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CHARACTERIZATION OF ORGANIC POLLUTANTS IN HIGHLY POLLUTED RIVER WATER

Snigdhendubala Pradhan[*1] & Rajesh Chandra[2]

[*1]Department of Civil Engineering, Dr. B. R. Ambedkar National Institute of Technology Jalandhar, Punjab, India

[2]Department of Polymer and Process Engineering, Indian Institute of Technology Roorkee, Roorkee, India

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ABSTRACT

The removal and transportation of hydrophobic and hydrophilic nature of organic pollutants in surface water is a major factor for adsorption. Hydrophobic and hydrophilic nature of organics was measured by octanol-water partition coefficients (KOW) by shake flask method and specific UV absorbance (SUVA). This study was done in water samples of river Kali and river Krishni in Uttar Pradesh, India. River Kali and Krishni are the tributaries of river Hindon. It was observed that dissolved organic carbon (DOC) of river Kali and Krishni is 429.6 and 339.2 mg/L but the values of log KOW and SUVA are less in river Kali and Krishni. Values of log KOW and SUVA was represented the nature of river Kali, and Krishni is hydrophilic. Organic compounds are also identified individually by gas chromatography and mass spectroscopy (GC-MS) and characterized by their reported log KOW values. GC-MS study verified most of the organics present in river Kali and Krishni are hydrophilic in nature.

INTRODUCTION

Rivers water is an important water resource for domestic, industrial and irrigation purposes. The organic compounds discharged from municipal and industrial wastewater and runoff from agricultural land are the major role in assimilation or carrying of river pollution. It subsequently impact on the quality of the bank-filtered water (Sontheimer, 1980). The fate and transport of organic contaminants are mainly affected by the hydrophobic and hydrophilic nature of organics present in surface water Vega et al., 1998; Schwarzenbach et al., 1983; Ahel et al., 1996). Mixture of organics in surface water composed of humic (humic and fulvic acids) and nonhumic substances (amino acids and carbohydrates) and abundant in aquatic environments (Frimmel 1998). Organics in surface water is biodegradable and non biodegradable (Marmonier et al., 1995). Octanol water partition coefficient (K_{OW}) and specific UV absorbance (SUVA) are two surrogate parameters by which the hydrophobic and hydrophilic nature of organics can be monitored. K_{OW} can be also be used to estimate organic carbon-normalized partition coefficient (K_{oc}) (Karickhoff et al., 1979) in adsorption process, composition of mixtures of organics (Klopman et al., 1992), aqueous solubility (S) (Karickhoff et al., 1979; Burgess et al., 1996) and toxic effects of organics (Burmaster et al., 1991).

K_{OW} become a key parameter for the regulation and management of organics in natural flow condition. Important application for monitoring of mixture of organics in surface water by K_{OW} is for environmental and ecotoxicological interest. K_{OW} is the accepted physicochemical property for measuring the hydrophobic and hydrophilic nature of single organics (Sangster, 1987). In pharmaceutical and biochemical industry K_{OW} was measured in drug design and toxicology, in industrial chemistry for optimization of production and waste treatment and in food chemistry for purification and extraction of sugars, fat or caffeine (Rydberg et al., 1992). So monitoring of this parameter is important for the surface water quality improvement.

Another practical parameter that provides information about the nature of organics is specific ultraviolet absorbance (SUVA). It is the ratio of UVA at wavelength λ (usually 254 nm) to the concentration of DOC in the water, i.e. UV (m^{-1})/DOC (mg L^{-1}) for natural water sample. SUVA provides a quantitative measure of aromatic content per unit concentration of organic carbon and it characterizes the hydrophobic and hydrophilic nature of organics (Karanfil, 2002; Pradhan et al., 2013). According to Johnson et al. (2002) SUVA value is correlated with molecular weight of organic compounds. SUVA has received increasing attention among drinking water researchers since it indicates the amenability of DOC removal during water treatment. Moreover, SUVA is a valuable characterization parameter for the surface water quality improvement. The main purpose of the study

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was to monitor the nature of organics in polluted water by K_{OW} and SUVA and also compare the organics identified by GC-MS and their individual K_{OW} values.

MATERIALS AND METHOD

Study Area

This study was done by collecting three river water samples. Water samples were collected from river Kali, and Krishni that are situated in Uttar Pradesh, India. These two rivers are highly polluted due to the discharge of treated and untreated industrial effluents and also municipal wastes. Fig. 1 shows the map of river Kali, and Krishni with the sampling locations. River Kali originates in the Doon valley and passes through Saharanpur, Muzaffarnagar and Bagpat districts, before merging with Hindon River at Barnawa. The total length of the river from its origin up to its confluence with the Hindon River is 150 km. The Colour of the water is blackish. Several industrial discharges of treated and untreated sewage and effluents from major cities Meerut and Muzaffarnagar enters in to this river. There are 31 industries within Meerut district, including sugar mills, paper mills, textile and distilleries, along with villages and slaughter houses that discharge their effluent into the river. The main point sources, which contributes the water pollution includes municipal waste and wastes of Deoband town and sugar waste mill in Muzaffarnagar. Agricultural input is another source for contribution of organic pollutants in the river. Disposal of organic wastes polluted River Kali and also river Hindon, which is harmful for aquatic life, human health and environment. The sample collected from the downstream of the river near the village of Pithlokar village, carrying the industrial effluents of the Rohana sugar mill and the Shubham paper mill.

Krishni River merged with river Hindon at the downstream of Barnawa and upstream of Daruhera at Shaikhpur village in Baghpat district. The total length of river Krishni is 78 km. Discharge of treated and untreated industrial effluents from four sugar mills (Kisan Sehkari Sugar Mills Limited, Bajaj Hindustan Limited, Shamli Distillery and Chemical Works and Ramala Sehkari Sugar Mills), one dairy plant, one distillery and three paper mills at Sikka enters into the river Krishni.

Water samples collected from the sampling location of Pitholkar in river Kali, Shaikhpur of river Krishni. Samples were collected to the laboratory for the analysis of different parameters. The temperature and pH of water samples of river Kali and Krishni were measured in the laboratory condition. As per Standard Methods (2005) for DOC measurement, a part of each sample was filtered through a fiberglass filter (0.45 µm). DOC was determined by Shimadzu-TOC-V_{CSN} analyzer. UV-A of filtered samples was measured at 254 nm by the Hach DR-5000 UV-VIS Spectrophotometer with 10 mm quartz cell.

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Fig.1. Sampling locations (of river Kali and Krishni, India

K_{OW} and SUVA measurement: K_{OW} of filtered water samples were measured at octanol to water ratio of 1:1, 1:2, 2:1 in accordance with the procedure described by Pradhan et al., 2013. SUVA of these samples also measured at 254 nm.

GC-MS Analysis: Organic compounds present in the water samples were identified by GC-MS (Varian 450-GC and 240-MS). The work presented here is based on GC/MS screening analysis. For this the water samples were extracted by n-hexane as per liquid/liquid extraction process. Hexane extraction was applied to 500 ml water samples with 50 ml n-hexane in a separating funnel. After separation of phase the organic layers were combined, dried by filtration over 1 g of anhydrous granulated sodium sulphate (Merck, India). The extract volume was used for the identification of individual compounds based on retention time.

RESULTS AND DISCUSSION

It was observed that water samples of river Kali and Krishni contains high DOC values, corresponding to less UVA (Table 1). It was observed that in three different ratios as 1:1, 1:2 and 2:1 in two river water samples the log K_{OW} and SUVA value are significant. From the tabulated data it was found that log K_{OW} and SUVA value does not affect the ratio of octanol to water. SUVA values <2 shows the organics present in the river are nonhumic substances and hydrophilic in nature. In both the rivers the water samples have less log K_{OW} and SUVA values. The SUVA at 254 nm found approximately equal to the initial water samples. In both the ways the water samples which contain variety of mixture of organic compounds are hydrophilic in nature (Table 2). The slope between K_{OW} and $SUVA_{254\ nm}$ is ~ 3.28 in water samples of river Kali. Whereas at the location of Shaikhpur of river Krishni water sample the slope was observed 2.62. In another study at the location of Barnawa of river Hindon the slope of K_{OW} and $SUVA_{254\ nm}$ was found 3.04. It, therefore, suggests that the behavior of a mixture is organic compounds at sampling location Pithlokar and Barnawa are approximately same.

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Table 1: Physico chemical parameters of water samples

Sampling location	pH	Temperature (°C)	DOC (mg/L)	UV (m^{-1})	$SUVA_{254}$ (m-1mg/L-1)
Kali	7.92	30	429.6	485.9	1.138
Krishni	8.23	32	339.2	323	0.952

Table 2: K_{ow} and SUVA values of river Kali and Krishni

Water samples	C_{wf} (mg/L)	C_o (mg/L)	K_{OW}	log K_{ow}	Mean log K_{ow} ± SD	UV (m^{-1})	SUVA ($m^{-1}mg/L^{-1}$)	K_{OW}/ $SUVA_{254\ nm}$ (mg m L^{-1})	Log K_{OW}/ $SUVA_{254\ nm}$ (mg m L^{-1})
Kali (C_{wi}=429.6)									
1:1	102.0	327.6	3.21	0.51	0.53 ± 0.01	99.8	0.978	3.282	0.52
2:1	197.1	232.5	3.36	0.53		201.2	1.021	3.291	0.52
1:2	132.2	297.4	3.45	0.53		142.1	1.075	3.209	0.49
Krishni (C_{wi}=339.2)									
1:1	136.8	202.4	1.48	0.17	0.18 ± 0.01	86.7	0.634	2.334	0.26
2:1	81.93	257.2	1.57	0.20		79.3	0.601	2.612	0.33
1:2	191.1	148.1	1.55	0.19		139.6	0.731	2.930	0.25

The Organic compounds identified by GC-MS are tabulated in Table3. Organic compounds as Valeric anhydride, Ethylenediamine, 2-Pyrrolidinone, 2-Hydroxyethyl acrylate etc. are found in river Kali, Krishni and also in river Hindon water sample. Most of the compounds present in river kali and Krishni are hydrophilic in nature except four hydrophobic compounds.

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Table 3 Organic compounds identified by GC-MS in river water samples

Name of the compound	Molecular Formula	log K_{OW} (Sangster, 1989)	Kali	Krishni
Methyl phenyl sulphoxide	C_7H_8OS	0.55	√	√
Valeric anhydride	$C_{10}H_{18}O_3$	2.15	√	×
Dimethyl sulphoxide	$C_2H_6O_6$	-1.35	×	√
Ethyl maleate	$C_6H_7O_4$	0.89	√	×
N-methyl benzamide	C_8H_9NO	0.86	√	×
N-N-diethylethanamide	$C_6H_{13}NO$	0.34	√	√
2-Methyl-2-nitropane	$C_4H_9NO_2$	1.01	√	√
2-6-diethyl aniline	C10H15N	0.95	√	×
4-Aminobenzoic acid	$C_7H_7NO_2$	0.68	√	×
2- methyl pyridine	C_6H_7N	0.32	√	√
Cyclohexamide	$C_{15}H_{23}NO_4$	0.55	√	×
2-Pyrrolidinone	C_4H_7NO	-0.39	×	√
2-aminopyrimidine	$H_2NC_5H_4N$	-0.22	×	√
Hydroquinone	$C_6H_6O_2$	0.55	√	×
3-Cyclobut-1-enyl-3-hydroxy-2-methyl-propionic acid	$C_8H_{12}O_3$	0.59	√	×
Ethylenediamine	$C_2H_8N_2$	0.19	×	√
2-Hydroxyethyl acrylate	$C_5H_8O_3$	0.54	√	×
2-Phenoxybutyric acid, (octahydroquinolizin-1-yl)methyl ester	$C_{20}H_{29}NO_3$ 331	1.09	√	×

CONCLUSION

K_{OW} and SUVA at 254 nm of water samples of polluted river which contains mixture of organics were measured for the first time. Both SUVA and K_{OW} do not depend on the ratio of octanol to water used for partitioning and the concentration of water samples. These parameters reveal the hydrophilic and/or hydrophobic nature of the water sample. The ratio of log K_{OW} to SUVA at 254 nm shows a narrow range of variation in river Kali and Krishni due to the presence of little different type of organics. The identification of compounds by GC-MS and K_{OW} values shows hydrophilic nature of the river Kali and Krishni water samples where as in river Elbe it shows hydrophobic in nature. The outcome of this study can be used to estimate residence time for the natural purification of organics in the polluted water. It will require suitable design for the removal of such organics by adsorption.

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