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Research Article

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Determination of Organic Pollutants Concentrations in Water along Wulmi River in Pankshin Local Government, Plateau State, Nigeria

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Abstract Persistent and toxic substances (PTS) are group of compounds that has been attracting attention of environmental scientists for decades because of their potential for both long-range transport and adverse effects. The aim of the research is to determine the concentration of organic pollutants in water from Wulmi River at two sampling points (S_1-S_2) at interval of 1km from the extract of semi permeable membrane Device (SPMD) placed at each sampling point monthly from May to August, 2017. The extract from the SPMD were recovered using non-polar solvent Methylene chloride and combined with the triolein fraction, enriched and analyzed using GCMS. The analyzed organic pollutants were classified into twelve (12) groups namely: Aliphatic hydrocarbons, Aromatic acids, Esters, Aldehydric compounds, alcohols, fatty acids, phthalates, phenols, Sulphur and Nitrogen containing compounds, Benzene and its derivatives, Amide and Hydroxylated compounds. The concentration of Aliphatic hydrocarbons ranged between $2.4x10^6$µg/l – $1.524x10^8$µg/l at sampling point S_1 and $2.8\ x10^6$µg/l – $1.051x10^8$µg/l which are above the maximum limit of 1µg/l - 100 µg/l. Aromatic acids ranged between $2.53\ x10^7$µg/l - $2.374\ x10^8$µg/l at point S_1 and no aromatic acids was detected at point S2. The concentration at point S_1 is above the approved standard of 6.9 µg/l. Esters ranged between $2.30x10^7$µg/l - $6.06x10^7$µg/l at sampling point S_1which are well above the approved standard of 0.024 µg/l - 0.03µg/l. No esters was detected at point S_2. Aldehydric compounds ranged between $3.2\ x10^6$µg/l - $1.046\ x10^8$µg/l at point S_1 which are higher than the permissible range of 0.096-0.10µg/l. No aldehydric compounds was detected at point S_2. Alcohols ranged between $6.6\ x\ 10^6$ µg/l - $1.903\ x10^8$µg/l, at point S_1 and non was detected at S_2. The concentration of alcohols at point S_1 was above the limit of 0.0031µg/l, Fatty acids ranged between $8.2x10^6$ µg/l - $1.677x10^8$ µg/l at point S_1 and $3.4x10^6$µg/l – $1.644x10^8$µg/l at point S_2 above the limit of 1.48-1.50 µg/l , phthalates is $1.08x10^7$µg/l at sampling point S_1 and at point S_2 phthalates ranged between $2.17x10^7$µg/l – $1.595x10^8$µg/l all above the standard limit of 4.5µg/l. Phenols ranged between $1.38\ x10^7$µg/l - $1.157x10^8$µg/l at point S_1 and at point S_2 it ranged between $5.8x10^6$µg/l – $6.4x10^6$µg/l above the limit of 1 µg/l.Sulphur and Nitrogen containing compounds ranged between $2.4x10^6$ µg/l - $3.779\ x10^8$ µg/l at point S_1 and $6.02x10^7$µg/l at point S_2 and there is no established standard. Benzene and its derivatives ranged between $8.1x10^6$ µg/l - $1.205x10^8$µg/l at point S_1 and $8.2x10^6$µg/l – $2.37x10^7$µg/l with maximum concentration limit range of 0.011-0.68 µg/l, Amides ranged between $6.5x10^6$ µg/l - $3.38x10^7$ µg/l at point S_1 and $6.8x10^6$µg/l – $3.862x10^8$µg/l at point S_2 with permissible limit range of 0.21µg/l-0.74 µg/l .Hydroxylated compounds $1.55\ x10^7$ µg/l at point S_1 with maximum concentration limit of 0.37µg/l .

Keywords Wulmi River, persistent organic pollutants concentrations

Introduction

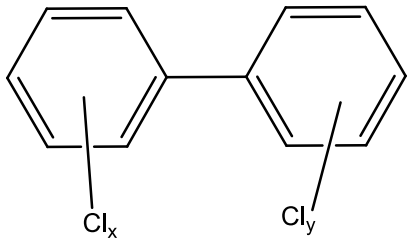
Wulmi, a village in Pankshin local government area of Plateau state is located at longitude 9o24’58.4712’’E and latitude 9o18’38.63096’’N is noted for rural agricultural practices. The farmers use fertilizers, herbicides etc as farming inputs and the run-off from those farms enter Wulmi River. There are no portable water supplies in the catchment areas of Wulmi, hence the inhabitants of villages along it depend on water sources mainly from the river for domestic, irrigation, and livestock activities.

Natural environment has been a subject of concern to the effects of various chemicals emitted during anthropogenic as well as natural processes. Such chemicals can originate from industrial production (often high-volume production) or be generated as unwanted by-products of chemicals synthesis or combustion processes (Masindi and Muedi, 2018).

Persistent and toxic substances (PTS) are group of compounds that have been attracting attention of environmental scientists for decades because of their potential for both long-range transport and adverse effects (Balali-Mood et al., 2021). They are generally thermally stable and chemically resistant. Their degradation rates are slow and thus their life times in the environment are very long. Majority of these compounds are lipophilic and, therefore, accumulate in biological tissues. They are also called Persistent bio-accumulative and toxic chemicals (PBT). Among them, an important subgroup consists of Persistent organic pollutants (POPs), some specific examples of persistent organic pollutants include: Polychlorinated biphenyls (PCBs), Polychlorinated naphthalenes (PCNs), Polybrominated- diphenyl ethers (PBDEs), Organochlorine Pesticides, and combustion by-products as Polychlorinated dibenzo-P-dioxins and dibenzofurans (PCDDs/Fs), and Polyaromatic hydrocarbons (PAHs). Even though PAHs do not represent typical POPs because they have higher reactivity and lower bioaccumulation potential, they are often included because of their high toxicity and high abundance at the same time (Jayaraj et al., 2016a)

PCBs are a class of synthetic organic chemicals used since 1930 in a large number of industrial applications (mainly as dielectric fluids in capacitors and transformers but also as flame retardants, ink solvent or plasticizers) (Erickson et al., 2017). PCBs exhibit fire resistance, having a low electrical conductivity, a high resistance to thermal decomposition and a high resistance to oxidants and other chemicals. PCBs were mostly use as technical mixtures known under commercial names as Aroclor, Pyralene, Chlorphen, Solvolor technical mixture produced in former Czechoslovakia – Delor (Yun et al., 2021), and the technical mixtures were produced by direct chlorination of technical biphenyl.

Since 1970s, PCB production was gradually terminated as it was found that they pose considerable threats to human health and environment. They are considered to be immuno-toxic and affect reproduction, gastrointestinal tract and thyroid gland, (Gupta et al., 2018). Once PCBs is released into the environment it has long-life times and can travel long distances (Montano et al., 2022).

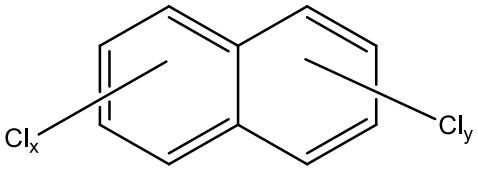


Scheme I: Structure of PCBs

Polychlorinated Naphthalenes (PCNs) are a group of 75 congeners with physicochemical properties similar to PCBs, PCNs have low flammability and medium to low volatility, their volatility decreases with increasing degree of chlorination (Wang et al., 2019).

They are chemically and thermally resistant and their technical mixtures as Halowax, Nibren or clonacire were used as capacitor, dielectrics, electrical insulators, engine oil additives, wood paper and fabrics impregnation, flame

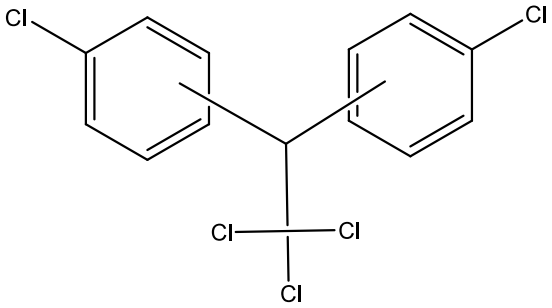
retardants, fungicides and even insecticides (Klimczak et al., 2023). PCNs are also formed during incineration processes involving chlorine, and they are found as impurities in technical PCBs mixtures. PCNs are known to cause chloracne, other common symptoms of intoxication involve digestive problems, anorexia, nausea and vertigo (Li et al., 2020).



Scheme II: Structure of PCNs

Dichlorodiphenyltrichloroethane (DDT), was first synthesized in 1874, however its insecticidal properties were found in 1930s. DDT was widely used during world war II to protect soldiers and civilians from malaria and other disease spread by insects, and after the war DDT usage went on to control disease and also in agriculture for crops protection. In former Czechoslovakia it was vastly applied on potato fields against mosquitoes in several countries, mainly in Africa, to control malaria (Azzouz et al., 2021).

Among toxic effect of DDT is egg-shell thinning among birds, especially birds of prey, its impact on bird populations had led to bans in many countries during the 1970s. Its residues are still present in the environment and the short – term acute toxic effects of DDT on humans are limited, but long – term exposures have been associated with chronic health effects, owing to its structure. DDT can mimic hormones, thus acts as endocrine disruptor and affect development (Bouwman et al., 2019).



Scheme III: Structure of DDT

Efficient techniques for the removal of high toxic organic compounds from water have drawn significant interest. A number of methods such as, filtration with coagulation, precipitation, ozonation, absorption, ion exchange, reverse osmosis and advanced oxidation processes have been used for the removal of organic pollutants from polluted water and wastewater. These methods have been found to be limited, since they often involve high capital and operational costs. On the other hand, ion exchange and reserve osmosis are more attractive processes because the pollutant value can be recovered along with their removal from the effluents (Jeirani et al., 2015).

Among the possible technique for water treatments, the absorption process by solid adsorbents shows potential as one of the most efficient methods for the treatment and removal of organic contaminants in wastewater treatment (Rathi and Kumar, 2021). Adsorption has advantages over the other methods because of simple design and can involve low investment in terms of both initial cost and land required

Persistent Organic Pollutants are group of chemicals typically found in all environmental compartments. They are generally thermally stable, chemically resistant and their degradation rates are slow thus their lifetimes in environment are very long. Majority of them are lipophilic, and they tend to accumulate in fatty tissues. In addition, even trace amounts of many of these compounds pose adverse effects on living organism. One important property of persistent organic pollutants is that of semi – volatility. This property confers a degree of mobility through the atmosphere and be transported over long distances, this moderate volatility does not result in the substance remaining permanently in the atmosphere where it would present little direct risk to humans and organism in the

environment. These substances may volatilize from hot regions but will condense and tend to remain in colder regions (Jayaraj et al., 2016b).

Anthropogenic influence from industrial, agricultural activities and natural processes like weathering and erosion affect the quality of waters and threaten their use for drinking, irrigation economic and social purpose.

The Stockholm convention on Persistent organic pollutants identified several classes of chemicals of environmental concern – chlorinated Pesticides, Polychlorinated biphenyls, Polychlorinated dioxins, furans and later developed policy criteria leading to the world-wide limitation or ban on the use of dozen chemicals in these classes (Srinivas et al., 2020). Waste water treatment plants (WWTPs) and industrial complexes, leaking septic tanks, rural and urban surface run off, and improper disposal of waters are all common sources of environmental contaminants (McCance et al., 2018). Diminishing fresh water has prompted a "use and reuse" practice where water is often used, treated and released back into a reservoir or river before being reuse again as drinking water by the same or downstream communities (McCance et al., 2018; Simons et al., 2015 and Srinivas et al., 2020). The pathways for removal of environmental contaminants from waste water streams or rivers are poorly understood and as result, many environmental contaminants survive conventional water treatment in drinking water supplies (Eggen et al., 2014) found that 52 of 98 environmental contaminants remained unaltered in chlorinated drinking water 10 days after treatment. Several common environmental contaminants are known or suspected to alter the endocrine function, feminization or masculinization of the opposite sex, and other anomalies (Samal et al., 2022). Since environmental contaminants (ECS) are released into the environment as complex mixtures, and not as single compounds, the concentration of ECS in water supplies are likely to be below any level of direct risk to humans; however the presence of antibiotics in the environment may result in the development of antibiotic resistant strains of bacteria which could become a serious threat to human health (Okeke et al., 2022; Parida et al., 2021and Patel et al., 2019). Materials made of polyethylene, rubber, tygon or other plastics should be avoided due to the potential for these materials to absorb or desorb targeted chemicals into the collected sample (Landrigan et al., 2023). The environmentalists have also carried out significant researches on as aspect Pertaining water management (Loucks et al.,2017).

Many of the effects of the toxic Persistent Organic Pollutants were first identified in fish –eating wildlife, but precise mechanisms of action and chemicals involved were subsequently elucidated in carefully – controlled experimental design in laboratory animals.

Materials and Methods

Chemical/Reagents The chemicals and reagents that were used for the research are of analytical grades and were used without further preparation. They include: Glycerol ($C_3H_8O_3$), Lipozyme ($C_{11}H_9N_3N_9O_2$), methylene chloride (CH_2Cl_2), Hydrochloric acid (HCl), anhydrous sodium sulphate (Na2SO4) and sulphuric acid (H2SO4).

Equipment Gas chromatography – mass spectrometer (GC-MS) with model number GCMS – QP2010SE SHIMADZU, JAPAN and Semi-permeable Membrane Device (SPMD) were used.

Study Area The study area for this research is Wulmi River in Pankshin Local Government of Plateau State. The River Sites span a wide range of Villages. Sampling points along the River are labeled:

S_1 = Wulmi River Sampling Point 1

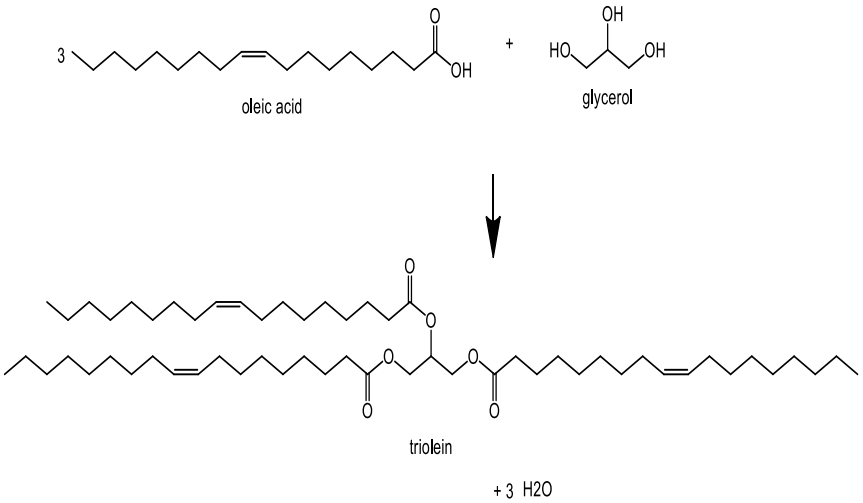
S_2 = Wulmi River Sampling Point 2

S_3 = Wulmi River Sampling Point 3

Sampling and Sample Collection Semi – Permeable membrane Device tube in a stainless cage filled with 1 ml of synthetic triolein was deployed monthly at three sampling points S_1-S_3 along Wulmi River at an interval of 1 km from May- August 2017. The membrane was removed and transported in a sealed can to the laboratory and was mechanically cleaned from biofouling using cold water and dried. The membrane was inserted into a glass column and 100 ml of methylene chloride was added and left to dialyse for 24 hours. 100 ml of methylene chloride was added again and left to dialyse for another 24 hours. The combined dialysates were evaporated to a small volume (approximately 0.5 ml) before GC-MS analysis.

Synthesis of Triolein ($C_{57}H_{104}O_6$) 0.5 g of oleic acid and 0.0543 g of glycerol were mixed with 0.05 g of Lipozyme in an Eppendorf tube kept open at 60 oC. The amounts of substrates must correspond to the exact stoichiometric amounts necessary to synthesize 100 % triolein. The consumption of oleic acid will start immediately after the addition of the enzyme into monolein and diolein. The reaction may be completed after 60 hours. Triolein which may be slowly formed than the other two glycerides may go up to 100 % within 60 hours (Y. Li et al., 2021).

Extraction of Compounds At environmental sampling Technologies the lipid fraction of each SPMD was removed and combined with other



lipid fractions from the sampling point. Trip blanks were extracted along with the other SPMDs. The extract were recovered dialytically with a non polar solvent, Methylene chloride from the lipid portion of the SPMD. This extract was reduced, cleaned up, and enriched. From the clean up procedure gel-permeation chromatography was used. This process removes any lipid that was carried out during the dialysis extraction.

Isolation of Analytes Before analysis, the sealed loops were removed and exposed membranes were carefully mechanically cleaned from biofouling using cold tap water. The surface of membranes was then rinsed with small amounts of Methylene chloride, 1M HCl and distilled water and dried.

Dialysis Membrane was rolled, inserted into the glass column and after addition of 100 ml of methylene chloride was left to dialyse for 24 hours. The dialysate was collected passing through the layer of anhydrous sodium sulphate, 100 ml portion of methylene chloride was added again and left to dialyse for another 24 hours. Combine dialysates were evaporated to a small volume (approximately 0.5 ml) and the remaining solvent was ramoved using a gentle nitrogen stream.

Clean-Up The residue left after removing of extraction solvent was dissolved in 10 ml of GPC mobile phase (cyclohexane: ethylacetate mixture, 1.1, v/v) containing 5ng per ml of PCB congener No. 112, a recovery internal standard. The aliquot of 2 ml of this solution was loaded onto the Bio-beads S-X_3 column to separate triolein and other interferences from analytes (the capacity of the GPC column used in this study was 200 mg of lipids per injection). Under applied experimental conditions, all the target analytes were eluted in 16 ml fraction corresponding to elution volumes 14-30 ml at a flow rate 0.6 ml per min.

Chromatographic Analysis of Organic Compounds Gas chromatography/mass spectrometry detection (GC/MS) analysis of the extracts was done. One microliter (1μL) of each sample was injected in the splitless mode using an auto injector. Separation of the compounds was accomplished with a fused- silica capillary column of 5 percent phenyl methyl silicone (ultra-2) with a film thickness of 0.33 μm (micrometer),30 m (Meter)$\times$0.2 mm (millimeter) inside diameter. Confirmation of the compounds was based on the presence of the molecular ion and confirming ions, a retention-time match was compared to external standards, and correct area ratios of the confirming ions.

Trip blanks was analyzed exactly as deployed samples and was used to define contamination of the SPMD concentrations during transportation and handling. Any concentrations that was detected in trip blanks was subtracted from the SPMD concentration from the water sampling sites.

Identification and Quantification of Analytes Eluate collected from gel-permeation chromatography column was vacuum evaporated, the remaining solvent was removed using a gentle nitrogen stream and then 1ml of syringe internal standard mixture containing 40 ng per ml tonalide D3 was added. Approximately 500 µL of the sample was treated with concentrated H_2SO_4 and then the upper layer was carefully transferred into GC vials for organic pollutants analyses sample equivalent of 1µL injected for GC analysis corresponded to 0.02 % of total SPMD extract. Organic compound pollutant content were determined by GC/MS method with EI Ionization in SIM (Selected Ion Monitoring) mode. Internal standard calibration technique was used for quantification of these analytes (concentrations of syringe internal standards tonalide D_3 in calibration standards was 40 ng per ml 150 octane). The solutions used for calibration were in the range 0.2 – 100 ng/ml.

Table 1: Concentration (µg/l) of Organic Pollutants at sampling point S_1 in Wulmi River in May 2017

Peak	Compound	Mw (g/mol)	Area	Area%	Conc. (µg/l)
1	o-Xylene	106	436367	0.81	8.1×10^6
2	Benzene, (1-methylethyl)-	120	437676	0.82	8.2×10^6
3	Benzene, 1,2,4-trimethyl-	120	592862	1.11	1.11×10^7
4	Methylene chloride	84	134222	0.25	2.5×10^6
5	Thioindigo	296	5308874	9.91	9.91×10^7
6	Thioindigo	296	4816862	8.99	8.99×10^7
7	Hexadecanoic acid, methyl ester	270	1088802	2.03	2.03×10^7
8	Eicosanoic acid	312	890177	1.66	1.66×10^7
9	Silane, dimethylisobutoxydocosyloxy-	456	3077672	5.75	5.75×10^7
10	Cholest-2-en-3-amine, N,N-diethyl-, (5.alpha	441	2052404	3.83	3.83×10^7
11	Octadecanoic acid, 9,10-epoxy-18-(trimethylsiloxy	400	440156	0.82	8.2×10^6
12	Dimethyl[bis(undecyloxy)]silane	400	8160914	15.24	1.524×10^8
13	2-methylhexacosane	380	4362526	8.15	8.15×10^7
14	Behenyl chloride	344	5535098	10.33	1.033×10^8
15	Nonadecan-1-ol trimethylsilyl ether	356	10194942	19.03	1.903×10^8
16	Octadecane, 3-ethyl-5-(2-ethylbutyl)-	366	944784	1.76	1.76×10^7
17	1-Chloroeicosane	316	5084602	9.49	9.49×10^7
			53558940	**100.00**	

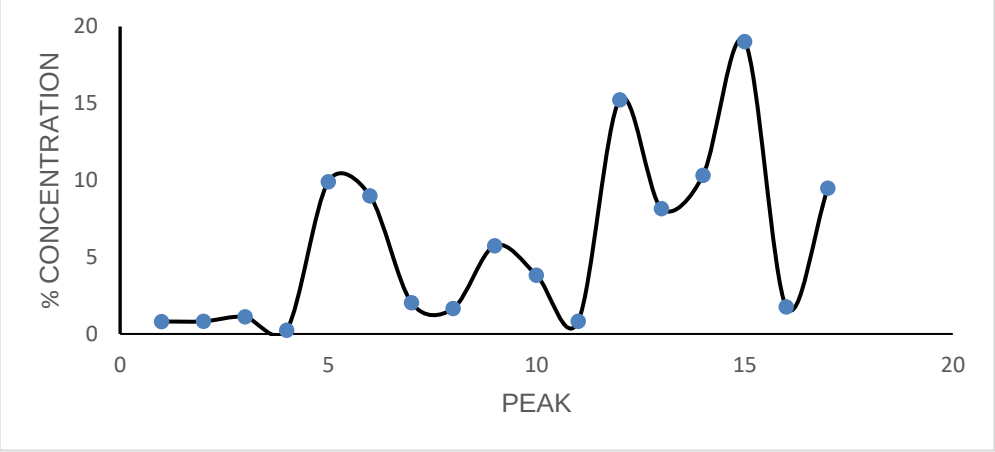


Figure 1: % Concentration (µg/l) of Organic Pollutants at sampling point S_1 in Wulmi River in May 2017

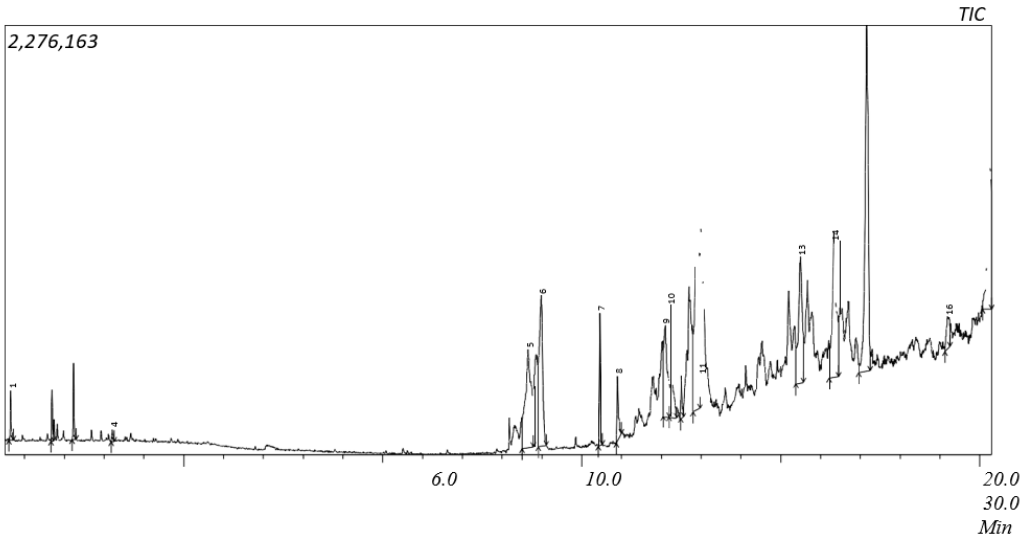


Figure 2: Chromatogram of Organic Pollutants in Wulmi River at sampling points S1 in May 2017

Table 2: Concentration (µg/l) of Organic Pollutants at sampling point S_1 in Wulmi River in June 2017

Peak	Compound	Mw (g/mo)	Area	Area%	Conc. (µg/l)
1	o-Xylene	106	1383145	3.82	3.82×10^7
2	Benzene, 1-ethyl-2-methyl-	120	1903170	5.26	5.26×10^7
3	Benzene, 1,2,3-trimethyl-	120	3480559	9.61	9.61×10^7
4	Benzene, 1,4-diethyl-	134	1342255	3.71	3.71×10^7
5	Benzene, 4-ethyl-1,2-dimethyl-	134	1103692	3.05	3.05×10^7
6	Benzene, 1-methyl-2-(2-propenyl)-	132	1344167	3.71	3.71×10^7
7	Azulene	128	757231	2.09	2.09×10^7
8	Phenol, 2,4-bis(1,1-dimethylethyl)-	206	1623621	4.48	4.48×10^7
9	1,2-Benzenedicarboxylic acid, bis(2-methylp	278	8597545	23.74	2.374×10^8
10	n-Hexadecanoic acid	256	2521747	6.96	6.96×10^7
11	l-Norvaline, N-(2-methoxyethoxycarbonyl)-,	429	360235	0.99	9.9×10^6
12	cis-Vaccenic acid	282	5420168	14.97	1.497×10^8
13	Oleic Acid	282	1282068	3.54	3.54×10^7
14	Z-11-Pentadecenol	226	392305	1.08	1.08×10^7
15	15-Hydroxypentadecanoic acid	258	938104	2.59	2.59×10^7
16	9-Octadecenal, (Z)-	266	2819269	7.79	7.79×10^7
17	15-Hydroxypentadecanoic acid	258	940807	2.60	2.60×10^7
			36210088	**100.00**	

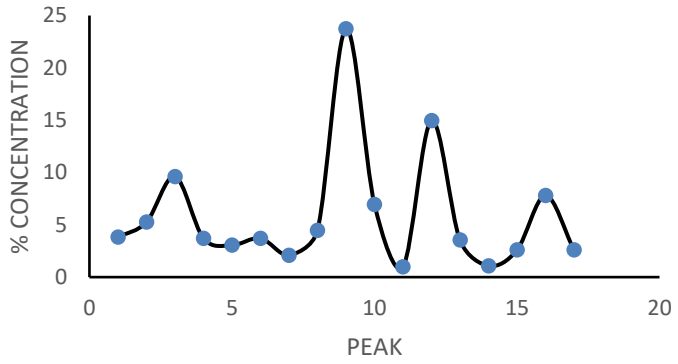


Figure 3: % Concentration (µg/l) of Organic Pollutants at sampling point S_1 in Wulmi River in June 2017

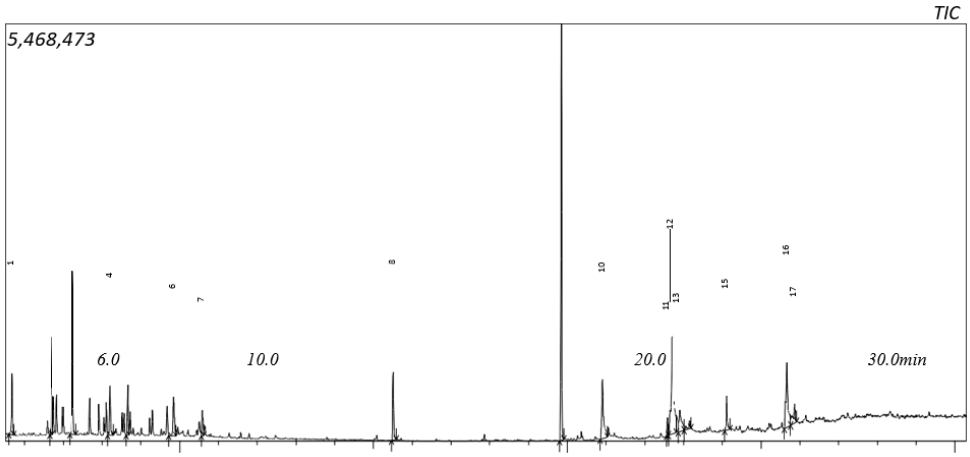


Figure 4: Chromatogram of Organic Pollutants in Wulmi River at sampling point S1 in June 2017

Table 3: Concentration (µg/l) of Organic Pollutants at sampling point S_1 in Wulmi River in July 2017

Peak	Compound	Mw (g/mo)	Area	Area%	Conc. (µg/l)
1	p-Xylene	106	1729067	5.01	5.01×10^{7}
2	Benzene, 1-ethyl-2-methyl-	120	2406049	6.97	6.97×10^{7}
3	Benzene, 1-ethyl-2-methyl-	120	995555	2.89	2.89×10^{7}
4	Benzene, 1,2,4-trimethyl-	120	1039984	3.01	3.01×10^{7}
5	Benzene, 1,2,3-trimethyl-	120	4158673	12.05	1.205×10^{8}
6	Benzene, 1,2,3-trimethyl-	120	961759	2.79	2.79×10^{7}
7	Benzene, 1,4-diethyl-	134	1559646	4.52	4.52×10^{7}
8	Benzene, 4-ethyl-1,2-dimethyl-	134	1371608	3.97	3.97×10^{7}
9	Benzene, 1-methyl-2-(2-propenyl)-	132	1594117	4.62	4.62×10^{7}
10	Azulene	128	1039270	3.01	3.01×10^{7}
11	Phenol, 2,4-bis(1,1-dimethylethyl)-	206	475638	1.38	1.38×10^{7}
12	(CH3)3CSC(O)OCH3	148	82449	0.24	2.4×10^{6}
13	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl	278	2307748	6.69	6.69×10^{7}
14	n-Hexadecanoic acid	256	1895753	5.49	5.49×10^{7}
15	cis-Vaccenic acid	282	5788201	16.77	1.677×10^{8}
16	Oleic Acid	282	1578803	4.58	4.58×10^{7}
17	15-Hydroxypentadecanoic acid	258	1025685	2.97	2.97×10^{7}
18	9-Octadecenal, (Z)-	266	3608027	10.46	1.046×10^{8}

19	15-Hydroxypentadecanoic acid	258	352813	1.02	1.02×10^7
20	2H-Pyran, 2-(2-heptadecynyloxy)tetrahydro-	336	535239	1.55	1.55×10^7
			34506084	**100.00**	

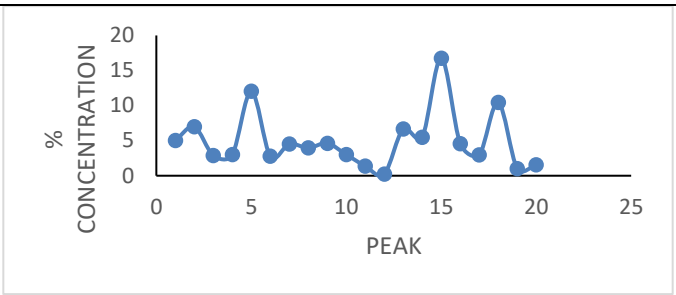


Figure 5: % Concentration (µg/l) of Organic Pollutants at sampling point S_1 in Wulmi River in July 2017

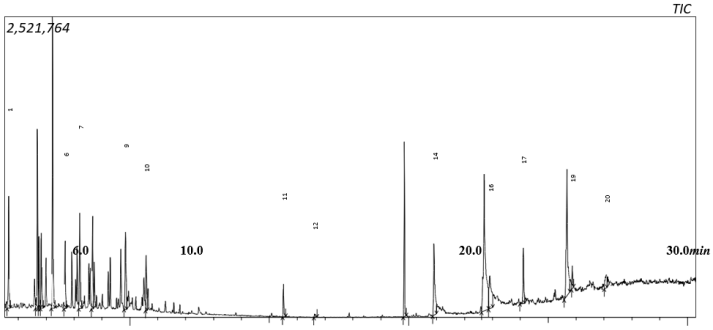


Figure 6: Chromatogram of Organic Pollutants in Wulmi River at sampling point S1 in July 2017

Table 4: Concentration (µg/l) of Organic Pollutants at sampling point S_1 in Wulmi River in August 2017

Peak	Name	Mw (g/mol)	Area	Area%	Conc. (µg/l)
1	o-Xylene	106	23255281	1.67	1.67×10^7
2	Benzene, 1-ethyl-3-methyl-	120	34619681	2.49	2.49×10^7
3	Benzene, 1,2,4-trimethyl-	120	52074705	3.75	3.75×10^7
4	Benzene, 1,2,3-trimethyl-	120	13354131	0.96	9.6×10^6
5	Benzene, 2-ethyl-1,4-dimethyl-	134	21685029	1.56	1.56×10^7
6	Benzene, 4-ethyl-1,2-dimethyl-	134	17428081	1.25	1.25×10^7
7	Benzene, 1-methyl-2-(2-propenyl)-	132	21949162	1.58	1.58×10^7
8	Azulene	128	11278020	0.81	8.1×10^6
9	Phenol, 4-bromo-2-chloro-	206	160901866	11.57	1.157×10^8
10	S,S'-Diethyl methylphosphonodithioate	184	22986463	1.65	1.65×10^7
11	o-Butyl O,O-diethyl phosphorothioate	226	16227037	1.17	1.17×10^7
12	Eicosane	282	12191147	0.88	8.8×10^6
13	Benzaldehyde, 3-phenoxy-	198	19697493	1.42	1.42×10^7
14	1,2-Benzenedicarboxylic acid, bis(2-methylpr	278	35107844	2.53	2.53×10^7
15	5-Fluoro-1-triacetylribofuranosylimidazole-4	388	7005371	0.50	5.0×10^6
16	2,6-Dimethyl-1,3,5,7-octatetraene, E,E-	134	13163225	0.95	9.5×10^6
17	Dimethyl[bis(tridecyloxy)]silane	456	19629309	1.41	1.41×10^7
18	Profenofos	372	525341936	37.79	3.779×10^8
19	Profenofos	372	8507629	0.61	6.1×10^6
20	1-Phenanthrenecarboxaldehyde, 1,2,3,4,4a,9	284	4423649	0.32	3.2×10^6
21	9-Octadecenamide, (Z)-	281	51394241	3.70	3.70×10^7
22	Octadecanamide	283	9053398	0.65	6.5×10^6
23	Di-n-octyl phthalate	390	15072580	1.08	1.08×10^7

24	9-Octadecenamide, (Z)-	281	9719063	0.70	7.0×10^6
25	2-Propyn-1-ol, triisobutylsilyl ether	254	9230711	0.66	6.6×10^6
26	2,2,4-Trimethyl-3-(3,8,12,16-tetramethyl-heptadeca	428	3319834	0.24	2.4×10^6
27	Cypermethrin	415	84231403	6.06	6.06×10^7
28	Cypermethrin	415	8114285	5.84	5.84×10^7
29	Cypermethrin	415	54329044	3.91	3.91×10^7
30	Cypermethrin	415	32022218	2.30	2.30×10^7
			1390342402	**100.00**	

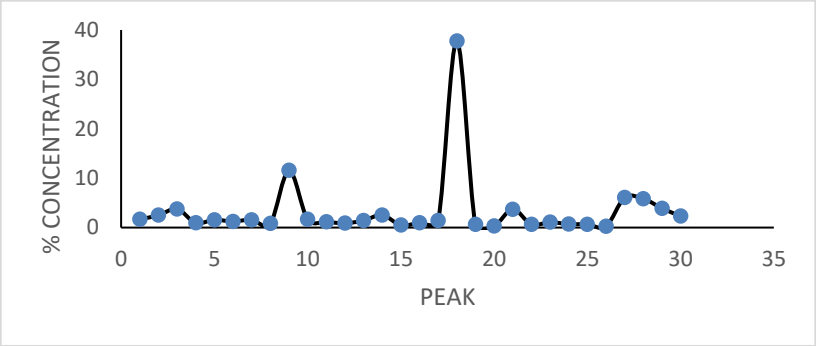


Figure 7: % Concentration (µg/l) of Organic Pollutants at sampling point S_1 in Wulmi River in August 2017

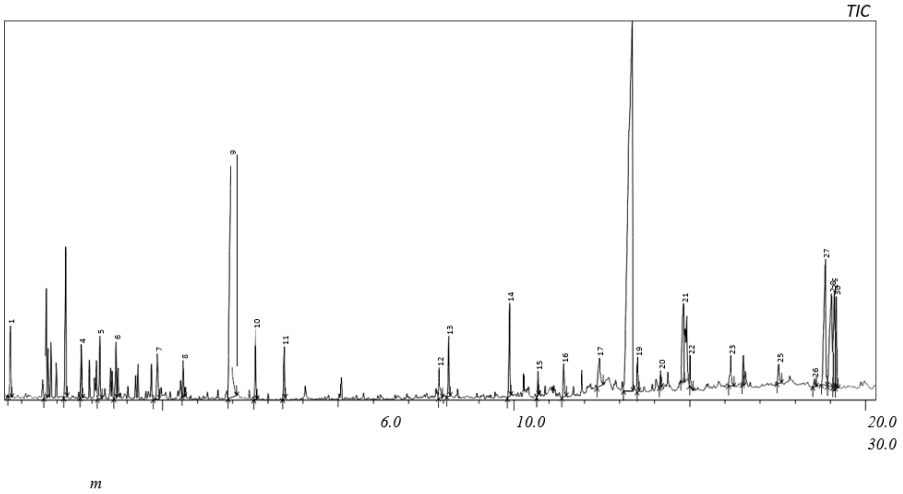


Figure 8: Chromatogram of Organic Pollutants in Wulmi River at sampling point S1 in August 2017

Table 5: Concentration (µg/l) of Organic Pollutants at sampling point S_2 in Wulmi River in May 2017

Peak	Compound	Mw (g/mol)	Area	Area%	Conc. (µg/l)
1	Acetophenone	120	72110	1.96	1.96×10^7
2	Ethanone, 1-(4-methylphenyl)-	134	59797	1.62	1.62×10^7
3	1-Pentanone, 1-(4-methylphenyl)-	176	58223	1.58	1.58×10^7
4	Benzene, (2-methylcyclopropyl)-	132	61944	1.68	1.68×10^7
5	1H-Indene, 2,3-dihydro-1,1-dimethyl-	146	38569	1.05	10.5×10^7
6	Pentanoic acid, 5-hydroxy-, 2,4-di-t-butylph	306	30910	0.84	8.4×10^6
7	Pentanoic acid, 2-methyl-	116	22408	0.61	6.1×10^6
8	2-Methylheptanoic acid	144	18599	0.51	5.1×10^6
9	Hexadecanoic acid, methyl ester	270	536669	14.58	1.458×10^8
10	Benzenepropanoic acid, 3,5-bis(1,1-dimethyl	292	56453	1.53	1.53×10^7
11	9,12-Octadecadienoic acid, methyl ester	294	106158	2.88	2.88×10^7

12	9-Octadecenoic acid, methyl ester, (E)-	296	605228	16.44	1.644×10^7
13	9-Octadecenoic acid (Z)-, methyl ester	296	245252	6.66	6.66×10^7
14	Methyl stearate	298	152085	4.13	4.13×10^7
15	Heptanamide, 4-ethyl-5-methyl-	194	250044	6.79	6.79×10^7
16	Butanoic acid, 2-methyl-	171	21049	0.57	5.7×10^6
17	9-Octadecenamide, (Z)-	281	1182073	32.11	3.211×10^8
18	Tetradecanoic acid, 10,13-dimethyl-, methyl e	270	12498	0.34	3.4×10^6
19	Amylene hydrate	88	85193	2.31	2.31×10^7
20	Butanoic acid, 2-methyl-	102	20972	0.57	5.7×10^6
21	Trimethyl[4-(1,1,3,3,-tetramethylbutyl)phenoxy	278	21307	0.58	5.8×10^6
22	Trimethyl[4-(1,1,3,3,-tetramethylbutyl)phenoxy	102	23572	0.64	6.4×10^6
			3681113	**100.00**	

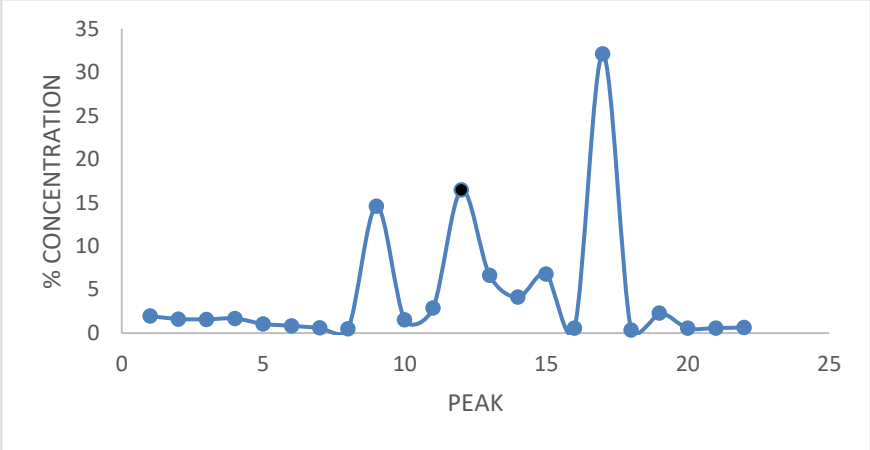


Figure 9: % Concentration (µg/l) of Organic Pollutants at sampling point S_1 in Wulmi River in May 2017

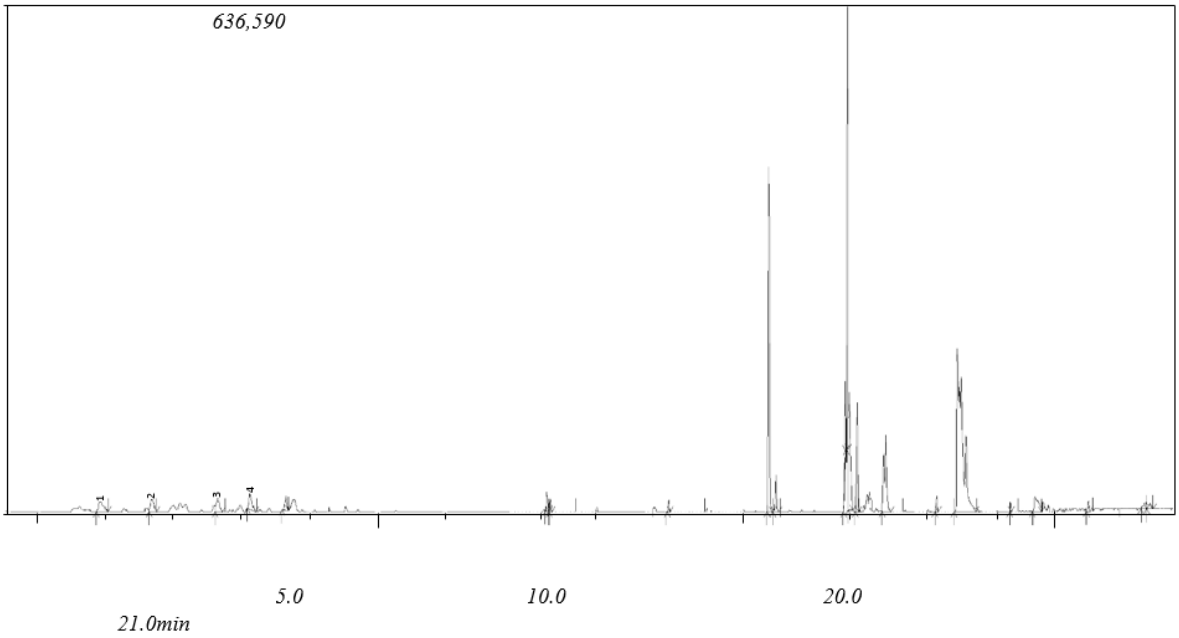


Figure 10: Chromatogram of Organic Pollutants in Wulmi River at sampling point S2 in May 2017

Table 6: Concentration (µg/l) of Organic Pollutants at sampling point S_2 in Wulmi River in June 2017

Peak	Compound	Mw (g/mol)	Area	Area%	Conc. (µg/l)
1	Acetophenone	120	49442	0.76	7.6×10^6
2	1-Pentanone, 1-(4-methylphenyl)-	176	33234	0.51	5.1×10^6
3	p-Cymene	134	35862	0.55	5.5×10^6
4	1-Pentanone, 1-(4-methylphenyl)-	176	34546	0.53	5.3×10^6
5	Benzene, (2-methylcyclopropyl)-	132	53177	0.82	8.2×10^6
6	Hexadecanamide	255	214986	3.32	3.32×10^7
7	9-Octadecenamide, (Z)-	281	2497350	38.62	3.862×10^8
8	Sulfurous acid, 2-propyl tridecyl ester	306	389076	6.02	6.02×10^7
9	Bis(2-ethylhexyl) phthalate	390	1031372	15.95	1.595×10^8
10	3-Heptadecanol	256	354956	5.49	5.49×10^7
11	2-Bromotetradecane	276	679777	10.51	1.051×10^8
12	Nonane, 1-iodo-	254	325411	5.03	5.03×10^7
13	1,4-Epoxynaphthalene-1(2H)-methanol, 4,5,7-	344	767760	11.87	1.187×10^8
			6466949	**100.00**	

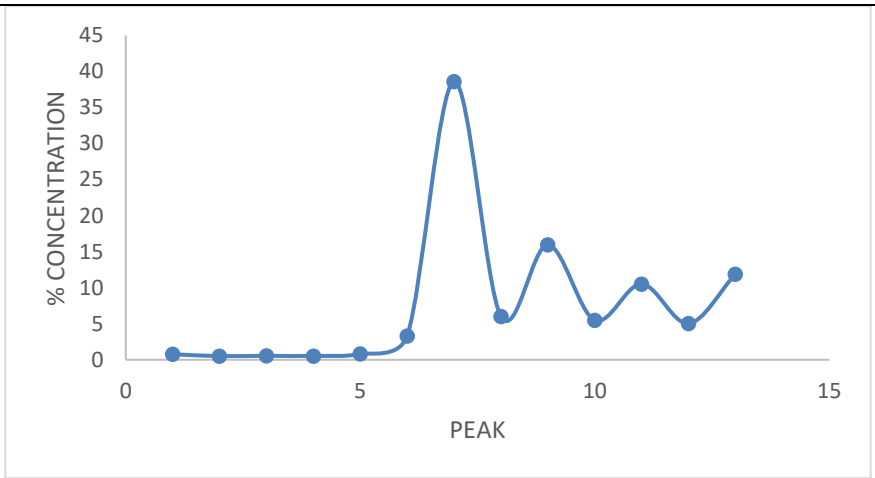


Figure 11: % Concentration (µg/l) of Organic Pollutants at sampling point S_1 in Wulmi River in June 2017

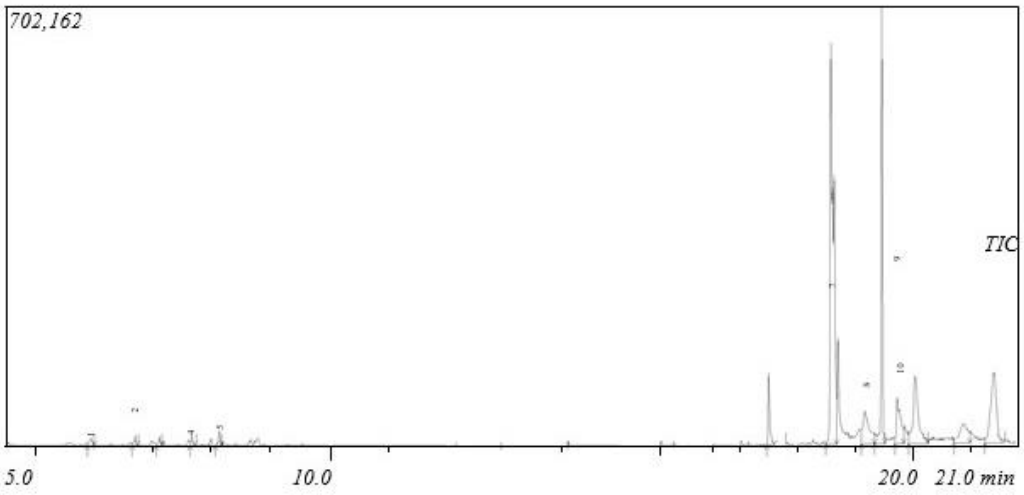


Figure 12: Chromatogram of Organic Pollutants in Wulmi River at sampling point S_2 in June 2017

Table 7: Concentration (µg/l) of Organic Pollutants at sampling point S_2 in Wulmi River in July 2017

Peak	Compound	Mw (g/mol)	Area	Area%	Conc. (µg/l)
1	Acetophenone	120	56611	7.70	7.70×10^7
2	Ethanone, 1-(4-methylphenyl)-	134	41587	5.65	5.65×10^7
3	Ethanone, 1-(4-methylphenyl)-	134	19066	2.59	2.59×10^7
4	o-Cymene	134	38566	5.24	5.24×10^7
5	1H-Indene, 1-hexadecyl-2,3-dihydro-	342	18307	2.49	24.9×10^7
6	1-Pentanone, 1-(4-methylphenyl)-	176	41057	5.58	5.58×10^7
7	Benzene, (2-methylcyclopropyl)-	132	17414	2.37	2.37×10^7
8	Indan, 1-methyl-	132	63000	8.56	8.56×10^7
9	1,3-Cyclopentadiene, 5-(trans-2-ethyl-3-me	146	43899	5.97	5.97×10^7
10	4-Amino-3-ethylbenzonitrile	146	64633	8.79	8.79×10^7
11	N-Isovaleroylglycine	159	5854	0.80	8.0×10^6
12	1,2,4-Triazine-3,5(2H,4H)-dione, 6-fluoro-	131	9386	1.28	1.28×10^7
13	Methane, isocyanato-	57	2091	0.28	2.8×10^6
14	Formamide, N-formyl-N-methyl-	87	5038	0.68	6.8×10^6
15	Isobutylene carbonate	116	188725	25.65	2.565×10^8
16	Phthalic acid, di(hept-4-yl) ester	362	28951	3.94	3.94×10^7
17	1,4-Epoxynaphthalene-1(2H)-methanol, 4,5,	344	91493	12.44	1.244×10^7
			735678	**100.0**	

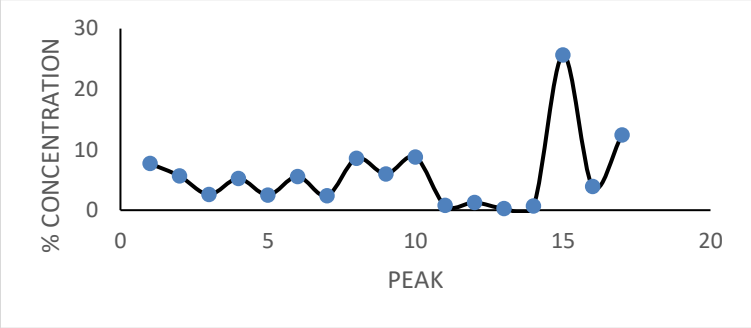


Figure 13: % Concentration (µg/l) of Organic Pollutants at sampling point S_1 in Wulmi River in July 2017

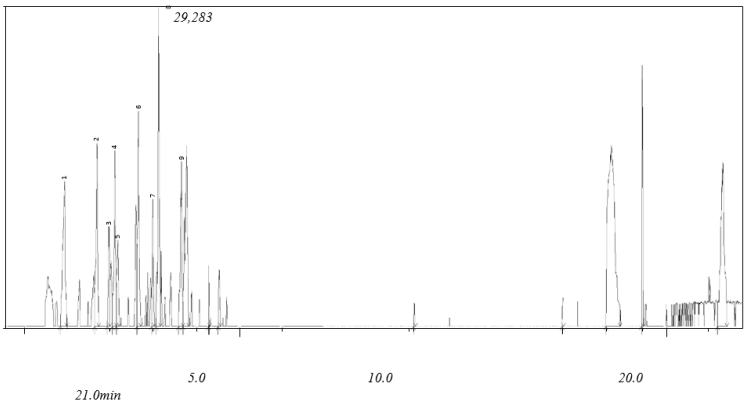


Figure 14: Chromatogram of Organic Pollutants in Wulmi River at sampling point S2 in July 2017

Table 8: Concentration (µg/l) of Organic Pollutants at sampling point S_2 in Wulmi River in August 2017

Peak	Compound	Mw (g/mol)	Area	Area%	Conc. (µg/l)
1	Acetophenone	120	40618	2.29	2.29×10^7
2	Ethanone, 1-(4-methylphenyl)-G	134	71297	4.01	4.01×10^7
3	o-Cymene	134	51724	2.91	2.91×10^7

4	1-Pentanone, 1-(4-methylphenyl)-	176	61627	3.47	3.47×10^7
5	2,4,6,9-Dehydroadamantane	132	49026	2.76	2.76×10^7
6	Indan, 1-methyl-	132	113197	6.37	6.37×10^7
7	4'-Methylpropiophenone	148	27192	1.53	15.3×10^7
8	1H-Indene, 2,3-dihydro-1,1-dimethyl-	146	94639	5.32	5.32×10^7
9	1H-Indene, 2,3-dihydro-1,1-dimethyl-	146	141350	7.95	7.95×10^7
10	Silane, trimethyl(1-methylpropoxy)-	146	19979	1.12	1.12×10^7
11	4-Amino-3-ethylbenzonitrile	146	22654	1.27	1.27×10^7
12	1,2,4-Triazine-3,5(2H,4H)-dione, 6-fluoro-	131	7663	0.43	4.3×10^6
13	Naphthalene, 1-methyl-	142	7053	0.40	4.0×10^6
14	Butane, 2,2-dimethyl-	86	9528	0.54	5.4×10^6
15	Butane, 2,2-dimethyl-	86	27743	1.56	1.56×10^7
16	Butane, 2,2-dimethyl-	86	7341	0.41	4.1×10^6
17	Furo[2,3-c]pyridine, 2,3-dihydro-2,7-dimeth	149	36118	2.03	2.03×10^7
18	Heptanoic acid, 2-methyl-, methyl ester	158	17705	1.00	1.00×10^7
19	Isobutylmethylketone benzyloxime	205	39999	2.25	2.25×10^7
20	1,1'-(4-Methyl-1,3-phenylene)bis[3-(5-benzyl-1	556	6151	0.35	3.5×10^6
21	5,10-Pentadecadien-1-ol, (Z,Z)-	224	33123	1.86	1.86×10^7
22	Pentanamide	101	40043	2.25	2.25×10^7
23	9-Octadecenamide, (Z)-	281	184044	10.36	1.036×10^8
24	Bis(2-ethylhexyl) phthalate	390	38494	2.17	2.17×10^7
25	1,4-Epoxynaphthalene-1(2H)-methanol, 4,5,	344	628968	35.39	3.539×10^9
			1777276	**100.0**	

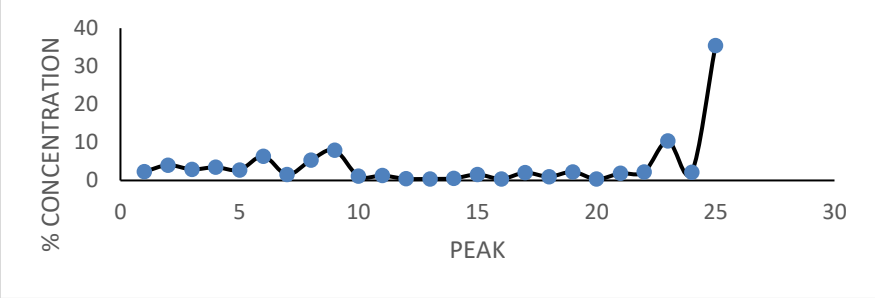


Figure 15: % Concentration (µg/l) of Organic Pollutants at sampling point S_1 in Wulmi River in August 2017

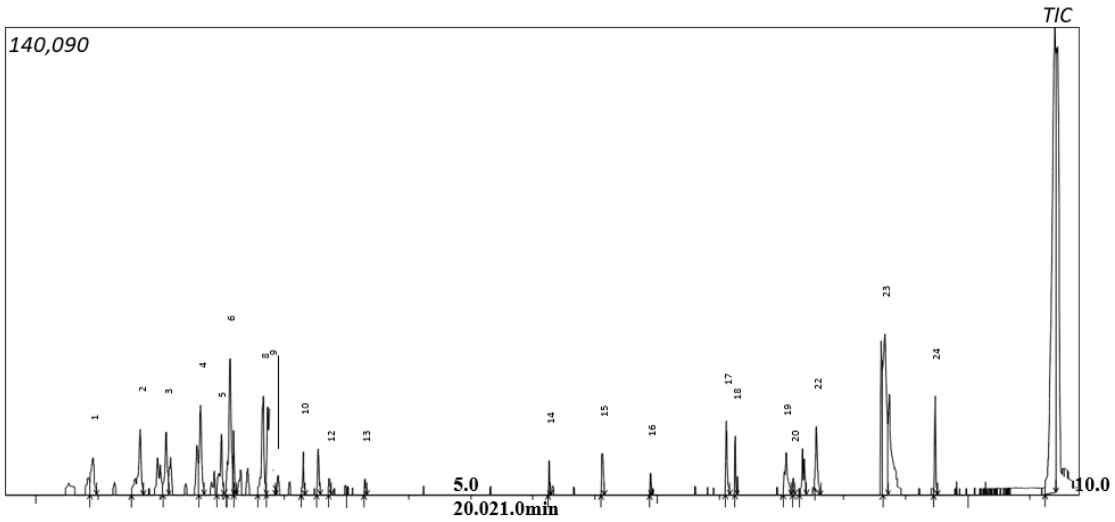


Figure 16: Chromatogram of Organic Pollutants in Wulmi River at sampling point S2 in August 2017

Discussion

From the GC-MS analyses of the samples obtained from water in Wulmi River, a wide variety of organic contaminants were identified. The relative quantities and presence of these organic contaminants are discussed under the following sub-headings.

Aliphatic Hydrocarbons As seen in table 1, concentration of hydrocarbons at sampling point S_1 ranged between $2.4x10^6$ µg/l for 2,2,4-trimethyl-3- (3,8,12,16-tetramethylheptadecane) to $1.524x10^8$ µg/l for dimethyl [bis(undecyloxy)] silane, sampling point S_2 ranged between $2.8x10^6$µg/l for isocyanatomethane to $1.051x10^8$ µg/l for 2-bromotetradecane. These concentrations are above the maximum permissible limit range of 1-100 µg/l set by International Commission for the Protection of the Danube River (ICPDR, 2009). Aliphatic hydrocarbons increase occurrence of cancer and respiratory disorder in humans, reduces photosynthesis ability of plants. Majority of these hydrocarbons came from combustion of fuel (petroleum), municipal sewage, or from herbicides and insecticides used on farm land around the river (Eggen *et al.*,2014).

Aromatic Acids Concentration of aromatic acids were only found at the sampling location S_1. At sampling point S_1 the concentration ranged between $2.53x10^7$ µg/l for bis(2-methylpropenyl)-1,2-benzenedicarboxylic acids to $2.374x10^8$ µg/l for Bis(2-methylpropenyl)-1,2,-benzenedicarboxylic acid. Sampling point S_2 has no aromatic acids. The concentration of aromatic acids at S_1 are above the approved standard of 6.9 µg/l for set by ICPDR (2009). Aromatic acids are carcinogenic especially cancer of the bladder. They May cause mild to moderate irritation of the skin. They may also cause narcosis with symptoms of hallucinations, excitement, euphoria, distorted perceptions and headache (Patel *et al.*,2019).

Esters Esters was detected at sampling points S_1 . At sampling point S_2 Esters was not detected . The concentrations of Esters at sampling point S_1 ranged between $2.30x10^7$ µg/l for cypermethrine to $6.06x10^7$ µg/l for cypermethrine,. These concentrations are higher than the permissible limit range of 0.024 µg/l-0.03 µg/l (ICPDR, 2009).

Esters are narcotics at high concentrations. Their vapors are irritants to the eye and mucous membrane (Haffner and Schecter,2014).

Aldehydric Compounds Aldehydric compounds was detected at sampling point S_1 . The concentrations of Aldehydric compounds at sampling point S_1 ranged between $3.2x10^6$ µg/l for 1,2,3,4a,9-1-phenanthrene carboxaldehyde to $1.046x10^8$ µg/l for (Z)-9-Octadecenal. At sampling point S_2, no Aldehydric compound was detected. These concentrations are higher than the permissible limit range of 0.096 µg/l – 0.10 µg/l (ICPDR, 2009). Aldehydric compounds have irritative effect. They cause Ocular and olfactory irritation, cancer and respiratory difficulties (Azzouz *et al*.,2021).

Alcohols There was absence of alcohols at sampling point S_2 . The concentration of alcohols at sampling point S_1 ranged between 6.6x10 ^{6}µg/l for triisobutylsilylether-2-propyn-1-ol to 1.903x10^8 µg/l for Trimethylsilyl ether nonadecan-1-ol. (ICPDR, 2009) gave the concentration limit of alcohols in water to be 0.0031 µg/l which is far less than the concentration of the compounds detected. The alcohols may be irritant to the eyes and mucous membrane. They may also cause liver damage (Azzouz *et al*.,2021).

Fatty Acids Fatty acids are resultant of bio-degradation of petroleum hydrocarbons, animals and vegetables fats (saturated) e.g. n-hexadecanoic acid and unsaturated such as cis-vaccenic acid and oleic acid.

Varieties of fatty acids was detected all through the months investigated. The concentration of fatty acids at sampling point S_1, ranged between 8.2x10^6 µg/l for 9,10,epoxy-18-trimethylsiloxyoctadecanoic acids to 1.677x10^8 µg/l for cis-vaccenic acid, S_2 ranged between 3.4x10^6 µg/l for 10, 13-dimethyl-methyltetradecanoic acid to 1.644x10^8 µg/l for methyl ester (E) -9-octadecenoic acid.. The maximum permissible limit range of fatty acids in water is set to be 1.48 µg/l - 1.50 µg/l (ICPDR, 2009). Fatty acids appear to be innocuous but increase plasma cholesterol (Samal *et al*.,2022).

Phthalates Most phthalates are frequently used in many industries as plasticizers of polymeric materials, insecticides and cosmetics etc. as a result of the daily use of these phthalates, they are mostly found in waters.The concentration of the phthalates at the sampling point S_1 is 1.08x10^7 µg/l for di-n-octyl phthalate. S_2 ranged between 2.17x10^{7}µg/l for bis (2-ethylhexyl)phthalate to 1.595x10^8 µg/l for bis (2-ethylhexyl) phthalate.. The maximum permissible limit is 4.5µg/l (ICPDR, 2009) which is less than the concentrations of the phthalates detected. Phthalates are characterized by reproductive toxicity in humans. They can cause infertility and reproductive problems in males. Some phthalates are endocrine disruptors (Raslan *et al*.,2018).

Phenols Phenols was detected at sampling point S_1.. The concentrations of phenol at sampling point S_1 ranged between 1.38 x10^{7}µg/l for 2,4-bis (1,1- dimethylethyl- phenol) to 1.157x10^8 µg/l for 4-bromo-2-chlorophenol, S_2 has a concentration of 5.8x10^6 µg/l for trimethyl [4-(1,1,3,3-tetramethylbutyl) phenoxy to 6.4x10^6 µg/l trimethyl [4-(1,1,3,3-tetramethylbutyl) phenoxy.. These concentrations are higher than the maximum limit of 1µg/l (ICPDR, 2009). Phenol is a bit carcinogenic and can cause kidney damage. It is a violent systematic poison. It causes anorexia, progressive weight loss, and diarrhea (Samal *et al*.,2022).

Sulphur and Nitrogen Containing Compounds The concentration of the sulphur and nitrogen containing compounds at S_1 ranged between 2.4x10^6 µg/l for methylxanthines to 3.779x10^8 µg/l for profenotos. The S2 has a concentration of 6.02 x 10^7 µg/l for 2-propyl tridecyl ester sulfurous acid There is no established standard limit from literature in which to compare these concentrations with. However, they are carcinogenic. Profenotos can cause respiratory failure (Samal *et al*.,2022).

Benzene and its Derivatives The relative abundance of alkyl-substituted benzene represents the degradation products of petroleum hydrocarbons coming from oil pollutants from combustion of fuels. Quite a range of these alkyl-substituted benzene compounds were found in several concentrations from the two sampling locations (S_1, S_2,). The concentrations of the benzene and its derivatives at sampling point S_1 ranged between 8.1x10^6 µg/l for o-xylene to 1.205x10^8 µg/l for 1, 2, 3-trmethylebenzene, S_2 ranged between 8.2x10^6 µg/l for 2-methylcyclopropyl-benzene to 2.37x10^7 µg/l for 2-methylcyclopropyl-benzene. Maximum permissible limit ranged of these compounds is 0.011 µg/l - 0.68 µg/l (ICPDR, 2009). Benzene and its derivatives are classified as carcinogens, which increases the risk of cancer and other sicknesses, and it is also a notorious cause of born marrow failure (Raslan *et al*.,2018).

Amides Various isomers of deceamide and decanamide was detected. The concentrations of the amides at sampling point S_1 ranged between 6.5x10^6 µg/l for octadecanamide to 3.38x10^7 µg/l for N,N-diethyl-5,alphacholest-2-en-3-amine.S_2 ranged between 6.8x10^6 µg/l for N-formyl-N-methyl-formamide to 3.862x10^8 µg/l for(Z) -9-octadecenamide.The maximum permissible limit range is set to be 0.21 µg/l – 0.74 µg/l (ICPDR, 2009). Amides are human carcinogens and tetragens. They also have neurologic effects (like tingling of fingers, excessive sweating of hands and feet, peeling of skin). Also cause liver and kidney damage in animals (Raslan *et al*.,2018).

Hydroxylated compounds 2-(2-heptadecynyloxy) tetrahydro-2H-pyran was the only hydroxylated compound detected at sampling S_1 at concentration of 1.55x10^{7}µg/l, none of the compounds was detected at sampling point S_2. The maximum concentration limit range of hydroxylated compounds in water is set at 0.37 µg/l (ICPDR, 2009).

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