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Role of aquifer media in determining the fate of polycyclic aromatic hydrocarbons in the natural water and sediments along the lower Ganges river basin

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Abstract

Groundwater-sourced drinking water quality in South Asia, specifically India, is extremely stressed, mostly from the presence of many pervasive and geogenic pollutants. The presence and behavior of anthropogenic pollutants like polycyclic aromatic hydrocarbons (PAHs) are poorly investigated on a regional or basin-wide scale. The present study provides one of the first documentation of the presence and behavior of PAH in the aquifer sediments in the Ganges river basin. Lower and medium molecular weight PAHs e.g., naphthalene, phenanthrene, and fluoranthene were detected in 79, 36 and 13% of samples (n=25). The PAH level in groundwater was approximately five times lower than river water. The sorption behaviour of PAHs were studied in experiments in presence/absence of organic carbon and by simulating advective transport of low to medium molecular weight PAHs e.g., naphthalene, phenanthrene and fluoranthene in aquifer sediments collected from agricultural, peri-urban and

urban areas. Naphthalene and phenanthrene adsorbed on quartz and kaolinite, but not on clay minerals like kaolinite. Fluoranthene adsorbed more favourably on kaolinite. Numerical modeling of the advective transport of PAHs in aquifers suggest up to 25 times faster movement of pollutants from irrigation-induced pumping, indicating the strong control of hydraulics on the spatial distribution of PAHs in sub-surface.

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Keywords

Land use; Sediment; Groundwater; Ganges River; Contamination; Transport; Extraction; Pyrogenic; Petrogenic; Pumping

Introduction

The mobility, persistence, and extensive consumption of polycyclic aromatic hydrocarbons (PAHs) have resulted in widespread drinking water contamination^[1]. Accumulation of contaminants like PAHs in aquifers and the use of contaminated groundwater for irrigation further deteriorates the situation, and raises concern about their exposure to the public^[2]. The introduction of such toxic organic chemicals in aquifer sediments and groundwater has troubled the natural catabolic processes and threaten human health^[3]. For example, the study conducted in the Vhembe district, South Africa showed that prevalence of higher molecular weight PAHs are elevated in industrial effluents, which are eventually transported into surface and groundwater bodies, and pose a challenge to human health issues^[4]. The sources of these compounds are primarily anthropogenic. Vehicles release wide-ranging organic and inorganic compounds from incomplete combustion of fossil fuels, leakage, and operation of catalytic converters. In particular, PAHs present in petroleum hydrocarbons and wood preservatives like creosote are toxic to the ecosystem because of their lipophilic character and detrimental effects to resulting in mutagenic and carcinogenic changes^[5,6]. PAHs adsorb to sediments because of their high hydrophobicity and solid-water distribution ratios^[7,8]. In addition, the sorption of PAHs is influenced by its degradation and transport in aquatic environments^[9]. This phenomenon is related to the retention capacity of PAHs in sediments which varies between the compounds.

PAHs have been intensely investigated over the last few decades due to their widespread occurrence and persistence in nature^[10–13,8]. PAHs reported in different locations from the world including the present study area are given in Table 1.

In India, several studies have investigated the spatial distribution of PAHs. For example Mitra et al^[14] studied the surface sediments (0–5 cm) in the Hooghly River estuary in the

Western Bengal basin. Anthropogenic activities resulted in the introduction of different point and non-point source PAHs in drinking water in the area. While different sources of PAHs and its distribution in natural waters and sediments have been investigated, PAH sorption behavior in these environments are rarely explored.

The Ganges River basin is a densely populated region with an areal extent of about 21,000 km² [15,16]. Approximately 2% of the world's population resides in this region. Groundwater in major parts of the Ganges River basin has been studied for inorganic geogenic pollutants such as arsenic and fluoride. Although the presence of various anthropogenic-sourced pollutants has been indicated in the Ganges river basin, there is a dearth of detailed or site-specific information. In particular, the prevalence and fate of PAHs in the arsenic-contaminated aquifers of the Western Bengal basin is largely unknown.

The primary objectives of this study are to 1) provide a detailed understanding of spatial distribution of PAHs in groundwater, and 2) examine sorption phenomenon of commonly occurring PAHs on surface sediments from the Western Bengal basin. Specifically, the distribution and quantification of PAHs derived from industrial sources and vehicular emissions were examined in this study. The influence of land-use on PAH distribution arising from pumping of groundwater that is mainly used for agriculture was determined using advective transport modeling. This study documents for the first time detailed information on the spatial distribution of PAHs on a basin-wide scale and impacts of groundwater pumping to sustain the high agricultural demands. The information generated in this study will be useful for land management and land-use practices to safeguard the groundwater and surface water resources in the Ganges River basin.

Materials and Methodology

Sample collection

Approximately, 1L groundwater (n = 235) and river water (n = 32) samples were collected for analyses of PAHs during 2015 for two seasons in pre-cleaned high-density polyethylene bottles (HDPE) following EPA Method 680 (Table 1S – 3S). The sediment samples were collected from three different depths (0–30 cm) in 25 locations across the Western Bengal basin. Few sites (n = 14) were close to national highways and they were situated in peri-urban and urban areas. Some of the samples (n = 11) were collected adjacent to agricultural lands (Fig. 1).. Sediments were collected in a sealed and sterilized bottle. The samples were homogenized and passed through a 2 mm sieve and oven-dried and stored in air-tight containers.

Extraction of PAHs from water and sediment samples

16 PAHs (ΣPAH_{16}) in both river water and groundwater samples were extracted from 1 L of water sample, by passing through methanol and de-ionized water pre-conditioned 6 mL C18-solid-phase cartridges (*Thermo Scientific*). Subsequently, the ΣPAH_{16} in the aforesaid air-dried C18 cartridge was eluted using 6 mL of methanol. The eluent was further concentrated using a rotary evaporator with nitrogen purging. The residue was dissolved in 3 mL of n-hexane and dichloromethane (50:50 volume ratio) and taken to near dryness under N flow. The extract was redissolved in 300 μL of hexane and refrigerated until further analysis.

Dried and homogenized 5 g of sediment was extracted with a mixture of dichloromethane and n-hexane (9:1 v/v). A Dionex® Accelerated Solvent Extractor 300 was used by programming it for three extraction cycles at 1000 psi and 100°C^[19,20] followed by solid-phase extraction (SPE) using 6 mL C18 SPE glass cartridges, pre-rinsed with methanol and dichloromethane^[21].

PAH analyses in water and sediment samples

The PAHs and their alkylated derivatives in the sediment and water samples were analyzed by using a gas chromatograph-mass spectrometer (*Agilent® 7890A*). Sample injection was done in split-less mode into an ion trap *Agilent 7890A* gas chromatograph mass spectrometer, equipped with a DB5-MS column (30 m × 0.25 mm inner diameter × 0.25 µm film). GC oven temperature was varied from 70 to 200°C at 20 °C/min. The increase in temperature was up to 310°C (with a hold time of 15 min), and up to a final temperature of 315°C (with a hold time of 4 min) at 5°C/min. Quality control was done by analyzing solvent blanks and routine blanks, along with a five-point calibration curve using DCM and hexane based standards (NIST 16 PAH mix, 1000 µg/L) to quantify 16 PAHs (Σ PAH_{S16}). PAH identification was done based on their retention time and mass spectra. The limits of detection (LOD) for PAHs were in µg/kg concentrations and accuracy and precision, using triplicates were better than ±5%. From a batch of 25 sediment samples, five samples were selected for sorption studies based on the detailed mineral and elemental characterization.

Mineral characterization was carried using PANalytical X'pert Powder. Samples were packed in the flat sample stage holder, and the XRD pattern was obtained on the instrument using Cu K α radiation equipped with a diffracted – beam monochromator in the range of 5-75° (2 Θ) at the rate 0.00013°. Results were evaluated by Highscore Plus to detect the most abundant peaks and relative quantification. Each sample was analyzed three times to improve the signal-to-noise ratio [22].

Sorption experiments

Sorption phenomenon of selected PAHs was studied on natural sediments and laboratory-grade synthetic minerals using a batch equilibrium technique based on OECD Guideline 106 [23]. Glass vials with Teflon cap were used for the experiment. The solid to liquid ratio in the

experiment was 0.4 for laboratory kaolinite and 1.0 for quartz since it has a low surface area. Based on the mineral characteristics, quartz and kaolinite the dominant minerals in these sediment were considered for the sorption study. About 5 g of homogenized sediments were equilibrated with 4 mL of ultrapure water for 24 hours. 1 mL of each PAH solution was added to both and glass tubes were placed on a horizontal shaker. The suspension was centrifuged at 4000 rpm for 30 min and the supernatant was set aside for further analysis. Each sample was prepared in triplicate for the sorption experiment. Five different concentrations have been considered for the isotherm study. Two PAH solutions were prepared with concentration ranging from 0.25 to 1 mg/L. The experiment was conducted for 30 hours and PAH concentrations in sediments was analysed at 3-hr intervals. A similar procedure was followed for the laboratory-grade kaolinite and quartz powder. Langmuir and Freundlich isotherm model was used to demonstrate monolayer adsorption of PAHs onto natural sediments as well as on laboratory-grade kaolinite and quartz powders.

The results for adsorption of PAHs were analysed using the Langmuir and Freundlich models. The Langmuir isotherm has been used by previous workers for studying sorption of different compounds^[24]. The model assumes a uniform adsorption energy on the surface and no transmigration of adsorbate on the plane of the surface. The Langmuir adsorption isotherm is mathematically represented as equation 1:

$$\frac{1}{q_e} = \frac{1}{q_{\max} + 1} \frac{1}{b} q_{\max} C_e \quad (1)$$

where, q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L) and $Q_{\max}$ and b are the Langmuir constants related to maximum adsorption capacity and adsorption energy, respectively.

The adsorption data for PAHs were also analysed using the Freundlich model. The Freundlich adsorption isotherm is mathematically represented by Equation 2:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L) and K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively^[25].

Quality assurance and quality control

The quality assurance and quality control (comprised laboratory quality control procedures including analysis of the reference material (laboratory grade sand and kaolinite), field blanks and laboratory blanks, and spiked (1 µg/L) PAHs (naphthalene, phenanthrene, and fluoranthene) added to the samples. Laboratory-grade kaolinite and quartz were considered for laboratory blanks. Deuterated-perylene and chrysene were injected with a concentration of 0.5 and 1 µg/L respectively (Table 4S and 5S). The recovery percentages were 79% for the water samples and 74% for the sediment samples. Laboratory blanks were also used for extraction and PAH analyses were conducted following the similar procedure.

Statistical analysis

All values were specified as a mean of three determinations. The Student's t-test established the comparison between the mean of total PAH concentrations; $p < 0.05$ was considered as statistically significant. The t-statistics value was analysed from the coefficient ratio of an independent variable and standard error. A t -value of 0 indicates that the sample supports the null hypothesis. As the difference between the sample data and the null hypothesis increases, the absolute magnitude of t -value increases. The p -value (probability value) was calculated using the probability density function which describes the likelihood of a t -value and whether

it is statistically significant ^[26]. Spearman correlation coefficient ^[27] was used to observe the relationship between PAHs in 25 sediment samples. Multivariate statistics using hierarchical cluster analyses (HCA) were done on the original data set (without any weighting or standardization) ^[28]. The HCA dendrogram was constructed by Ward's method with squared Euclidean distance ^[29]. HCA was used to investigate relationships between the locations. HCA was also analyzed by E-views statistical software (v. 9.5).

Advective transport

High-resolution calibrated 3D-groundwater flow modeling in seasonal scale was used to replicate the groundwater flow path through anisotropic and heterogeneous aquifers in the study area following Mukherjee et al. ^[16] in a finite difference grid using MODFLOW codes ^[29] in dynamic-equilibrium mode. The entire model domain of the 21,000 km² lower Ganges basin was numerical gridded, with a horizontal resolution of 1000 m (x) and 1000 m (y), with 22 vertical layers from surface to 300 below ground level, and a resolution of 15 m (z). Details of the regional hydrostratigraphy were screened from Mukherjee et al. ^[16] and information from 141 lithologs. Hypothetical, conservative PAH particles were simulated using MODPATH ^[30] for advective transport to target wells at 50 m depth, from time t_l (infiltration time at the source) to t_n (transport time to the targeted drinking water well) that were nested on telescopically-refined grids (100 m $\times$ 100 m $\times$ 10 m, 31 layers) of the aforesaid groundwater flow path model and calibrated boundary conditions and hydraulic properties. The hypothetical source-particles were designed to be present horizontally between 10 m to 1500 m and at depths of 50 m from topographic elevation. For the particle transport simulations, base-line conditions of no irrigational pumping and present-day pumping conditions were included.

Results and discussion

Distribution of PAHs

Σ PAHs₁₆ were detected in the groundwater with a mean concentration of 3.45 and 5.31 $\mu\text{g/L}$ in river water samples during 2015. The Σ PAHs₁₆ concentrations in groundwater and river water across the study area varied from 0.01 to 8.01 $\mu\text{g/L}$ and 0.02 to 6.22 $\mu\text{g/L}$, respectively (Fig. 2, Table 3S). In order to detect the extent of low, medium and high molecular weight PAHs in different groundwater and river water samples, PAH compounds were divided into three groups: 2 + 3 rings or low molecular weight PAHs (LMs), 4-rings or medium molecular weight PAHs (MMs) and 5 + 6 rings or high molecular weight PAHs (HMs). The percentage of LMs to total PAHs was higher than that of MMs and HMs in groundwater samples, indicating that LMs were predominant in water samples. Naphthalene and phenanthrene were the dominant LMs. MMs were detected but at low levels HMs such as six-ring PAHs were detected in trace amount in both groundwater and river water samples. The total and individual concentrations of PAHs detected in river and groundwater samples ($\mu\text{g/L}$) from the Western Bengal basin are listed in appendix A. Among 235 groundwater samples, naphthalene was predominant in 79% samples followed by fluoranthene (26% of samples) and phenanthrene (3% of samples). Groundwater indicated that naphthalene was the dominant PAH with a maximum concentration of 8.25 $\mu\text{g/L}$. Presence of alkylated PAHs such as 2-methyl naphthalene (55%), 1-methyl naphthalene (22%), and 1, 3-dimethyl naphthalene (31%) was also detected in the study area. The PAH levels in groundwater were approximately five times lower than river water (Fig. 2). Low molecular weight PAHs (2-3 rings) were predominant in surface water samples in river water and, on average, accounted for 75% of the total PAHs. Naphthalene was the most common PAH found in river water samples (84% of the samples) followed by phenanthrene (29% of the samples) among 32 river water samples. Three-ring PAHs were predominant among individual PAHs, and six-ring PAHs were not detected. It was

noted that naphthalene was the dominant individual PAH. The highest concentration of naphthalene exceeded $>3 \mu\text{g/L}$ at 5 locations in river water samples.

While the predominant PAH was naphthalene its alkylated derivatives including 1, 3-dimethyl naphthalene, 2, 6-dimethyl naphthalene, 1-methyl naphthalene, and 2-methyl naphthalene and fluoranthene were also found in river water. The abundance of alkylated PAHs in river water samples were as follows: 2-methyl naphthalene (12%), 2, 6-dimethyl naphthalene (10%), 1, 3-dimethyl naphthalene (4%), 1-methyl naphthalene (2%) and fluoranthene (2%) in. Anthracene and chrysene were detected in trace amounts in groundwater and river water. The spatial distribution of four predominant PAHs is shown in Figure 3.

According to Koh et al. and Khairy et al. ^[32, 33], it has been observed that medium molecular weight (MM) PAHs are predominant in sediments whereas, low molecular weight PAHs (LMs) are dominant in water samples. LMs such as naphthalene and phenanthrene are more soluble and also degradable, whereas HMs such as pyrene and benzo(a)anthracene are comparatively more stable ^[33,34]. Overall, HMs are hydrophobic and more resistant to degradation (Bakhtiari et al., 2009). As a result, HMs readily adsorb to sediments and eventually settle down and accumulate in bottom sediments.

PAH concentrations in sediment from different depth intervals (0–10 cm, 10–20 cm, and 20–30 cm) indicated distinct differences (Fig. 4, Table 6S). The sediment samples collected from 0–10 cm showed the maximum PAH concentration ($2.22 \mu\text{g/kg}$ dry weight). Sediment samples collected from 10–20 cm and 20–30 cm depth intervals indicated a total PAH concentration of 2.02 and $1.95 \mu\text{g/kg}$, respectively. Naphthalene was the most common PAH in these sediments. The sediment sample collected from 0 – 10 cm consisted of mostly naphthalene (79%), phenanthrene (36%), fluoranthene (13%), and benzo (a) pyrene (9%). However, sediments collected from 10–20 cm and 20–30 cm depth indicated a high

concentration of naphthalene (58.3% at 10–20 cm depth and 49% at 20–30 cm depth), but relatively low phenanthrene concentration.

Possible explanations for the dissimilarities include diverse sorption capacity in the soils at sampling sites and different organic carbon content and mineral composition. Naphthalene frequently occurred in the 0–10 cm interval (min: 0.12 and max: 2.33 $\mu\text{g/kg}$) followed by phenanthrene (min: 0.63 and max: 1.6 $\mu\text{g/kg}$), and fluoranthene (min: 0.50 and max: 2.96 $\mu\text{g/kg}$). Soil particles with PAHs adsorbed on the surface can be transported into the deeper intervals within the soil column by recharge water or tilling of soil. The concentrations of all ΣPAH_{16} were low in the deeper layers (10–20 cm and 20–30 cm) compared to the surface soils. These variations in PAH distribution can be established by comparing the PAH profiles. While the medium molecular weight (MMW) PAHs, i.e. primarily anthracene and fluoranthene, are transported mainly in the particle-bound state, transport of naphthalene and phenanthrene occurs preferably in the dissolved or gaseous states. The concentrations of some of the lower molecular weight (LMW) (naphthalene and phenanthrene) and MMW (fluoranthene) PAHs show significant positive correlation with the organic carbon content ($r_{\text{nap}} = 0.91$, $r_{\text{phe}} = 0.84$, and $r_{\text{flu}} = 0.89$, $p < 0.05$). No significant correlation occurred between the higher molecular weight (HMW) PAHs and organic carbon in the whole study area. Adsorption of PAHs from topsoil was due to the organic carbon content, which adsorbed PAHs quite efficiently; only a small percentage of PAHs which pass through the surface are eventually transported into the deeper sub-surface layers.

Sorption experiment sand PAHs isotherms

Amongst the 25 sediment samples, in 13 samples, kaolinite was dominant. Muscovite and illite were the commonly occurring minerals in most of the samples. Seven samples from the southern part of the lower Ganges river basin showed high quartz content. Sorption study

for naphthalene and fluoranthene showed higher adsorption on quartz dominated sediments and laboratory-grade quartz. However, phenanthrene showed higher adsorption on kaolinite dominated sediment samples and laboratory-grade kaolinite. The present study indicated linear adsorption and distribution co-efficient after normalization to the specific surface area. Monolayer adsorption of naphthalene and fluoranthene on quartz were evident. The previous research showed that cation- π interaction played an essential role in enhancing the sorption of PAHs to sediments primarily on kaolinite (Herbert et al., 2004). Cation- π bonding between free metal ions and electron-rich aromatic structures were well acknowledged [35,36]. Isotherms for the three PAHs indicate that the Langmuir isotherm model was best for explaining the observed trends. All the isotherm parameters for naphthalene, phenanthrene, and fluoranthene are listed in table 7S-9S. The results of the experimentation and computation analysis of kinetic modeling of adsorption of naphthalene, phenanthrene, and fluoranthene contaminated sediments help to understand the sorption processes in sedimentary environments. The adsorption isotherms of Σ PAH₃ to kaolinite and quartz dominated sediments are presented in Figure 1S-3S.

The experiments indicated that ca. 66.6% of naphthalene adsorbed by 30 hrs on quartz dominated natural sediment. After this, the desorption phenomenon was observed (Figure 1S). A similar pattern was observed for laboratory-grade quartz. Kaolinite showed very low adsorption of naphthalene compared to quartz (8.9% at 30 hrs).

About 70% of fluoranthene was adsorbed by 30 hrs on quartz dominated natural sediment. After this, the desorption phenomenon was observed (Figure 2S). A similar pattern was observed for laboratory-grade quartz. Kaolinite showed very less adsorption of naphthalene compared to quartz (~ 9% at 30 hrs). Unlike naphthalene and fluoranthene, phenanthrene did not show any adsorption on quartz dominated sediment samples. Sorption

intensity indicated that soft transitional metal ions (Al^{3+}) generally favor the sorption of aromatic structures, which is consistent with cation π - π sorption mechanisms [36]. Na^+ , Al^{3+} , and Mg^{2+} which are dominant in kaolinite-rich sediment are primarily involved in such bonding. Therefore, the adsorption experiment for phenanthrene indicated different results from naphthalene and fluoranthene (Fig. 3S).

The organic carbon content in sediment samples, showed a significant correlation with PAHs. Among other physico-chemical parameters, organic carbon content is one of the crucial factors that may control the adsorption capacity of PAHs onto sediments [37]. For the adsorption process, equilibrium was attained faster in case of kaolinite than quartz for phenanthrene. The sorption process followed the first-order reaction kinetics. Based on the amount adsorbed and given the equal time needed for equilibrium to be attained, kaolinite can be described as a better adsorbing agent for phenanthrene.

The LMW naphthalene indicated better adsorption on quartz-rich sediments. The differences in sorption properties of fine-grained sediments (e.g., clay) in comparison to coarser sediments (sand) can be attributed to conducive hydraulic and surface properties. Quartz usually had medium to high porosity and very high permeability. Clay particles may have high porosity, but permeability is low [38]. As a result, water molecules lodged in between the clay particles may be associated with the contaminant solutes. Hence, hydraulic properties of sediments, e.g. porosity and permeability, can be an influential parameter in the presence of a potential volume of PAHs and other existing organic compounds.

Statistical analyses

Four major clusters were generated based on HCA to denote similarity and dissimilarity assessment among the sampling sites (Fig. 4S). Group one is made up of two districts namely Nadia and North-24 Parganas with the highest concentration of total PAHs and low molecular

weight-PAHs (primarily naphthalene). The second and third groups include South 24 Parganas including Kolkata with intermediate PAH concentrations. Group IV includes Murshidabad and few parts of South 24 Parganas with the lowest level of LMW PAHs; medium and high molecular weight PAHs were mostly absent. The study also includes control sites that are free from anthropogenic activity such as industrial influence and minimal vehicular traffic. The PAH input at these sites are mainly due to domestic waste incineration and disposal of sewage waste.

The highest concentration of total PAHs (ΣPAH_3) occurs in Group I (Nadia and North 24-Parganas), whereas the South 24-Parganas belong to Group II. The control site was the area with the lowest total PAH concentration and was classified as Group III, which primarily belonged to Murshidabad. The effect of flooding and possible dilution might be the reason for the observed differences in the clusters for the two sampling events. Group I indicating agricultural land use indicated the dominance of low molecular weight of PAHs. The southern part of the study area which comprises of urban areas including Kolkata and location of nearby petroleum refineries indicated high molecular weight of PAHs of petrogenic origin. PAHs of pyrogenic rarely include vehicular emissions. Therefore, agricultural and peri-urban areas indicated a higher abundance of low molecular weight PAHs, i.e. naphthalene, unlike the urban regions.

The Western Bengal basin mostly consists of clay minerals, and southern parts of the basin are dominated by sand and silt. Sediments collected from the peri-urban areas of South 24 Parganas contain a higher amount of naphthalene. However, clay-dominated sediment samples collected from Nadia and North 24 Parganas indicated higher concentrations of phenanthrene and fluoranthene. The present results indicated significant differences in the PAH concentrations in sediment samples. PAH ratios, such as $\text{An}/(\text{An}+\text{Phe})$ and $\text{Flu}/(\text{Flu}+\text{Py})$, calculated imply presence of both pyrogenic and petrogenic PAH inputs ^[39–41]. $\text{An}/(\text{An}+\text{Phe})$

ratio <0.1 suggests a petrogenic provenance for PAHs, whereas values >0.1 suggest pyrogenic PAHs. Flu/(Flu+Py) ratio <0.4 are derived from petrogenic source and >0.5 indicate pyrogenic sources ^[42]. In the present study, An/(An+Phe) ratios for six sediment samples SS5, SS7, SS9, SS19, SS21, and SS23 were lower than 0.1, which suggests some of the major sources of petrogenic PAHs can be released from motor oil, gasoline and other substances associated with vehicular transport and emissions. However, the rest of the sediment samples indicated the presence of pyrogenic PAHs. Pyrolytically formed material usually converts into more stable six-member rings PAHs (Fig. 5). Flu/(Flu+Py) ratio in five sediment sites (SS6, SS8, SS20, SS21 and SS22) was less than 0.4 which suggests that the PAHs sources were of petrogenic origin, whereas the other fifteen sediment samples showed pyrolytic PAHs. Five samples showed the Flu/ (Flu+Py) ratio within 0.4 and 0.5 (SS2, SS5, SS7, SS9, and SS23) which suggests the combustion of petroleum products as the source of these PAHs.

It has been observed that sediment samples from the South 24 Parganas were contaminated with PAHs due to petroleum spills in the recent past (Mitra et al.,^[14]). In contrast, PAHs sources in sediment samples from other districts were derived either from incomplete combustion of woods or from the local release of motor oil (vehicular emissions from incomplete combustion). It is proposed from the sorption kinetics that naphthalene is adsorbed to quartz, and as a result, naphthalene concentration is higher in sediments dominated by sand situated in the southern part of the Western Bengal basin. The urban areas in Nadia and North 24 Parganas showed a higher amount of phenanthrene in kaolinite dominated sediments. This trend is consistent with the results obtained from the sorption study.

Impact of pumping on PAH pollution

Advective transport modeling for PAHs particle shows the migration of these compounds in an aquifer under existing simulated groundwater flow conditions across the study area. The

present study on the influence of irrigational pumping on PAH distribution was hypothesized with imaginary conservative contaminant particles to simulate advective transport in a contaminated public drinking water well in an area found to be the most contaminated and hydraulically vulnerable to PAH contamination as reported earlier ^[43]. Assuming the PAH molecule as a conservative contaminant particle, the model assessed the vulnerability of the aquifer to contamination. As per the regional flow simulation, the presented and projected pumping scenarios indicated a cone of depression with a vertical gradient of up to ~ 0.25 m/m at present which is expected to increase up to ~ 0.36 m/m under the present rate of groundwater withdrawal (Mukherjee et al.,^[18]).

The simulated site is located near Kamgachi village in Nadia district (Fig. 6). In this area, the present-day annual pumping rates from public drinking water wells are ~ 100 m³/h for 6 h/day; pumping rates in heavy-duty mechanized irrigation wells are 150–200 m³/hr for 6–15 hr/day and varies seasonally. Simulated hypothetical particles from depths of near-surface to >50 m below land surface in the vertical direction, and up to ~ 75 m horizontal distance, could advectively travel to the target depth of the water source, which is up to 20–25 times faster under an induced vertical hydraulic gradient (Fig. 6). This clearly suggests that the pervasive irrigational pumping which is a common practice in the study area could be a potential reason for the transport of PAHs, as it enters into the sub-surface by natural hydrological processes like groundwater recharge. The presence of hypothetical particles emphasizes the advective transport of solutes by groundwater during the simulation for groundwater pumping. This trend demonstrated the potential of PAH molecules being transported from a near-surface (associated with agricultural or industrial activities) to potable groundwater abstraction depths ranging from ~ 15 m to >150 mbgl (meter below ground level) in the study sites. The simulation provides an insight into the potential causes of PAH pollution in agricultural and industrial areas in the region that can be extended to other sites as a monitoring tool.

Conclusions

The distribution and advective transport of anthropogenic-sourced PAH pollution in aquifers extending over ~21,000 km² of the lower reaches of the Ganges river basin, were studied in order to understand the availability of safe and sustainable groundwater-sourced drinking water in an area. This area is already exposed to wide-scale geogenic groundwater arsenic pollution. All sampled waters were found to have at least one or more of the 16 priority PAHs [e.g., naphthalene (4.9 – 10.6 µg/L), phenanthrene (3.32 – 6.61 µg/L)]. Naphthalene, phenanthrene and fluoranthene were detected in 79, 36 and 13% of the sampled sediments (n=25) in the area. The lithological setting of the lower Ganges River basin consists of four major types of unconsolidated sediments: gravel, clay, sand, and silt. The PAH concentrations in the sub-surface soils are generally dominated by naphthalene, followed by phenanthrene. PAH concentrations in the top soil (0–10 cm), is different from those in the deeper soil intervals (20–30 cm). The organic carbon content was also higher in surface soils (0–10 cm) than the deeper layers. As organic carbon content decreases with depth, the adsorption of PAHs decreases. The present study indicates that the potential sources of PAHs were primarily of pyrogenic origin in rural agricultural areas. In contrast, PAHs mostly originated from petroleum combustion processes in urban areas.

Sorption behavior and advective transport of PAH help to develop a mechanistic understanding of the contaminant transport that is influenced by dominant minerals in the sediment matrix (i.e., quartz (sand) vs. clay minerals), sediment characteristics (carbon content), and land use (agriculture, peri-urban and urban areas). The numerically simulated advective transport mechanism in a well-investigated aquifer within the study area (cite the ref here), was found to be vulnerable to PAH pollution. Transport of PAH from the surface to a

drinking water target depth, suggests up to ~25 times faster movement of the contaminant particle under influence of irrigation-induced pumping regimes.

Besides providing a possible explanation for regional and local patterns in the distribution of PAHs in shallow aquifers, our observations have two practical inferences. First, the study represents the sorption of PAHs on predominant minerals in aquifer sediments which would influence the distribution of PAHs. In particular, the different physicochemical properties in sediments indicate the influence on migration of PAHs. Secondly, the mobility of PAHs in groundwater wells is affected by irrigational pumping. The hypothetical advective transport modeling indicates the development of a depression cone during pumping which enhances PAHs transport. These two scenarios can help in assessing the overall vulnerability of PAH contamination in the study area.

The study highlights the correlation between aquifer sediment properties, land use, and PAH contamination. In particular, groundwater abstraction practices and use can have a significant impact on redistribution and spreading of anthropogenic pollutants including PAHs in the sub-surface. Implementation of legislation and other activities to restrict the use of solid fuels for domestic purposes may reduce the PAH emissions and deposition on surface sediments and provides vision on groundwater monitoring and assessment.

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1 **TABLE CAPTIONS**

2 **Table 1:** PAHs detected at various study across the world including that at the present site

Location	Range (ng/g)	Mean (ng/g)	References
<i>Biscay Bay, France</i>	20 – 5159	–	<i>Fernandes et al.</i> ^[44]
<i>Northwest Mediterranean Sea</i>	86.5 – 48,090	–	<i>Benlahcen et al.</i> , ^[45]
<i>West Mediterranean Sea</i>	1.5–20,440	–	<i>Baumard et al.</i> , ^[46]
<i>Meizhou Bay, China</i>	196.7 – 299.7	256.1	<i>Zhu et al.</i> , ^[47]
<i>Izmit Bay, Marmara Sea, Turkey</i>	3.0×10^4 – 1.67×10^6	6.01×10^5	<i>Telli-Karakoç et al.</i> , ^[48]
<i>Santander Bay, Spain</i>	1620 – 344,600	–	<i>Viguri et al.</i> , ^[49]
<i>Black Sea coast, Turkey</i>	10–530	–	<i>Readman et al.</i> , ^[50]
<i>Hsin-ta Harbour, Taiwan</i>	156 – 3382	–	<i>Fang et al.</i> , ^[51]
<i>Porto Torres, Sardinia, Italy</i>	70 – 1210	–	<i>De Luca et al.</i> , ^[52]
<i>Narragansett Bay, USA</i>	569–216,000	21,100	<i>Hartmann et al.</i> , ^[53]
<i>Gomti River, India</i>	208–3365		<i>Malik et al.</i> , ^[54]
<i>Yamuna River, India</i>	4,502 - 23,527	14014.5	<i>Agarwal et al.</i> , ^[55]
<i>Barcelona Harbour, Spain</i>	16,300 – 10,320		<i>Martínez-Lladó et al.</i> , ^[56]
<i>Liaodong Bay, China</i>	276.26 – 1606.89	743.03	<i>Men et al.</i> , ^[57]
<i>San Francisco Bay, USA</i>	2653 - 27680		<i>Pereira et al.</i> , ^[58]
<i>Leizhou Bay, China</i>	21.72 – 319.61	103.91	<i>Luo et al.</i> , ^[59]
<i>Zhanjiang Bay, China</i>	41.96 – 933.90	315.98	<i>Huang et al.</i> , ^[60]
<i>Alang-sosiya, India</i>	5020–981,000	345,000	<i>Dudhagara et al.</i> ^[61]
<i>Gulf of Kutch, India</i>	118,280–1,099,410	321,635	<i>Rajpara et al.</i> , ^[62]
<i>Hooghly river estuary, India</i>	3.26 - 628.61	168.28	<i>Mitra et al.</i> , ^[14]
<i>Sunderbans mangrove, eastern coast of India</i>	15.4 to 1731	-	<i>Zanardi-Lamardo et al.</i> , ^[63]
<i>Western Bengal basin, India</i>	1.15 – 23.13	3.68	<i>Present study</i>

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9 FIGURES CAPTIONS

10 **Figure 1.** Map showing study area located in India (a) four districts vis-à-vis major rivers in
11 Western Bengal basin in India [blue lines proposed river path] and sediment (n = 25) and river
12 water(n = 32) sampling locations; (b) groundwater sampling locations (n = 235)

13 **Figure 2.** Graph showing detection frequencies of detected polycyclic aromatic hydrocarbons
14 (PAHs) for river water and groundwater

15 **Figure 3.** Spatial distribution of predominantly detected four PAHs in (a) groundwater and (b)
16 river water, viz. naphthalene, phenanthrene, fluoranthene and anthracene across the Western
17 Bengal basin

18 **Figure 4.** Graph showing the PAH concentration ($\mu\text{g/kg}$) in twenty five sediment samples
19 collected from Western Bengal basin

20 **Figure 5.** PAHs cross plot for the ratios of $\text{Flu}/(\text{Py} + \text{Flu})$ and $\text{An}/(\text{An} + \text{Phe})$

21 **Figure 6.** Advective transport of hypothetical PAH particles during pumping
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Fig. 1

Fig. 2

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35 **Fig. 3a**

Fig. 3b

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40 **Fig. 4**

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Fig. 5

Fig. 6

Supporting Information

Figure 1S. Naphthalene concentration ($\mu\text{g/kg}$) adsorbed onto natural sediment having dominant mineral quartz and kaolinite along with laboratory grade quartz and kaolinite

Fig.1S

Figure 2S Phenanthrene concentration ($\mu\text{g/kg}$) adsorbed onto natural sediment having dominant mineral quartz and kaolinite along with laboratory grade quartz and kaolinite

Fig.2S

Figure 3S. Fluoranthene concentration ($\mu\text{g/kg}$) adsorbed onto natural sediment having dominant mineral quartz and kaolinite along with laboratory grade quartz and kaolinite

Fig.3S

Figure 4S. Hierarchical Cluster Analysis (HCA) for PAHs present in different land uses

Fig.4S

70 **Table 1S:** Groundwater sampling locations across Western Bengal basin

Murshidabad			Nadia			North 24 Parganas			South 24 Parganas		
Sample ID	Latitude	Longitude	Sample ID	Latitude	Longitude	Sample ID	Latitude	Longitude	Sample ID	Latitude	Longitude
S1	24.2598	88.6592	S89	23.7639	88.3789	S154	22.7219	88.4006	S178	22.4867	88.3636
S2	24.2597	88.6590	S90	24.0329	88.7140	S155	22.774	88.3961	S179	22.4878	88.3646
S3	23.9901	87.9140	S91	24.0421	88.7105	S156	22.8928	88.5535	S180	22.4878	88.3646
S4	23.9912	87.9128	S92	23.5507	88.3827	S157	22.5735	88.5016	S181	22.4879	88.3642
S5	24.1187	88.6566	S93	23.5475	88.3887	S158	23.1635	88.8907	S182	22.4038	88.1504
S6	24.1131	88.6382	S94	22.9932	88.5477	S159	22.7361	88.535	S183	22.1879	88.2254
S7	24.1150	88.6442	S95	22.9931	88.5478	S160	22.7382	88.403	S184	22.1871	88.2245
S8	24.1167	88.6506	S96	22.9595	88.5661	S161	22.7342	88.4029	S185	22.1879	88.2256
S9	24.1142	88.6458	S97	22.9353	88.5415	S162	22.5931	88.4895	S186	22.1893	88.2266
S10	23.8511	88.2598	S98	23.0277	88.5888	S163	22.9253	88.7969	S187	22.1843	88.2261
S11	23.8506	88.2562	S99	23.0380	88.5144	S164	22.9233	88.7891	S188	22.1864	88.2280
S12	23.8545	88.2524	S100	23.2906	88.3689	S165	22.8083	88.5154	S189	22.1832	88.2267
S13	23.8662	88.2485	S101	23.2321	88.5233	S166	22.8886	88.7404	S190	22.1863	88.2272
S14	23.8227	88.2637	S102	23.2868	88.3590	S167	22.8897	88.7376	S191	22.3947	88.2042
S15	24.1586	88.6473	S103	23.6890	88.5292	S168	22.8886	88.7404	S192	22.3912	88.2139
S16	24.1534	88.6468	S104	23.6902	88.5306	S169	22.8897	88.7376	S193	22.3953	88.2046
S17	24.1587	88.6438	S105	23.6912	88.5306	S170	23.0543	88.8071	S194	22.3948	88.2042
S18	24.1548	88.6479	S106	23.2327	88.4965	S171	23.0572	88.7926	S195	22.3949	88.2042
S19	23.9296	88.0470	S107	23.2385	88.4590	S172	22.8456	88.7442	S196	22.4063	88.2186
S20	23.9282	88.0471	S108	23.3936	88.6581	S173	22.8471	88.7501	S197	22.4062	88.2187
S21	23.9453	88.0405	S109	23.3904	88.6524	S174	22.8487	88.7493	S198	22.4060	88.2188
S22	23.9441	88.0405	S110	23.3415	88.4152	S175	22.8369	88.6949	S199	22.4060	88.2188
S23	24.1720	88.6056	S111	23.3373	88.4190	S176	22.8391	88.6964	S200	22.4061	88.2193
S24	24.1723	88.6063	S112	23.3542	88.4235	S177	22.8376	88.6965	S201	22.4064	88.2196
S25	23.9435	88.0229	S113	23.3538	88.4247				S202	22.4065	88.2195
S26	23.9433	88.0238	S114	23.3552	88.4212				S203	22.4068	88.2192
S27	23.9199	88.0533	S115	23.0232	88.5990				S204	22.4067	88.2193
S28	23.9193	88.0554	S116	23.0233	88.6002				S205	22.4068	88.2193
S29	23.9171	88.0611	S117	23.0053	88.6023				S206	22.4342	88.2916
S30	23.9299	88.0458	S118	23.0092	88.6028				S207	22.4307	88.2997

S31	23.8963	88.4624	S119	23.0124	88.6051	S208	22.4332	88.2994
S32	24.1078	88.6361	S120	23.0133	88.6048	S209	22.4358	88.3007
S33	24.1080	88.6367	S121	23.3656	88.3382	S210	22.4339	88.2979
S34	23.8988	87.9343	S122	23.2503	88.5389	S211	22.4349	88.2983
S35	23.8986	87.9342	S123	23.2528	88.5396	S212	22.3881	88.2467
S36	24.0495	88.6330	S124	23.2549	88.5250	S213	22.4270	88.3020
S37	24.0658	88.6049	S125	23.2528	88.5225	S214	22.4268	88.3068
S38	24.0712	88.6026	S126	23.2525	88.5339	S215	22.4336	88.2977
S39	23.9625	87.9275	S127	22.9964	88.4909	S216	22.3964	88.2081
S40	23.9614	87.9286	S128	22.9826	88.4904	S217	22.3995	88.2083
S41	23.9724	87.9281	S129	23.7691	88.2672	S218	22.3948	88.2042
S42	23.9192	88.3620	S130	23.6210	88.3137	S219	22.3948	88.2068
S43	24.0063	88.0241	S131	23.7682	88.2666	S220	22.4339	88.2979
S44	23.7708	88.2194	S132	23.6202	88.3143	S221	22.4336	88.2977
S45	24.0420	88.5520	S133	23.7707	88.2611	S222	22.3881	88.2467
S46	24.0428	88.5500	S134	23.7696	88.2587	S223	22.4270	88.3020
S47	24.0429	88.5488	S135	23.6219	88.3129	S224	22.4268	88.3068
S48	24.0420	88.5518	S136	23.7671	88.2590	S225	22.4357	88.2999
S49	24.0431	88.5523	S137	23.6151	88.3265	S226	22.4351	88.3004
S50	24.0097	88.5350	S138	23.7699	88.2649	S227	22.4349	88.2983
S51	24.0103	88.5327	S139	23.6384	88.2657	S228	22.4332	88.2994
S52	24.0089	88.5330	S140	23.6184	88.3121	S229	22.4339	88.2979
S53	23.9355	88.1099	S141	23.7680	88.2583	S230	22.4336	88.2977
S54	23.9321	88.1085	S142	23.6315	88.2609	S231	22.3881	88.2467
S55	23.9301	88.1063	S143	23.7880	88.2505	S232	22.4270	88.3020
S56	23.9277	88.1068	S144	23.7877	88.2508	S233	22.4307	88.2997
S57	23.9323	88.1069	S145	23.5933	88.3415	S234	22.4268	88.3068
S58	24.0312	87.8844	S146	23.5871	88.3353	S235	22.4336	88.2977
S59	24.0077	88.4952	S147	23.5974	88.3474			
S60	23.8967	87.9282	S148	23.7580	88.3100			
S61	23.8914	87.9151	S149	23.7596	88.3102			
S62	23.8913	87.9143	S150	23.5325	88.4034			
S63	24.0848	88.0711	S151	23.5344	88.4013			
S64	23.8636	88.4632	S152	23.6892	88.3030			

S65	23.8630	88.4633	S153	23.6885	88.2997
S66	23.9530	88.0752			
S67	23.9534	88.0722			
S68	23.8214	88.4240			
S69	24.0914	88.6283			
S70	24.0907	88.6269			
S71	24.0928	88.6226			
S72	24.0931	88.6217			
S73	23.8211	88.4244			
S74	23.8211	88.4244			
S75	24.0949	88.6217			
S76	23.8183	88.4231			
S77	23.8183	88.4231			
S78	23.8195	88.4242			
S79	23.8195	88.4242			
S80	23.8216	88.4233			
S81	23.8216	88.4233			
S82	24.0926	88.6250			
S83	24.0943	88.6227			
S84	23.8184	88.4230			
S85	23.8149	88.4214			
S86	23.9531	88.2154			
S87	23.9531	88.2151			
S88	24.3408	88.3023			

72 **Table 2S:** River water sampling locations across Western Bengal basin

Sample ID	Latitude	Longitude
WBB1	24.75	87.74
WBB2	24.63	87.97
WBB3	24.59	88.02
WBB4	24.53	88.06
WBB5	24.44	88.09
WBB6	24.31	88.18
WBB7	24.19	88.24
WBB8	24.10	88.23
WBB9	23.94	88.23
WBB10	23.84	88.23
WBB11	23.68	88.15
WBB12	23.56	88.33
WBB13	23.49	88.38
WBB14	23.43	88.32
WBB15	23.36	88.34
WBB16	23.29	88.36
WBB17	23.23	88.46
WBB18	23.17	88.46
WBB19	23.06	88.49
WBB20	23.01	88.45
WBB21	22.92	88.39
WBB22	22.85	88.37
WBB23	22.76	88.36
WBB24	22.67	88.36
WBB25	22.62	88.30
WBB26	22.57	88.24
WBB27	22.53	88.16
WBB28	22.47	88.12
WBB29	22.40	88.09
WBB30	22.32	88.09
WBB31	22.26	88.07
WBB32	22.20	88.17

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Table 3S: Detailed information on mineralogical characteristics, pH and average organic carbon content (mg/kg) for 25 sediment samples

Sampling site	Mineral characterization	pH	Average organic carbon content
SS1	Quartz, Silica	8.1	0.92
SS2	Quartz, Silica	7.9	1.93
SS3	Quartz, Feldspar	8.0	2.18
SS4	Quartz, Silica	7.3	0.60
SS5	Illite, Smectite	7.5	3.21
SS6	Calcite	7.2	2.10
SS7	Muscovite	7.0	2.13
SS8	Muscovite	6.9	2.09
SS9	Kaolinite, Kaolinite	6.7	1.69
SS10	Albite , Muscovite	6.5	1.51
SS11	Quartz, Silica	7.3	1.19
SS12	Muscovite, Illite	8.1	0.93
SS13	Orthoclase	6.9	1.21
SS14	Sanidine	6.8	1.15
SS15	Orthoclase, Berlinite	6.8	1.75
SS16	Anorthite	6.7	1.69
SS17	Calcite	7.6	0.97
SS18	Muscovite, Kaolinite	7.6	0.91
SS19	Quartz, Silica	7.5	1.51
SS20	Quartz, Feldspar	6.4	2.11
SS21	Kaolinite, Orthoclase	7.3	2.05
SS22	Muscovite, Illite	7.3	0.67
SS23	Albite, Muscovite	7.2	0.61
SS24	Anorthite, Illite	7.1	1.21
SS25	Muscovite, Illite, Kaolinite	7.1	1.15

86 **Table 4S:** Minimum detection limit and extraction recoveries for the polycyclic aromatic
87 Hydrocarbons (PAHs) in water samples

Compounds	Detecti on limit (µg/L)	Internal standard injected	Internal standard recovered	Reco very (%)	Internal standard injected	Internal standard recovered	Recov ery (%)
Naphthalene	0.3	0.5	0.32	64	1	0.89	66
Acenaphthylene	0.5	0.5	0.39	78	1	0.91	77
Acenaphthene	0.5	0.5	0.41	82	1	0.93	83
Fluorene	0.5	0.5	0.46	92	1	0.98	96
Phenanthrene	0.5	0.5	0.43	86	1	0.95	88
Anthracene	0.3	0.5	0.32	64	1	0.84	50
Fluoranthene	0.3	0.5	0.39	78	1	0.91	77
Pyrene	0.2	0.5	0.33	66	1	0.85	55
Benz(a)anthracene	0.2	0.5	0.42	84	1	0.82	82
Chrysene	0.2	0.5	0.39	78	1	0.91	77
Benzo(b)fluoranthene	0.2	0.5	0.41	82	1	0.93	83
Benzo(k)fluoranthene	0.2	0.5	0.37	74	1	0.89	70
Benzo(a)pyrene	0.1	0.5	0.32	64	1	0.84	50
d-Perylene (Istd)*	0.1	0.5	0.42	84	1	0.94	86
Perylene	1.0	0.5	0.4	80	1	0.92	80
Indeno(1,2,3)pyrene	0.2	0.5	0.29	58	1	0.81	34
Dibenzo(a,h)anthracene	0.9	0.5	0.39	78	1	0.91	77
Benzo(g,h,i)perylene	0.9	0.5	0.36	72	1	0.89	69
1,3-dimethylnaphthalene	0.25	0.5	0.32	64	1	0.69	69
1-methylnaphthalene	0.4	0.5	0.47	94	1	0.75	75
2-methylnaphthalene	0.39	0.5	0.45	90	1	0.74	74
2,6-dimethylnaphthalene	0.42	0.5	0.45	90	1	0.89	89

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Table 5S: Minimum detection limit and extraction recoveries for the PAHs in sediment samples

Compounds	Detection limit (µg/kg)	Internal standard injected	Internal standard recovered	Recovery (%)	Internal standard injected	Internal standard recovered	Recovery (%)
Napthalene	0.3	0.5	0.34	68	1	0.67	66
Acenaphthylene	0.5	0.5	0.41	82	1	0.85	77
Acenaphthene	0.5	0.5	0.43	86	1	0.87	83
Fluorene	0.5	0.5	0.48	96	1	0.92	96
Phenanthrene	0.5	0.5	0.45	90	1	0.89	88
Anthracene	0.3	0.5	0.34	68	1	0.68	50
Fluoranthene	0.3	0.5	0.41	82	1	0.85	77
Pyrene	0.2	0.5	0.35	70	1	0.79	55
Benz(a)anthracene	0.2	0.5	0.44	88	1	0.86	82
Chrysene	0.2	0.5	0.41	82	1	0.85	77
Benzo(b)fluoranthene	0.2	0.5	0.43	86	1	0.87	83
Benzo(k)fluoranthene	0.2	0.5	0.39	78	1	0.76	70
Benzo(a)pyrene	0.1	0.5	0.34	68	1	0.65	50
d-Perylene (Istd)*	0.1	0.5	0.44	88	1	0.88	86
Perylene	1.0	0.5	0.42	84	1	0.86	80
Indeno(1,2,3)pyrene	0.2	0.5	0.31	62	1	0.65	34
Dibenzo(a,h)anthracene	0.9	0.5	0.41	82	1	0.85	77
Benzo(g,h,i)perylene	0.9	0.5	0.38	76	1	0.79	69
1,3-dimethylnaphthalene	0.25	0.5	0.29	58	1	0.61	61
1-methylnaphthalene	0.4	0.5	0.44	88	1	0.74	74
2-methylnaphthalene	0.39	0.5	0.41	82	1	0.69	69
2,6-dimethylnaphthalene	0.42	0.5	0.43	86	1	0.83	83

Table 6S: Polyaromatic Hydrocarbons (PAHs) concentration ($\mu\text{g/L}$) in river water samples for four districts of Western Bengal basin

Components	Murshidabad			Nadia			North 24 Parganas			South 24 Parganas		
	Med	Min	Max	Med	Min	Ma	Med	Min	Max	Me	Min	Max
Naphthalene	7.41	5.80	9.01	23.13	12.21	34.0	4.30	2.60	6.00	8.33	1.34	15.32
Phenanthrene	5.83	4.90	6.76	4.84	1.54	8.14	5.71	3.86	7.57	5.67	2.99	8.35
Anthracene	3.10	3.06	3.14	1.16	0.56	1.76	2.14	1.03	3.25	0.33	0.11	0.55
Fluoranthene	3.65	3.57	3.74	3.90	2.91	4.90	7.22	5.38	9.07	1.70	1.16	2.24
Chrysene	0.36	0.07	0.65	0.12	0.07	0.17	0.22	0.14	0.31	0.09	0.04	0.13
Pyrene	0.20	0.09	0.30	0.10	0.10	0.10	0.01	0.00	0.01	0.16	0.10	0.21
1,3-dimethyl naphthalene	4.60	3.58	3.70	4.96	3.16	6.75	2.18	1.86	2.50	1.59	1.02	2.16
1-methyl naphthalene	4.60	4.56	4.63	1.20	0.93	1.48	2.23	1.71	2.74	1.44	1.22	1.66
2-methyl naphthalene	3.50	3.43	3.57	3.80	2.61	5.00	5.04	0.83	9.24	0.89	0.44	1.33
2,6-dimethyl naphthalene	3.87	3.63	4.11	2.49	1.31	3.66	4.61	2.43	6.78	0.71	0.53	0.90

Table 7S: Polyaromatic Hydrocarbons (PAHs) ($\mu\text{g/kg}$) concentration in sediment samples collected across the study area

Components	Murshidabad			Nadia			North 24 Parganas			South 24 Parganas		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Naphthalene	3.38	2.64	4.11	10.55	5.57	15.53	1.96	1.19	2.74	3.80	0.61	6.99
Phenanthrene	2.66	2.24	3.08	2.21	0.70	3.71	2.61	1.76	3.45	2.59	1.36	3.81
Anthracene	1.41	1.40	1.43	0.53	0.25	0.80	0.98	0.47	1.48	0.15	0.05	0.25
Fluoranthene	1.67	1.63	1.70	1.78	1.33	2.24	3.29	2.45	4.14	0.78	0.53	1.02
Chrysene	0.16	0.03	0.30	0.06	0.03	0.08	0.10	0.06	0.14	0.04	0.02	0.06
Benzo(a)anthracene	1.86	1.69	2.03	2.82	2.63	3.01	1.51	1.09	1.92	3.18	3.09	3.26
Pyrene	0.09	0.04	0.14	0.05	0.04	0.05	0.00	0.00	0.00	0.07	0.05	0.10
1,3-dimethyl naphthalene	1.66	1.63	1.69	2.26	1.44	3.08	0.99	0.85	1.14	0.73	0.47	0.99
1-methyl naphthalene	2.10	2.08	2.11	0.55	0.42	0.68	1.02	0.78	1.25	0.66	0.56	0.76
2-methyl naphthalene	1.60	1.56	1.63	1.73	1.19	2.28	2.30	0.38	4.22	0.40	0.20	0.61
2,6-dimethyl naphthalene	1.77	1.66	1.87	1.14	0.60	1.67	2.10	1.11	3.09	0.33	0.24	0.41

104 **Table 8S:** Isotherm parameters for Langmuir and Freundlich models for naphthalene

Isotherm Model For naphthalene	Estimated isotherm parameters	Estimated isotherm parameters			
		Quartz	Kaolinite	Laboratory grade quartz	Laboratory grade kaolinite
Langmuir	$q_{\max}$ (mg/g)	25.95	16.51	22.41	18.68
	b	0.39	0.00	0.05	0.01
	R^2	0.93	0.91	0.98	0.98
Freundlich	n	0.68	0.40	0.77	0.28
	K_f	9.67	2.43	8.60	11.53
	R^2	0.91	0.89	0.98	0.97

105 **Table 9S:** Isotherm parameters for Langmuir and Freundlich models for fluoranthene

Isotherm Model for fluoranthene	Estimated isotherm parameters	Estimated isotherm parameters			
		Quartz	Kaolinite	Laboratory grade quartz	Laboratory grade kaolinite
Langmuir	$q_{\max}$ (mg/g)	17.06	11.51	17.41	12.68
	b	1.63	0.02	0.21	0.02
	R^2	0.95	0.94	0.96	0.97
Freundlich	n	0.30	0.65	0.50	0.74
	K_f	8.54	81.30	14.47	10.40
	R^2	0.91	0.89	0.92	0.93

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Table 10S: Isotherm parameters for Langmuir and Freundlich models for phenanthrene

Isotherm Model for phenanthrene	Estimated isotherm parameters	Estimated isotherm parameters			
		Quartz	Kaolinite	Laboratory grade quartz	Laboratory grade kaolinite
Langmuir	$q_{\max}$ (mg/g)	23.89	27.67	22.57	13.84
	b	0.80	0.008	0.10	0.02
	R^2	0.99	0.95	0.99	0.98
Freundlich	n	0.84	0.24	0.83	0.34
	K_f	9.10	81.86	15.04	10.96
	R^2	0.91	0.87	0.97	0.96

Table 11S: Physical properties of collected groundwater samples across the Western Bengal basin

Sample Name	pH	TDS	Hardness	Sample Name	pH	TDS	Hardness	Sample Name	pH	TDS	Hardness	Sample Name	pH	TDS	Hardness
S1	7.1			S26	8	722	112	S51	8.38	1924	104	S76	7.4	332	120
S2	5	405	107	S27	8.2	794	116	S52	7	593	108	S77	7.8	317	120
S3	7.9	586	120	S28	8	1532	120	S53	8	587	100	S78	6.9	294	120
S4	8.1	624	120	S29	8.1	836	120	S54	7	486	120	S79	6.9	295	126
S5	7.9	562	120	S30	8	624	116	S55	7	575	108	S80	8.3	405	120
S6	7.9	592	116	S31	8	624	116	S56	7	611	100	S81	7.5	408	120
S7	7.9	624	120	S32	8	756	116	S57	7.5	632	104	S82	8.3	627	120
S8	7.8	654	116	S33	8	892	120	S58	7.5	632	104	S83	8.3	627	120
S9	7.5	323	116	S34	8.1	884	112	S59	7.5	472	120	S84	8.3	388	120
S10	7	427	100	S35	8.1	698	112	S60	8.5	561	120	S85	6.8	299	120
S11	7.7	377	116	S36	7.8	702	112	S61	7.5	566	120	S86	6.9	299	112
S12	8.1	390	120	S37	7.5	664	120	S62	7.5	664	120	S87	7.2	299	112
S13	7.0	764	104	S38	7.5	913	100	S63	7.5	913	100	S88	6.9	299	112
S14	7.5	611	112	S39	8	838	120	S64	8	838	120	S89	8.1	594	112
S15	7.5	661	120	S40	7	715	120	S65	7	715	120	S90	7.9	542	116
S16	8.3	650	116	S41	7	560	104	S66	8	560	104	S91	8	598	112
S17	8	564	120	S42	7.5	464	100	S67	8	560	104	S92	8	598	116
S18	6.6	47	12	S43	7.5	464	100	S68	7.5	464	100	S93	8.08	500	100
S19	7.9	620	120	S44	7.5	464	100	S69	7.5	464	100	S94	8.5	688	100
S20	7.9	832	116	S45	7.5	563	120	S70	7.5	563	120	S95	7.74	383	100
S21	8.2	738	120	S46	7.5	480	108	S71	7.5	480	108	S96	7.77	598	112
S22	8.2	732	120	S47	7.5	562	120	S72	7.5	562	120	S97	7.5	689	116
S23	7.8	740	120	S48	7.8	286	108	S73	7.5	562	120	S98	7.5	685	100
S24	8.1	708	108	S49	8	359	104	S74	7.4	299	112	S99	7.88	624	116
S25	8.2	732	120	S50	7.4	299	112	S75	7.2	405	120	S100	7.72	591	100
	8.3	812	120		7.2	405	120		7.2	405	120		8.62	598	112
	8.2	800	116		7.2	405	120		7.2	405	120		8.62	598	112

Sample Name	pH	TDS	Hardness	Sample Name	pH	TDS	Hardness	Sample Name	pH	TDS	Hardness	Sample Name	pH	TDS	Hardness
S101	7.5	683	100	S126	8.1	618	108	S151	7.4	612	116	S176	8.19	744	116
S102	7.5	411	100	S127	7.9	656	120	S152	8	660	120	S177	8.16	716	120
S103	8.2	253	100	S128	7.6	568	116	S153	8.2	764	120	S178	7.74	687	116
S104	8.0	253	100	S129	7.9	568	116	S154	8.2	756	112	S179	8.13	764	116
S105	7.9	273	120	S130	7.96	982	108	S155	8.1	784	112	S180	8.16	712	104
S106	8.0	247	100	S131	7.83	998	110	S156	7.8	600	104	S181	8.16	714	104
S107	7.6	591	100	S132	8	604	120	S157	7.6	395	118	S182	8.12	724	116
S108	7.7	591	100	S133	7.7	582	120	S158	7.4	386	116	S183	7.86	736	116
S109	8	676	100	S134	8	712	112	S159	7.9	356	106	S184	8.12	857	116
S110	7.5	570	100	S135	7.5	586	108	S160	7.9	568	108	S185	7.93	812	108
S111	7.3	481	100	S136	8.1	640	120	S161	8.1	768	120	S186	7.72	616	116
S112	7.4	507	104	S137	8.1	648	112	S162	8.2	1251	100	S187	8.12	1026	108
S113	7	434	120	S138	7.2	546	116	S163	7.8	1173	110	S188	7.96	1064	116
S114	7.5	493	100	S139	8.1	684	116	S164	7.8	1016	116	S189	7.86	1076	116
S115	7.5	390	120	S140	8	608	120	S165	7.8	746	112	S190	8.12	964	116
S116	7.5	387	100	S141	7.9	572	120	S166	8.1	664	116	S191	7.78	1032	116
S117	7.5	520	120	S142	8	632	116	S167	8.1	716	120	S192	8.24	808	116
S118	7.7	409	120	S143	8	688	112	S168	8.1	708	116	S193	8.24	764	116
S119	7.5	397	120	S144	8.2	658	112	S169	8.2	640	108	S194	8.14	856	116
S120	8	606	100	S145	8	588	120	S170	8.1	984	120	S195	8.29	1230	120
S121	7.5	519	100	S146	7.9	574	112	S171	8.4	927	100	S196	8.12	638	108
S122	8	538	120	S147	8.2	726	112	S172	7.8	974	116	S197	7.96	732	104
S123	8.2	632	120	S148	8	596	112	S173	7.9	736	120	S198	8.13	628	104
S124	8.2	812	116	S149	7.6	756	112	S174	7.9	824	116	S199	7.92	649	112
S125	7.7	546	112	S150	7.8	626	126	S175	7.9	684	120	S200	7.78	671	120

Sample Name	pH	TDS	Hardness	Sample Name	pH	TDS	Hardness
S201	7.84	652	104	S226	6.9	273	108
S202	7.36	648	104	S227	6.8	286	112
S203	7.98	862	104	S228	6.9	312	120
S204	8.12	893	116	S229	7.4	276	108
S205	7.86	748	116	S230	7.2	550	104
S206	7.79	718	100	S231	8.12	523	116
S207	7.5	501	120	S232	8.03	313	108
S208	7.53	598	100	S233	8.21	268	106
S209	7.5	512	120	S234	7.79	309	110
S210	7.78	820	120	S235	8.18	285	100
S211	7.16	741	120				
S212	7.86	742	116				
S213	7.84	720	116				
S214	7.71	824	120				
S215	7.96	724	116				
S216	7.83	820	116				
S217	8.1	840	120				
S218	7.96	960	120				
S219	7.51	960	120				
S220	8.3	806	120				
S221	8.01	720	110				
S222	6.9	403	112				
S223	6.9	312	116				
S224	6.8	276	108				
S225	6.9	270	108				

Table 12S: Physical properties of collected river water samples across the Western Bengal basin

Sample Name	pH	TDS	Hardness
WBB1	7.72	424	120
WBB2	7.96	399	120
WBB3	7.84	373	116
WBB4	7.84	688	112
WBB5	8.39	435	110
WBB6	7.83	576	112
WBB7	7.99	545	108
WBB8	8.14	419	110
WBB9	7.92	456	120
WBB10	7.92	478	116
WBB11	7.86	496	108
WBB12	8.04	420	120
WBB13	7.93	471	120
WBB14	8.26	642	100
WBB15	7.96	685	120
WBB16	8.25	262	110
WBB17	8.21	408	100
WBB18	8.22	235	116
WBB19	7.71	651	120
WBB20	8.16	658	120
WBB21	8.18	436	116
WBB22	7.96	612	116
WBB23	8.12	367	108
WBB24	7.81	274	120
WBB25	8.25	344	110
WBB26	8.02	527	110
WBB27	7.8	262	120
WBB28	7.8	438	120
WBB29	8	404	100
WBB30	7.5	357	106
WBB31	8.1	469	120
WBB32	7.9	500	112