1±0.49	0.18
Chrysene (Chr)	0.01	335-3629	1465±531	64
Benzo(b)fluoranthene (BbF)	0.1	2.4-46	15±6.6	0.66
Benzo(k)fluoranthene (BkF)	0.1	29-87	54±9.1	2.36
Benzo(a)pyrene (BaP)	1	16-533	161±78	7
Benzo (g,h,i)perylene (BghiP)	0.01	1.6-8.7	3.5±1.1	0.16
Dibenzo(a,h)anthracene (DBA)	1	120-312	193±33	8
Indeno(1,2,3-cd)pyrene (Ind)	0.1	5.2-18	10±1.9	0.44
$\sum$16PAHs (mgTEQ kg^{-1})	-	0.64-4.9	2.3±0.66	100
$\sum$7PAH$_{Car}$ (mgTEQ kg^{-1})	-	0.52-4.2	1.9±0.59	84

Assessment of Sludge Toxicity Based on BaP$_{TEQ}$ Concentrations
Benzo(a) pyrene has been considered as potential reference carcinogen and a good index for PAH toxicity by the IARC (IARC, 2005). 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 concentration of individual PAH was multiplied by its corresponding BaP TEF for calculating the BaP$_{TEQ}$ (μg BaP$_{TEQ}$ kg^{-1}) (Table 2). The sum of the TEQs of individual PAHs was used to estimate the carcinogenic potency of the 16PAHs. The BaP$_{TEQ}$ for 16PAHs ranged from 0.64-4.9 mg BaP$_{TEQ}$ kg^{-1} with a mean value of 2.3±0.66 mg BaP$_{TEQ}$ kg^{-1} which is higher than those in textile sludge (70-1332 μg BaP$_{TEQ}$ kg^{-1}; mean 423 μg BaP$_{TEQ}$ kg^{-1}) and sewage sludge (31.38 - 74.38 μg BaP$_{TEQ}$ kg^{-1}) in China (Ning *et al.,* 2014; Liu *et al.,* 2017) but quite comparable to the BaP$_{TEQ}$ values in the urban drain sediment (21-4339 μg BaP$_{TEQ}$ kg^{-1}; 990±1542 μg BaP$_{TEQ}$ kg^{-1}). The sum of the BaP$_{TEQ}$ concentrations for the seven carcinogenic PAHs known as the BaP Total Potency Equivalent (BaP TPE) ranged from 0.52-4.2 mg BaP$_{TEQ}$ kg^{-1} with an average value of 1.9±0.59 mg BaP$_{TEQ}$ kg^{-1}, accounting for 84% of the total BaP$_{TEQ}$ concentrations in the sewage sludge.

Organochlorine Pesticides
The concentration of total and individual of HCH and DDT isomers in the sewage sludge from the selected STPs in Delhi are presented in Table 1. The total concentration of the OCPs ($\sum$HCH+DDT) ranged from 880-23564 μg kg^{-1}, with an average representation of 7952±3519 μg kg^{-1}. The concentration sum of HCH isomers ($\sum$HCHs) varied from 797-23397 μg kg^{-1} while the $\sum$DDTs varied from 84-398 μg kg^{-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 observed levels of OCPs in the present study were compared with some of their measurements on sewage sludge from the other countries. In Canada, none of the studied OCPs were detected in the sewage samples, with the exception of p,p'-DDE which ranged from 6-28μg kg^{-1} at an average value of 13μg kg^{-1} (Stevens *et al.,*2003), much lower than the present levels. DDE is the most representative metabolite of DDT after its breakdown under aerobic conditions. In Korea, most of the isomers of HCH and DDT were detected in the STP sludge from both rural and urban background. The ranges of levels found were between 0.09-

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0.11 µg kg^{-1}, 0.61-0.98 µg kg^{-1}, 1.15-1.66 µg kg^{-1},7.58-14.8 µg kg^{-1}for α-HCH, β-HCH, γ-HCH and p,p'-DDE, respectively. In the same study, all the studied OCPs were detected in sludge samples of wastewater treatment plants treating effluents of mainly industrial origin. One such sample from the WWTP having papermaking units as major source of input wastewater, contained all the seven studied isomers, α-HCH, β-HCH, γ-HCH, δ-HCH, p,p'-DDE, o,p'-DDT and p,p'-DDT at levels of 0.19 µg kg^{-1},0.28 µg kg^{-1},0.36 µg kg^{-1},0.06 µg kg^{-1},0.76 µg kg^{-1},0.23 µg kg^{-1}and 0.44 µg kg^{-1}, respectively. The presence of α-HCH, γ-HCH, p,p'-DDE and p,p'-DDT were also detected in municipal WWTP sludge of Madrid, Spain, where their levels varied from 43-160 ng g^{-1}; 58-274 ng g^{-1}, 12-128 ng g^{-1}, 33-100 ng g^{-1}, respectively (Sánchez-Brunete *et al.,*2008).

Possible Sources of HCHs and DDTs

The compositional profile of HCH and DDT isomers are used to identify their contamination sources in the environment. The pooled ratio of α-HCH/γ-HCH is used to differentiate between technical HCH and lindane (γ-HCH) input. Technical HCH is a mixture of five isomers with percent contribution of 55-80% (α-HCH), 5-14% (β-HCH), 8-15% (γ-HCH), 2-16 % (δ-HCH) and 3-5% (ε-HCH),while lindane formulations contain >90% γ-HCH. 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. It has been studied that γ-HCH can be transformed to α-HCH through biological degradation and photolysis (Walker *et al.,* 1999). The ratio of α-HCH/γ-HCH between 3 and 7 indicates fresh input of technical HCH while lower ratio of ≤1, indicates lindane application (Willett *et al.,* 1998). The α-HCH/γ-HCH ratio found in this study varied from 5-18at an average value of 10, 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 γ-HCH may be transformed by sunlight and through biological degradation into α-HCH, which is more stable (Malaiyandi and Shah, 1980). The study area is located under the Tropic of Cancer line with strong ultraviolet radiation and a biologically active environment suggesting the transformation from γ-HCH into α-HCH under such conditions. Other studies anticipated the use of technical HCH as well as lindane formulations in India with a significant correlation between α-HCH and γ-HCH (R^2= 0.78).

The ratios between the parent compound of DDT and its metabolites can be used to identify their possible sources in the environment. DDT can be volatilized in a few days (Atlas and Giam, 1988) after the DDT applications. It was reported that *p,p'*-DDT degraded to other metabolites much faster in a tropical environment. Parent compounds of DDT slowly get converted to DDE and DDD under aerobic and anaerobic conditions, respectively (Baxter, 1990). Hence, the ratio between the DDT and DDE is often used as an indicator for aged or recent source of DDT. The ratio of DDT/DDE greater than 1 suggest fresh input of DDT in last five years, while lower ratios indicates microbial degradation or aged DDT (Tavares *et al.,* 1999). 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. Elevated concentrations of *p,p'*-DDE have been interpreted as a result of DDT conversion to *p,p'*-DDE by UV radiation during atmospheric transport (Atlas and Giam, 1988). 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).

Chlorophenols (CPs)

The concentration of ∑CPs ranged between 40-57 mg kg^{-1} with a mean value of 49±2.4 mg kg^{-1} while the concentration of the individual compounds ranged from 5.5-7.8 mg kg^{-1} (mean:6.8±0.3 mg kg^{-1}), 3.4-7.7 mg kg^{-1} (mean:4.4±0.7 mg kg^{-1}), 4.2-13.4 mg kg^{-1} (mean:8.9±1.6 mg kg^{-1}), 24-40 mg kg^{-1} (mean:29±2.5

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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 (Table 1). Comparing the levels of individual CPs with those reported in sewage sludge by few studies, it was found that the present chlorophenol levels were much higher than that investigated in other countries. The wastewater sludge samples of Korea contained the four CPs within a range of 0.091-0.244 mg kg^{-1} (2-CP; mean:0.168 mg kg^{-1}), 0.013-0.092 mg kg^{-1} (2,4-DCP; mean:0.057 mg kg^{-1}), 0.007-0.287 mg kg^{-1}(2,4,6-TCP; mean:0.096 mg kg^{-1}) and 0.015-0.212 mg kg^{-1} (PeCP; mean: 0.074 mg kg^{-1}) (Ju *et al.,* 2009). Another study in Canada, reported even lower values for the concentration maxima of 2,4-DCP and PeCP in wastewater sludge at 0.15 and 0.04 μg kg^{-1}, respectively (Bright and Healy, 2003). PeCP has been detected in sewage sludge of Germany at concentrations < 1 mg kg^{-1} (Schnaak *et al.,* 1997).

Conclusion
The US EPA 16 priority PAHs, persistent organic pollutants such as DDT and HCH and priority pollutants such as chlorophenols were measured in sewage sludge collected from sewage treatment plants of Delhi.

The 3-4 ringed PAHs were most dominant in all the sludge samples with Fluorene accounting for the highest PAH content in the sewage sludge. Major source diagnostic ratios revealed possibilities of both petrogenic and pyrogenic activities responsible for the load of PAH in the sewage sludge. The targeted organochlorine pesticides and chlorophenols were also found to be present in all the sewage sludge. The isomeric ratios of DDT/DDE suggested past and ongoing usage of DDT while that of α-HCH/γ-HCH suggested possibilities of contamination from technical HCH usage in the past and current lindane application.

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