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Pops in Groundwater: Exposure Profiles of PAHs and OCPs at an Agricultural Site of a North Indian Terai Region

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Abstract **-** Our world is full of synthetic chemicals which pollute water, soil and food. Contamination of groundwater with synthetic organic materials is presenting major environmental problems in many areas of India and in other industrialized nations as well. In this regard, an investigation of persistent organic pollutants (POPs) in groundwater has been performed at selected locations in Gorakhpur (terai belt in the north part of India) in order to ascertain their contamination levels. Two different compounds were determined: polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs). High pressure liquid chromatography (HPLC) was used for PAH analysis whereas capillary gas chromatography (GC) with electron capture detector (ECD) was used for OCP analysis. A set of sixteen PAHs and eleven OCPs were determined in the groundwater of Gorakhpur city from agricultural area. Mean concentration of total PAH and OCP for the entire sample collected was 21.60 ng/L and 6.21 ng/L respectively. The median was 17.27 ng/L and 4.95 ng/L for PAHs and OCPs respectively. Results show that concentration of individual PAH is between 1-10 ng/L and is in the range given for the uncontaminated groundwater. The foremost PAHs found in present study were anthracene> fluoranthene>benzo(b)fluoranthene. T-OCP concentrations were highest at agricultural sites followed by residential sites and roadside sites. Trends of major OCP were pp-DDT > γ-HCH > Aldrin. Using a Toxic Equivalent Factors approach according to literature and USEPA, mean concentration of TPAH equates to about 1.86 ng/L of B(a)P with respect to carcinogenic potency.

***Keywords*:** POPs, PAHs, OCPS, Groundwater, Terai belt

1. Introduction

Contamination of groundwater with synthetic organic materials is presenting major environmental problems in many areas of India and in other industrialized nations as well. Persistent organic pollutants (POPs) are amongst the most dangerous substances released by humans into the environment. They include a wide range of substances, including organochlorine pesticides (OCPs) and their metabolites from agricultural activities/practices; industrial chemicals (e.g., PCBs); anthropogenic and natural combustion products, e.g. chlorinated dioxins/furans and polycyclic aromatic hydrocarbons (PAHs) [1]. They possess toxic characteristics and are persistent, resist degradation under natural conditions and remain unchanged in the environment for a long period. PAHs are neutral, non-polar organic molecules that comprise two or more benzene rings arranged in a linear, angular or cluster arrangement. Most of the PAHs released into the environment arise from anthropogenic sources [2]. Atmospheric deposition has been regarded as a main pathway for loading of PAHs to many water bodies. On entering the aquatic systems, most of the PAHs are adhered to suspended particles due to their hydrophobic properties, and therefore sink to the bottom and accumlate in sediments [3] and from a long-term source of potential pollution. Hence, the occurrence of PAH in groundwater can be hazardous even at low concentrations [4]. 16 PAHs have been chosen by the US federal water pollution control, US clean water act and USEPA (1980) as priority pollutants to be monitored in industrial effluents. Also, the world health organization [5]**,** has recommended limits for certain PAH in drinking water. The uncontaminated groundwater appears to have lowest PAH concentrations of all natural waters i.e. 0.001 to 0.010 ng/L [6]. OCPs are man-made insecticide, fungicide and antimicrobial chemicals containing multiple chlorine substitutions. They are potentially toxic, highly persistent and resistant to biodegradation and it readily accumulates in human body tissues, causing a variety of health hazards.

In the public health arena, pesticides are also used for control of domestic pests, e.g. cockroaches, flies, mosquitoes, ectoparasites including ticks, and other insects [7]. The occupational exposure could be during manufacture of pesticides in industrial settings and their distribution in field condition during application of pesticides. The non-occupational exposure or indirect toxic effects may be due to pollution of the ecosystem or habitat as a whole such as from water, air and food [4]. Thus, it is important to acquire information about this environmental compartment and its role in micro pollutant cycle. In India, sporadic studies have been reported for PAHs and OCPs. To our knowledge there has been a shortage of groundwater and soil POPs studies. Therefore, the aim of this study to determine groundwater contamination by PAHs and OCPs at an agricultural area of this terai belt in northern India.

2. Materials and Methods

2.1. Site Description

Gorakhpur (26°46´N 83°22´E) is located in the eastern part of the state of Uttar Pradesh in India, near the border with Nepal. It is located on the bank of river Rapti which is interconnected through many other small rivers. Gorakhpur city comes under the terai belt of eastern Uttar Pradesh, India. The present district of Gorakhpur, 265 Kms east of capital Lucknow, on National Highway -28, covers the geographical area of 3483.8 Sq. km having total population 10,61,428.

2.2. Extraction and Analysis

The water samples were collected from an agricultural area named Haiderganj. Water samples (250 ml) were extracted with hexane (30 ml) in a separating funnel thrice. Small amount of sodium sulphate was added to the extract to eliminate the presence of water. Silica-gel column was used for purification of the extract according to EPA method 3630 [8]. The extract was evaporated by a flow of Nitrogen and then extract was divided into two parts for PAH and OCP analysis. After drying the extracts was redissolved in 1ml of acetonitrile (PAH) and hexane (OCP) for analysis by HPLC and GC respectively. PAH analysis was carried out using a High Pressure Liquid Chromatography (HPLC) system (BGS-515, Waters) with UV visible detector (DAD-2487, Waters). The analytical column was of 250 mm length and 4.6 mm i.d; packed with totally porous spherical C-18 material (Particle size 5μm). A guard column (10 mm long and 4.6 mm i.d) preceded the analytical column. Acetonitrile-water mixture (70:30) was used as mobile phase in an isocratic mode at a flow rate of 1.5 ml/min. Samples of 20 μl were injected into the column through the sample loop (0.1 ml). OCP analysis was carried out by using capillary gas chromatography system (Agilent Technologies) 7890 with electron capture detector (GC-ECD, DL: 0.020 μg/L). The analytical column was of 30m HP5-MS fused silica capillary column (30×0.25mm×0.25 μm film thickness). Temperature programme used for pesticides analysis started from 60oC it was then raised to 180oC @ 30oC per min and then to 280oC @ 10oC per min and held for 10 min. In electron capture detector the radiation source was Ni63, detector temperature 350oC, carrier gas-hydrogen, make-up gas-nitrogen (99.99%).

3. Results and Discussion

The total PAH concentration ranged from 7.53 ng/L to 49.68 ng/L. The mean concentration of total PAH for the entire sample collected was 21.60 ng/L and the median was 17.27 ng/L. The average concentration for all the individual PAHs is shown in Table 1. Trends of the concentrations of the major PAH found in present study were anthracene (4.43 ng/L), followed by phenanthrene (3.23 ng/L), benzo(a)anthracene (2.45 ng/L), chrysene (2.45 ng/L) and fluoranthene (2.04 ng/L) respectively . The results shows that the concentration of individual PAH is between 1-10 ng/L and is in the range of safe drinking water given in the literature [6,3], for the uncontaminated groundwater. Trapido [9] estimated PAH content at agricultural site to be about 0.1 ng/L which is considered as background value for PAH. Observed values of total PAH at agricultural site are higher than the background levels which can be due to atmospheric transport of PAH from sources to remote sites. Table 1 also shows the residue levels of OCPs in the groundwater. Mean concentration of OCPs was found to be 6.21 ng/L with the range of 3.04 ng/L – 14.84 ng/L and the median was 4.95 ng/L. A total of eleven OCPs were found in groundwater of Gorakhpur. Average concentrations of total hexa chloro cyclohexanes: HCHs (α-HCH, ß-HCH, γ-HCH, δ-HCH) in the groundwater samples of Gorakhpur was found to be 0.50 ng/L whereas that of total dichlorodiphenyltrichloroethane: DDT (pp-DDE, pp-DDD, op-DDT, pp-DDT) were found to be only 0.92 ng/L. pp-

DDT has higher concentration (3.43 ng/L) in comparison to its metabolite DDE and DDD (dichlorodiphenyldichloroethane) indicating that particularly pp-DDT was used for years until it was banned.

Significant concentration levels of DDE in comparison to DDD may be attributed to the presence of various kinds of benthic organisms present in soil, which accelerate the biodegradation process of DDT to DDE. Average concentrations of total endosulfan (α-Endosulfan, ß-Endosulfan) were found to be 0.15 ng/L. Major OCP trends were pp-DDT > γ-HCH > Aldrin. The dominant OCP found in this study was pp-DDT having 55% followed by γ-HCH having 32% of the total OCP concentrations

Table 1: PAH & OCP exposure profiles in Groundwater at GKP (ng/L)

PAHs	**Mean±s.d.**	**OCPs**	**Mean±s.d.**
NAP	0.95±0.4	α-HCH	0.28±0.1
ACY	0.25±0.1	ß-HCH	0.09±0.02
FLU+ACE	0.56±0.2	γ-HCH	1.36±0.6
PHE	3.23±1.2	δ-HCH	0.26±0.1
ANT	4.43±1.3	Aldrin	0.25±0.1
FLT	2.04±1.0	α-Endosulfan	0.25±0.1
PYR	1.62±0.8	ß-Endosulfan	0.06±0.01
BAA+CHR	2.45±1.1	pp-DDE	0.08±0.01
B(k)F	0.98±0.5	pp-DDD	0.09±0.02
B(b)F	1.75±0.8	op-DDT	0.07±0.01
B(a)P	1.02±0.3	pp-DDT	3.43±1.5
D(a,h)A	0.89±0.1		
Ind(123cd)P+B(ghi)P	1.41±0.5		
TOTAL	**21.6±8.3**		**6.21±2.6**

Figure 1 illustrates the pattern of PAH & OCP in Groundwater at an agricultural area of Gorakhpur. High concentrations of pp-DDT at agricultural site can be attributed to its particular use for protecting plants in order to enhance the production due to its strong pesticidal action against a variety of pests.

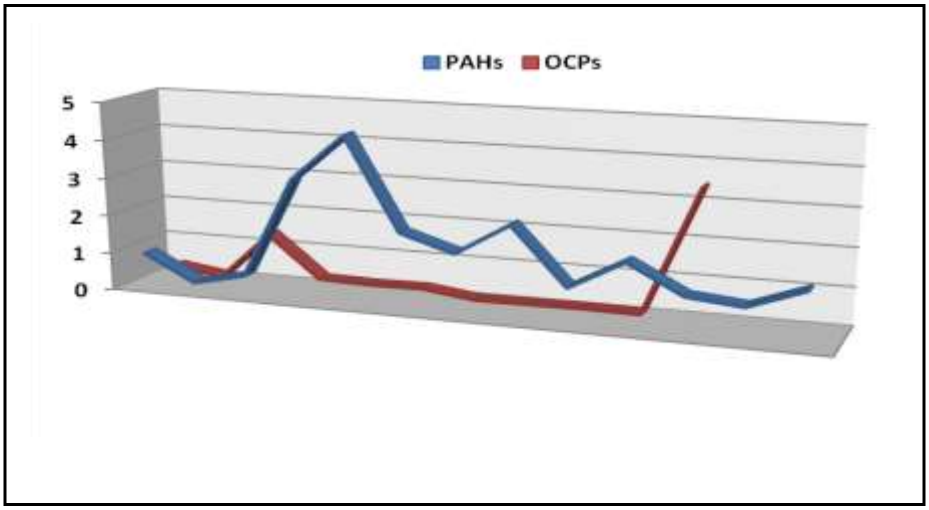
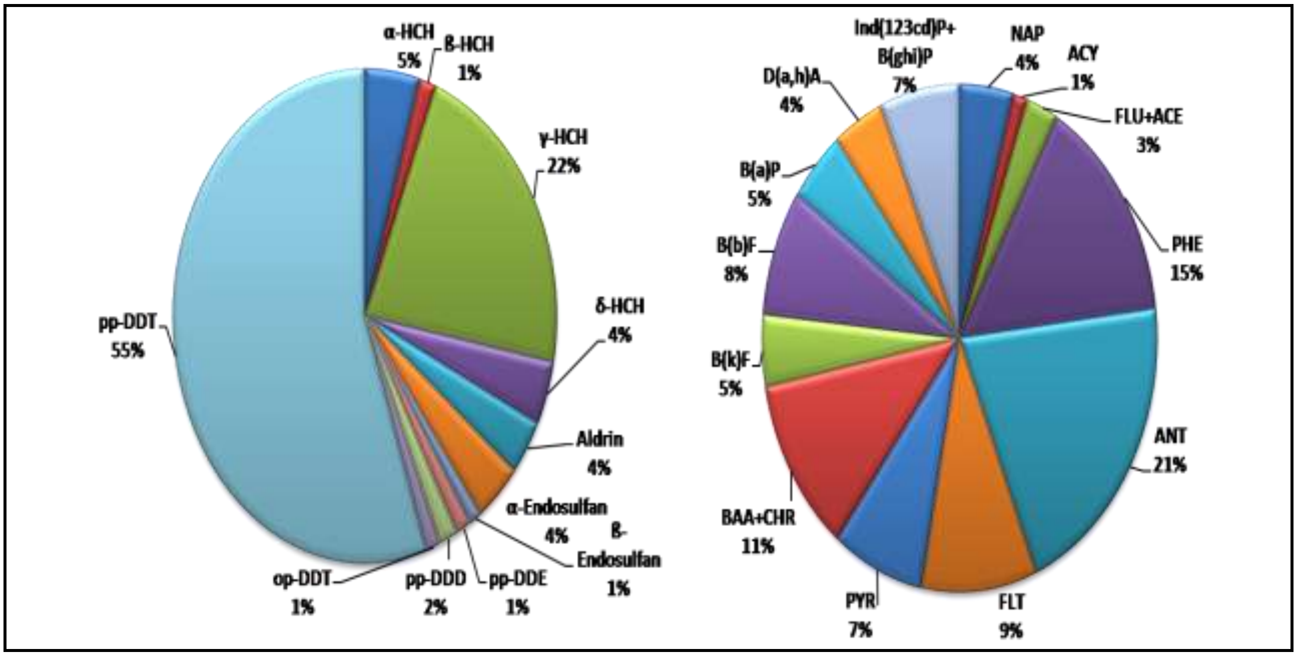


Figure 1: Pattern of PAH & OCP in Groundwater at GKP

Significant concentration levels of DDE in comparison to DDD may be attributed to the presence of various kinds of benthic organisms present in soil, which accelerate the biodegradation process of DDT to DDE. Average concentrations of total endosulfan (α-Endosulfan, ß-Endosulfan) were found to be 0.15 ng/L. Major OCP trends were pp-DDT > γ-HCH > Aldrin. The dominant OCP found in this study was pp-DDT having 55% followed by γ-HCH having 32% of the total OCP concentrations.



. Figure 2: Contribution (%) of individual PAH & OCP in Groundwater at GKP

Figure 2 shows percentage contribution (%) of different PAHs and OCPs in groundwater of Gorakhpur respectively. Average percentage of T-PAH based on benzene rings were 6% (2 ring), 39% (3 ring), 20% (4 ring), 20% (5 ring), and 15% (6 ring). 3-ring PAHs were found to be dominant in the groundwater of an agricultural area in Gorakhpur followed by 4-ring and 5-ring having 39%, 20% and 20% respectively of the T-PAH. Correlation analysis was performed by using

Univariate Pearson correlation coefficient for all pairs of PAH and OCP compounds separately which shows significant correlations among most of the PAHs and OCPs. One approach to estimating the carcinogenic potency associated with exposure to a given PAH compound is to assign a Toxic Equivalent Factor (TEF), a measure of its potency relative to that of B(a)P. TEF for B(a)P is set at 1.0. Concentration of each individual PAH compound is multiplied by its respective TEF to calculate the "B(a)P equivalent".

The mean concentration of T-PAHs in Gorakhpur to be 21.60 ng/L, which corresponds to a B(a)P equivalent exposure of 1.86 ng/L (Table 3) with respect to carcinogenicity, using TEFs given by Tsai [10]. B(a)P contributed the highest carcinogenic exposure equivalent (1.02 ng/L) followed by B(a)A (0.24 ng/L) and B(b)F (0.17 ng/L), accounting for approximately 55%, 13% and 9% of the total PAH carcinogenicity in groundwater of Gorakhpur, respectively.

Table 3: BaP toxic equivalency factors (TEFs) and BaP_{eq} exposure profiles (ng m^{-3})

PAHs	**MEAN**	***TEFs**	**BaP $_{exposure}$**
NAP	0.95	0.001	0.00095
ACY	0.25	0.001	0.00025
FLU	0.56	0.001	0.00056
ACE	0.56	0.001	0.00056
PHE	3.23	0.001	0.00323
ANT	4.43	0.01	0.04435
FLT	2.04	0.001	0.00204
PYR	1.62	0.001	0.00162
BAA	2.45	0.1	0.2455
CHR	2.45	0.01	0.0245
B(k)F	0.98	0.1	0.0985
B(b)F	1.75	0.1	0.1755
B(a)P	1.02	1	1.02
D(a,h)A	0.89	0.1	0.089
Ind(123-cd)P	1.41	0.1	0.1415
B(ghi)P	1.41	0.01	0.01415
TOTAL			**1.86**

TEFs cited by Tsai et al. (200

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Conclusion

A set of 16 PAHs and 11 OCPs were determined in the groundwater of Gorakhpur city from an agricultural area. Correlation analysis was performed using Univariate Pearson correlation coefficient for all pairs of PAH and OCP compounds separately which shows significant correlations among most of the PAHs and OCPs. It is probable that the chemistry of POPs in a tropical environment where temperature and relative humidity are higher coupled with abundant sunshine may differ from that of temperate regions which should be investigated in future studies.

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