



Physico-Chemical Characterization and Quantification of Selected Persistent Trace Organic Pollutants Containing Wastewater Samples

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Received: 11 July 2015;

Accepted: 25 August 2015;

Published online: 5 December 2015;

AJC-17675

Release of untreated effluents from industries and domestic sources deteriorates the water quality of receiving water bodies and drains. Hence, characterization of wastewater holds an important place as it can help the use of this wastewater for other purposes. For this purpose, wastewater analysis of the selected parameters and quantitative validation was performed to determine the presence of persistent trace organic pollutants in samples collected from different sources of Lahore city of Pakistan. Total suspended solid for the respective samples was found to be exceeding the NEQS limits. Chemical oxygen demand for the wastewater samples was 896, 166, 419, 812 and 610 mg/L, respectively, all in excess of NEQS (150 mg/L). Similarly, the biological oxygen demand values were also above NEQS limits (80 mg/L). Trace organic pollutants selected for analysis included five pesticides/insecticides and three polycyclic aromatic hydrocarbons. The results showed the presence of 1,2-dichloropropane and 1,3-dichloropropane in all the wastewater samples, pesticides was identified in housing society sample and textile industry sample. Finis and bifenthrin were detected in housing society and Hudaira drain wastewater samples. In case of polycyclic aromatic hydrocarbons, phenanthrene was identified in textile industry sample. Anthracene was detected in samples of housing society, PET bottles industry and pharmaceutical industry.

Keywords: HPLC studies, Lahore, Wastewater.

INTRODUCTION

Wastewater released from different industrial and domestic sources contain different types of contaminants ranging from inorganic pollutants (*e.g.* nitrates, phosphates, heavy metals) and various organic compounds (*e.g.* hydrocarbons, persistent organic pollutants (POPs)). Presence of these pollutants in fresh water deteriorates the water quality and also poses risk for consumption [1]. The untreated industrial and municipal effluents released into the irrigation system has an effect on the quality of soil and crops as well as a threat to human health. An estimate shows that around 800 to 1000 hectares area is being irrigated with untreated effluents from the Lahore city, Pakistan [2].

Persistent organic pollutants are an important class of water contaminants due to their hazardous effects. These are synthetic chemical substances which are persistent, don't degrade easily and become widely distributed geographically. They can bioaccumulate and also bio-magnify through the food chain and pose severe hazards on human health and the environment. They have been linked with adverse effects on the nervous system, reproductive and developmental problems, immune response suppression, cancer and endocrine disruption [3].

Traces of these organic compounds are produced deliberately from pesticides, others are formed as by-products or accidentally such as polychlorinated dibenzo-1,4-dioxins and dibenzofurans (PCDD/Fs) [4]. Trace organic pollutants also include a widespread range of chemicals mainly from petroleum compounds and their derivatives like polycyclic aromatic hydrocarbons (PAHs) to fire retardants like polybrominated diphenylethers (PBDEs) and lately, the per-fluorinated and poly-fluorinated compounds which have been extensively used in surface applications on a variety of household and consumer items [5].

Organic pollutants usually enter into the water systems from sources such as agriculture runoff (pesticides), by-products of degradation or other chemicals from industries. They persist long enough in the environment and drift in various media to cause harmful effects, accumulate in reservoirs such as water, soil, sediments, *etc.* from where they are remobilized through various processes, switch form or speciation and become available to the biological food chain [6]. Literature shows that effluents from paper and pulp industries, textile units, pharmaceutical industries, agricultural runoff, leachates from solid waste dumping sites, *etc.* some of the

major persistent organic pollutants generation in water resources [7-10].

EXPERIMENTAL

Lahore profile: Lahore being capital of Punjab province is the second largest city of Pakistan with the population of approximately 12,500,000. It has been ranked as the 42nd most populated urban city in the world. The area of Lahore is increasing day by day due to development of new housing societies and has been estimated that Lahore has expanded almost double in area in the last twelve to fourteen years.

Introduction to study area: Quaid-e-Azam Industrial Estate (QIE) formerly known as KotLakhpat Industrial Estate is the oldest planned industrial estate in Punjab spread over 565 acres, the project started in 1960s. It has 477 industrial plots varying in size from 1 to 100 kanals. Quaid-e-Azam Industrial Estate is sited at a prime location, adjacent to Township in the city of Lahore. The various types of industries situated in QIS include pharmaceutical, textile, dyeing and printing, food and beverages, garments, plastics, auto parts, chemicals, steel, *etc.*

Three industries from Quaid-e-Azam Industrial Estate were selected for wastewater samples on the basis of literature present with respect to the sources that are responsible for the emission of polycyclic aromatic hydrocarbons and other trace organic pollutants in their effluent.

Domestic wastewater sample source was collected from a housing society located on Bedian road Lahore near DHA. The wastewater from the sewage system ultimately goes into the nearby Hudiara/Rohi drain. Hudiara drain which is one of the largest drains of Lahore, initiates from Batala of Gurdaspur district, India and enters Pakistan near Laloo village, passes through Lahore and eventually goes into Ravi river. The total length of Hudiara drain is 98.6 km; out of which 44.2 km is in India whereas 54.4 km in Pakistan. There are approximately 84 different industries located alongside Hudiara drain in Pakistan and all these industries discharge their wastewaters into this drain. Furthermore, effluents from small villages and some parts of Lahore city also enter in this drain [9].

HPLC grade chemicals were used in the experiment *i.e.* ethyle acetate, dichloromethane, sodium chloride, sodium sulfate and methanol. Pesticides/herbicides/insecticides and polycyclic aromatic hydrocarbons were detected qualitatively using high performance liquid chromatography technique under chromatographic conditions as listed in Table-1.

TABLE-1
CHROMATOGRAPHIC CONDITIONS TO
RUN SAMPLES AND STANDARDS

Column	Zorbax-Eclipse Plus C18, 4.6 × 100 mm, 3,5 μ
Column temperature	25 °C
Flow rate	1.0 mL/min
Injection volume	5.0 μ
Mobile phase	Water:acetonitrile (60:40)
Iso-gratic	Water:acetonitrile (60:40)
Post time	10 to 20 min
Detector	DAD diode
Maximum wavelength	245 nm
Reference	360 nm

Sample collection: There were three types of wastewater samples collected, in autoclaved bottles, from the different industries (PET bottle, pharmaceutical and textile) situated in Quaid-e-Azam Industrial Estate.

Sample preparation: Samples were prepared using dichloromethane and ethyl acetate. From the mixture of wastewater sample and organic solvents, desired portion was extracted and run under HPLC. Same procedure was repeated for all the samples and standards.

RESULTS AND DISCUSSION

The samples collected from the various sources were analyzed using the standard methods. Physico-chemical analysis helps to assess the quality of water and its compliance with the NEQS. Table-2 shows that pH for housing society wastewater (6.9), PET bottles industry wastewater (6.7), pharmaceutical industry wastewater (6.27), textile industry wastewater (7.18) and hudiara drain (7.9) were all within the NEQS range which is 6-9 [10]. The turbidity for all the samples was exceeding NEQS value of 5 FTU. The TSS for the samples was found to be 194 mg/L (housing society), 241 mg/L (PET bottles industry), 254 mg/L (pharmaceutical industry), 140 mg/L (textile industry) and 251 mg/L (hudiara drain) and it can be seen that the wastewater from PET bottles industry; pharmaceutical industry and hudiara drain are exceeding the NEQS (200 mg/L).

Chemical oxygen demand and biological oxygen demand results show that both parameters were exceeding the NEQS in all the five samples. Chemical oxygen demand for the wastewater samples from housing society, PET bottles industry, pharmaceutical industry, textile industry and Hudiara drain was 896, 166, 419, 812, 610 and 896 mg/L, respectively which is also not in compliance with NEQS (150 mg/L) in all the wastewater samples. Higher COD means higher organic and inorganic compounds in wastewater. A high COD level and relatively low BOD level was seen in all wastewater samples. This shows that the wastewater samples contain organic compounds which are non-degradable. Higher BOD results in lower dissolved oxygen and is directly indicating the high organic pollution level. The BOD was determined as 110.8 mg/L (housing society), 170 mg/L (PET bottles industry), 423 mg/L (pharmaceutical industry), 355 mg/L (textile industry) and 560 mg/L (Hudiara drain) which was exceeding the NEQS (80 mg/L) [11]. The chloride content was found out to be 71, 142, 124, 213 and 320 mg/L, respectively for the wastewater samples which were lower than NEQS value (1000 mg/L).

The HPLC results for various pesticides (Table-3) and polycyclic aromatic hydrocarbons (Table-4) showed that these contaminants were present in all the selected wastewater samples.

Pesticide *viz.*, 1,2-dichloropropane and 1,3-dichloropropane, which is a soil fumigant mostly used to control nematodes and extensively used in Pakistan. It was found in the amount of 0.0465 mg/L in housing society wastewater sample. The same was found 0.0176 mg/L in PET bottle industry, 0.0335 mg/L in pharmaceutical industry and 0.060 mg/L in textile industry. Literature showed that dichloropropane is used in oil and fat solvents, degreasing processes and dry cleaning

TABLE-2
PHYSICO-CHEMICAL ANALYSIS OF WASTEWATER SAMPLES

Parameters	NEQS Pakistan	Wastewater samples				
		Housing society	Industrial wastewater sources			Hudiara drain
			PET bottles	Pharmaceutical	Textile	
pH	6-9	6.9	6.7	6.27	7.18	7.9
Temperature (°C)	40	18	20	17	15	21
Turbidity (FTU)	5	59	199	201	36.87	65
TSS (mg/L)	200	194	241	254	140	251
TDS (mg/L)	3500	1166	1392	1386	1078	1860
COD (mg/L)	150	166	419	812	610	896
BOD (mg/L)	80	110.8	170	423	355	560
Chloride (mg/L)	1000	71	142	124	213	320

The highlighted areas in the table show that values are exceeding the NEQS limits.

TABLE-3
ESTIMATED AMOUNT OF PESTICIDES IN SAMPLES

Samples	Pesticides				
	D.D (mg/L)	Karate (mg/L)	Commando (mg/L)	Finis (mg/L)	Bifenthrin (mg/L)
AK	0.0465	0.0000324	0.0000483	0.000181	0.0333
PET Bottles	0.0176	Not detected	Not detected	Not detected	Not detected
Pharmaceutical	0.0335	Not detected	Not detected	Not detected	Not detected
Textile	0.060	0.000035	Not detected	Not detected	Not detected
Hudiara Drain	Not detected	Not detected	Not detected	0.00160	29.438

TABLE-4
ESTIMATED AMOUNT OF POLYCYCLIC AROMATIC HYDROCARBONS IN SAMPLES

Sample	Polycyclic aromatic hydrocarbons		
	Anthracene (mg/L)	Phenanthrene (mg/L)	Naphthalene (mg/L)
Housing society	0.000602	Not detected	Not detected
PET Bottles	0.000993	Not detected	Not detected
Pharmaceutical	0.00184	Not detected	0.0000224
Textile	Not detected	26.049	0.000170
Hudiara drain	Not detected	Not detected	0.000019

purposes. The chlorination of organic materials during disinfection of drinking water and wastewater can result in the formation of 1,3-dichloropropane [12]. This may be the reason of 1,2-dichloropropane and 1,3-dichloropropane presence in industrial wastewater samples. However, this pesticide was not detected in Hudiara drain samples.

Pesticide "Karate" was present in the concentration of 0.0000324 and 0.000035 in housing society and textile wastewater samples. The reason behind its presence in low concentrations may be the use of Karate in nearby agricultural fields for the pest control. Karate was not observed in any other samples. Commando (a spray with acephate) is herbicide which is mainly used in fields where herbs grow. Low concentration of 0.0000483 mg/L Commando was observed in housing society wastewater sample. As there are many small villages and agricultural fields nearby housing society, hence the use of Karate and Commando is quite common in these agricultural lands.

Finis being very common home insect killer in Pakistan was present in housing society wastewater and Hudiara drain samples. Very little amount of 0.000181 mg/L in housing society wastewater sample and 0.00160 mg/L in Hudiara drain wastewater sample was determined.

Another pesticide bifenthrin in the concentration of 0.0333 and 29.438 mg/L was detected in housing society and Hudiara

drain wastewater sample. Bifenthrin is mainly an insecticide usually used both in agricultural and residential areas. Therefore, its presence has been detected in both domestic and municipal wastewater samples. Products containing bifenthrin are used on cereals, cotton, corn, alfalfa, hay, grass seed, some fruits, ornamentals and vegetables [13,14]. Therefore, its presence in domestic/municipal wastewater source is due to the fact that wheat, vegetables, fruit fields, *etc.* are in the vicinity of housing society where farmers use bifenthrin. Hudiara drain passes through Lahore and many agricultural fields are situated along the length of this drain which is the presence of this compound was also seen there. Literature also supports that these results as many authors have been reported the presence of various pesticides in the wastewater samples from domestic and municipal/domestic sources [15,16].

Anthracene presence in housing society, PET bottles, pharma industry in the concentrations of 0.000602, 0.000993 and 0.00184 mg/L was detected. Standard phenanthrene was detected in only one sample of textile industry in the amount of 26.049.

The reason for their presence in industrial water might be the use of these chemicals in higher concentrations. Anthracene is needed for the production of anthraquinone.

Quantification showed the presence of naphthalene in industrial wastewater samples of pharma and textile in the

concentration of 0.0000224, 0.000170 and 0.000019 mg/L. Naphthalene was the only polycyclic aromatic hydrocarbon found in Hudiara drain sample but with low concentration. The reason that anthracene and phenanthrene were not found in Hudiara drain wastewater samples was because may be these chemicals are not as extensively in use as naphthalene. Hudiara drain receives wastewater from many different sources which includes domestic sewerage, industrial effluents and wastewater from agricultural fields. These chemical substances have the ability to settle down in the sediments and therefore their presence in the sediments is expected to be more as compared to in water.

Naphthalene in the form of naphthalene balls is used commonly in Pakistan as insect killer. Naphthalene is also used in the production of plastics, dyes, resins, lubricants and fuels [17]. Literature supported the fact that naphthalene has been detected in wastewater from dyeing industry, as well as lubricant oils and enters into water mainly due to discharges and spills during the storage, transportation and disposal of fuel oil and coal tar. On the other hand, anthracene can also be released into water from dyes used in textile industry as well as in application of pesticides [18,19]. Few researches have documented the presence of polycyclic aromatic hydrocarbons in PET bottles therefore these compounds are detected in PET bottles industry wastewater sample [20].

Conclusion

It can be concluded that although the use of synthetic pesticides and polycyclic aromatic hydrocarbons is highly toxic for the environment, they are still being used in Pakistan and their presence in wastewater means that these chemicals ultimately enter into the food chain. Pesticides and polycyclic aromatic hydrocarbons or their derivatives use with no proper treatment of wastewater from industrial and municipal sector prior to its discharge into the surface water bodies is contaminating the aquatic environment. One major legal issue is that the NEQS Pakistan has not addressed the issue of these contaminants into the environment yet which is a matter of worry, as these chemicals are toxic and lethal not only for the environment but also for the human beings and animals. These

chemicals when enter into the aquatic environment are either taken up by the fishes or settle down in the sediments hence polluting the water. This water is being used for the irrigation purposes, so these chemicals will enter into the soil, then to the food which is ultimately eaten by the human beings and animals, hence causing adverse health effects.

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