**ISSN-1996-918X**

**Pak. J. Anal. Environ. Chem. Vol. 15, No. 1 (2014) 42 – 65**

# GC/MS Based Non-target Screening of Organic Contaminants in River Indus and its Tributaries in Sindh (Pakistan)

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Received 04 February 2014, Revised 11 June 2014, Accepted 20 June 2014

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**Abstract**

To investigate presence of organic contaminants in river Indus and its tributaries screening studies were carried out. Two years screening studies were based on four sampling campaigns in 13 sampling points out of which 9 sampling points belong to river Indus and its tributaries, 4 to municipal sewerage and 1 to industrial sewerage. Deconvolution Reporting Software (DRS) was used to analyze scan data. Deconvolution is capable of screening the compounds whose peaks become invisible due to co-extracted compounds. Furthermore it significantly reduces analysis time and chromatographic resolution requirements. Results reveal that all the sampling points were greatly polluted with phthalate esters and tributyl phosphate (TBP). Apart from these, numerous long chain hydrocarbons, toxic phenols i.e. bisphenol A, analgesic i.e. ibuprofen and mefenamic acid, pesticides i.e. endosulfan, PCPIs, etc have significantly contaminated water bodies. In this screening analysis many compounds are identified that can be possible emerging contaminants and that are rarely documented. The identified contaminants are debated in accordance with their use, possible emission source and pathway. To the best of our knowledge this study holds first detailed screening of organic contaminants in river Indus and its tributaries. The information gathered in this analysis can be useful for future studies based on individual contamination in river Indus.

***Keywords:*** Emerging organic contaminants; Endocrine disrupting compounds (EDC); Environmental monitoring; Non target screening analysis; Deconvolution reporting software; River indus contamination.

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## Introduction

The nature has been affected by numerous new synthetic compounds that have been introduced by human activities and that are causing health problems by altering physiological functions [1]. For European citizens and environmental authorities, one of the most important environmental concerns is water pollution [2]. However in developing countries like Pakistan where treatment of wastewater is not practiced at all and where Industrial and Municipal sewerage is directly spilled into the fresh water resources, no concerns are shown to assessment of water contamination and its sources. Water pollution is one of the most imperative environmental concerns that should be given utmost importance in Pakistan.

Presence of enormous number of organic contaminants in the environment poses potentially dangerous consequences and there is great need for the urgent establishment of information that reveals the presence, amount, possible

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bioaccumulation path way, and conduct of these toxins in the atmosphere. Due to this reason many researchers have published screening reports for environmental waters. Antoni et al. [3] assessed presence of pharmaceuticals in Llobregat River (NE Spain) while Rikke et al. [4] and Kuster et al. [5] studied presence of alkyl phenolic contaminants, phytoestrogens, progestogens and estrogens in basin of European river and Rio de Janeiro (Brazil), respectively. However, these studies and most of other monitoring programs are limited to the targeted screening of preselected groups of dominantly priority pollutants because of need to eliminate intrusion from co-eluting peaks. To assure sensitivity, tandem mass spectrometry (MS/MS) or selective ion monitoring (SIM) mode are commonly used for analysis of trace organic contaminants. Yet, those methods are limited to pre-selected compounds and are unable to locate any other compound that is not in the target list. Monitoring programs are also restricted due to great diversity of organic contaminants that are not only PCPIs, pesticides, pharmaceuticals, industrial chemicals but also huge amount of emerging unknown contaminants. This new class of contaminants is mostly not considered in monitoring network programs due to scarce knowledge about its occurrence in environment. This inadequacy of screening programs can be resolved by non-target screening methodology that gives a chance to enlarge the information about unknown organic pollutants and unveils a profound knowledge about status of contamination [6,7]. The non-target screening can be accomplished by using full-scan mode that is advantageous over SIM or MS/MS mode because of its ability to identify non-target compounds that could be injurious and whose presence was not expected in the environment. Thus the water pollution research is now focusing on “emerging contaminants” or “new environmental contaminants” along with “priority” pollutants. Personal care product ingredients (PCPIs) are gaining much interest [8-11] because some of them were expected to be endocrine disrupting [8-12] moreover most of the PCPIs accumulate in the environment due to their lipophilic behavior [13,14]. The emerging contaminants include wide group of chemicals that are utilized in everyday life. They are synthetic fragrances, U.V-filters, antiseptics, antioxidants, insect repellents, etc. The aquatic environment is mainly contaminated from emerging compounds, which are utilized in modern society and are introduced to the water bodies by municipal or industrial discharge [11-15]. There are few reports in the literature that used full-scan mode to screen for non-target compounds in wastewater and surface waters [8,16].

A detailed non-target screening based on GC/MS has been performed on the aqueous samples obtained from river Indus, Sindh Province, Pakistan. The River Indus is a major and limited source of water in Sindh. However, the canals emerging from it, at Kotri Barrage run through residential, agricultural as well as industrial areas and are major sink for the contamination coming from these areas. Thus the variety of pollution sources introduce wide range of organic chemicals including hydrocarbons, pesticides, surfactants, plasticizers, PCPIs, etc., in the river water. We also analyzed samples from municipal and industrial sewerage drains that are directly falling into fresh water canals. The purpose of analyzing wastewater samples was to locate possible sources that are responsible for the contamination of fresh water bodies.

Another challenge in full-scan based systematic toxicological analysis using GC/MS is to locate compounds from background noise. The information obtained from full-scan MS is usually huge and requires automated assessment of recorded data files. AMDIS (Automated Mass Spectral Deconvolution and Identification System) is deconvolution software that not only identifies the hidden compounds but also speeds up the evaluation of GC/MS based full-scan analysis. AMDIS is reliable tool for evaluation of routine and toxicology analysis [17]. Thus, Deconvolution Reporting Software (DRS) is used to analyze scan data for this study as well.

## Materials and Methods

### *Chemicals and materials*

All the reagents used in this study were of analytical grade. Standards of analytes used for calibration and quantification studies, acetonitrile and dichloromethane were purchased from Fisher Scientific, UK., Milli-Q water was obtained from ELGA Milli-Q water System (Model: Classic

UVF), UK. Oasis® HLB cartridges 60 mg/3 mL were purchased from SUPELCO Bellefonte, USA. 0.45-µm cellulose acetate membrane filter (Micropore) was purchased from Sigma-Aldrich.

### *Sampling*

A sampling campaign at thirteen sampling points (Fig. 1) was carried out from January 2010 to June 2011 at K.B.Feeder, Pinyari and Phuleli canals, emerging from river Indus. Also samples were collected from the main municipal/industrial sewerage drains falling into these canals. Samplings were carried out in the months of January and June each year; hence total four samplings were executed in two years. Water samples underwent analysis for priority and emerging organic contaminants.

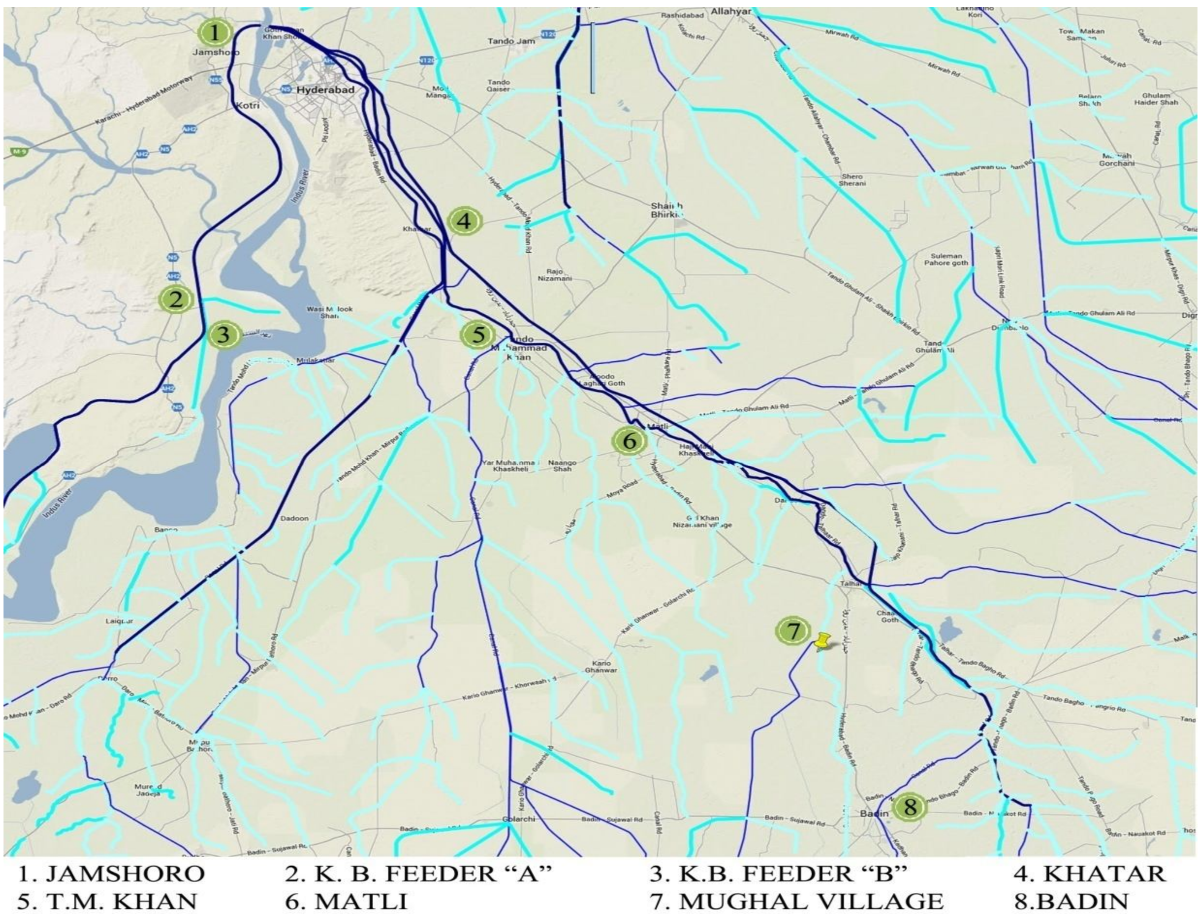


***Figure 1.*** **River Indus and its tributaries: map indicating sampling points**

### *Details of sampling sites*

River Indus originates in Tibet Autonomous Region and merges into the Arabian Sea near port city of Karachi in Sindh, flowing through whole country. It is Pakistan's longest river with total length of 2,900 kilometers and world's twenty first largest river with estimated annual flow of around 207 cubic kilometers. River Indus is a major supplier of water to Punjab and Sindh, which are the main agricultural provinces of Pakistan. The Kotri Barrage gives additional supplies for Karachi, Hyderabad, T. M. Khan, Badin, Matli etc, [18]. At Kotri Barrage the Indus is divided into three tributaries i.e. K.B.Feeder, Pinyari and Phuleli canals and all three canals receive the heavy input of industrial and urban wastewaters also surface runoff from agricultural areas while passing through the cities and agricultural lands. Detailed sampling sites and their description is given in Table 1.

*Table 1.* **Description of samples collected from the K.B. Feeder, Pinyari & Phuleli canals, and municipal/industrial sewerage drains from January 2010 to June 2011.**

| Sample Name | Sample Description | Sample Location |
|---|---|---|
| Jamshoro | River water | Combined channel at Jamshoro. |
| K.B feeder "A" | Canal water | K.B. feeder canal, before the entrance of Kotri industrial effluent. |
| Kotri drain | Industrial effluent | Main drain emerging from Kotri industrial area and falling into K.B.feeder canal. |
| K.B feeder "B" | Canal water | K.B.feeder canal, after the entrance of Kotri industrial effluent. |
| Deplai town drain | Municipal wastewater | Sewerage drain falling into Pinyari canal at Memon colony, back of Deplai town. |
| Hoor camp drain | Municipal wastewater | Hoor camp sewerage drain falling into Pinyari canal at Hoor camp |
| Kali mori drain | Municipal wastewater | Kali mori sewerage drain falling into Pinyari canal at Kali mori. |
| Main autobhan drain | Municipal & industrial wastewater | Main autobhan sewerage drain falling into Pinyari canal near Fateh industries |
| Khattar | Canal water | Pinyari canal at Khattar. |
| Tando.M.Khan | Canal water | Phuleli canal at Tando.M.Khan. |
| Matli | Canal water | Phuleli canal at Matli. |
| Mughal village | Canal water | Phuleli canal at Mughal village. |
| Badin | Canal water | Phuleli canal at Badin. |

### *Collection of samples*

Raw water from the K.B. Feeder, Pinyari, Phuleli canals and from municipal and industrial discharge points was collected in Pyrex borosilicate amber glass containers. The glass ware was baked at 320 °C for 8 h and rinsed with millipore water before use. Samples were stored at 4°C in the laboratory and extracted within 48 h.

### *Sample pre-treatment of water samples*

Samples were filtered through a 0.45-μm cellulose acetate membrane filter (micropore) and pre-concentrated on solid phase extraction cartridges using equipment: automated SPE system SUPELCO VISIPREP within 48 h of sampling in order to avoid any degradation of organic contaminants and loss of sample integrity.

The SPE procedure has been described in detail elsewhere [19]. Briefly, 3-mL cartridge columns packed with 60 mg of hydrophilic-lipophilic water-wettable reversed-phase sorbent (HLB cartridge) were activated and conditioned using $CH_2Cl_2$, acetonitrile and millipore water, respectively (6 mL each). 200 mL of each sample was maintained at pH 7 and 200 mL at pH 2. Both aliquots of each sample were extracted separately. Samples were loaded onto cartridge at flow rate of 6 mL/min and cartridges were rinsed with 1 mL of Millipore water soon after loading. Cartridges were dried under gentle stream of nitrogen. Elution was accomplished first with 1:1 mixture of dichloromethane and acetonitrile (2.5 mL) and then dichloromethane (3.2 mL), respectively. The eluent was concentrated through evaporation under gentle stream of nitrogen till the volume of 1 mL.

### *Instrumentation*

GC/MS analysis were performed with gas chromatograph Agilent 6900 connected to a mass spectrometer Agilent 5975 (Agilent technologies, US). A HP-5MS (30 m x 0.25mm i.d. with 0.25 $\mu$m film thickness) containing 5% phenyl methyl siloxane (model Agilent 19091S-433) was programmed from 100 (keeping this temperature for 01 min) to 300 °C at 10 °C/min (keeping this temperature for 10 min). The total analysis time was 31 min. Helium was used as the carrier gas at 10.52 psi. The splitless mode with injection volume of 1 $\mu$L was used.

## Results and Discussion

GC/MS based non-target screening analysis of the 52 samples was performed. The sampling was done from January 2010 to June 2011. The analysis revealed numerous compounds some of which are renowned contaminants and some are rarely documented or unknown. The main groups of identified compounds are; (1) carboxylic acids and esters (2) hydrocarbons and derivatives (3) imines, amines and amides derivatives (4) alcohol derivatives (5) phenol derivatives (6) heterocyclic aromatic compounds (7) benzene derivatives (8) ketone derivatives (9) cyclodienes (10) azole derivatives (11) aldehyde derivatives and (12) diphenyl ether derivatives. The selected contaminants that might be injurious to the environment are discussed with respect to their concentration, spatial distribution, source indication, applications, hazardous effects and pathways, if the information is available. Also, we made an attempt to quantify the compounds whose standards were available easily in our laboratory. The percent recovery of quantified compounds was calculated in ultrapure milli Q water as well as in synthetic wastewater prepared in laboratory. Synthetic wastewater sample was prepared by the method as reported earlier [20]. The milli Q water and synthetic wastewater were first spiked with 50 ng/L of each analyte to be quantified and then solid phase extraction was performed as explained above. Each analysis was performed in triplicates. Table 2 reveals that the percent recovery of compounds in synthetic wastewater is relatively low as compared to milli Q water. This may be due to the diverse composition of wastewaters, which is also considered to be the main cause of low percent recovery of real wastewater samples. Thus estimation of percent recoveries of quantified compounds in ultra pure water as well as in synthetic wastewater was very important to approximate real amount of analytes.

***Table 2.*** **% Recovery of quantified compounds obtained by spiking synthetic wastewater and milli Q water with 50 ng/L**

| Name | % Recovery in synthetic wastewater n=3 | RSD % | % Recovery milli Q water n=3 | RSD % | Name | % Recovery in synthetic wastewater n=3 | RSD % | % Recovery milli Q water n=3 | RSD % |
|---|---|---|---|---|---|---|---|---|---|
| **Carboxylic acids & esters** | | | | | **Hydrocarbons and derivatives** | | | | |
| Decanoic acid, methyl ester | 25 | 4.5 | 56 | 2.57 | Undecane | 39 | 4.7 | 57 | 2.6 |
| Dimethyl phthalate | 33 | 5.2 | 63 | 2.9 | Dodecane | 40 | 4.9 | 56 | 2.8 |
| Diethyl phthalate | 28 | 4.25 | 57 | 2.4 | Tridecane | 35 | 5.8 | 52 | 3.3 |
| Hexadecanoic acid, methyl ester | 20 | 5.3 | 50 | 3 | Tetradecane | 38 | 6.5 | 55 | 3.6 |
| Dibutyl phthalate | 60 | 4.7 | 80 | 2.7 | Pentadecane | 42 | 7.3 | 60 | 4.2 |
| Diisobutyl phthalate | 55 | 6 | 78 | 3.4 | Hexadecane | 45 | 7.6 | 62 | 4 |
| 9-Octadecenoic acid (Z)-, methyl ester | 23 | 5.7 | 55 | 3.3 | Heptadecane | 39 | 6.2 | 58 | 3.5 |
| Octadecanoic acid, methyl ester | 22 | 4.8 | 53 | 2.5 | Octadecane | 40 | 5.6 | 63 | 3.2 |
| Bis(2-ethylhexyl) phthalate | 70 | 5.6 | 87 | 2.9 | 1-Nonadecene | 25 | 6.7 | 45 | 3.8 |
| 1,2-Benzene-dicarboxylic acid | 25 | 6.5 | 56 | 3.5 | Pentadecane, 2,6,10,14-tetramethyl- | 48 | 7.3 | 70 | 4.2 |
| Benzoic acid, p-tert-butyl- | 35 | 5.2 | 60 | 2.25 | Nonadecane | 40 | 5.4 | 60 | 3.1 |
| Oleic Acid | 15 | 6.3 | 25 | 3.6 | Eicosane | 36 | 6.3 | 58 | 3.6 |
| | | | | | Heneicosane | 34 | 5.25 | 53 | 2.4 |
| **Phenols** | | | | | 1-Docosene | 30 | 7.3 | 49 | 3.6 |
| Phenol, p-tert-butyl- | 10 | 4.3 | 25 | 2.5 | **Alcohols** | | | | |
| Phenol, m-tert-butyl- | 11 | 3.9 | 25 | 2.2 | 1-Undecanol | 15 | 4.6 | 30 | 2.6 |
| **Diphenyl ether derivatives** | | | | | 1-Dodecanol | 18 | 5.2 | 35 | 3.1 |
| Diphenyl ether | 35 | 4.7 | 65 | 2.3 | 1-Hexadecanol | 16 | 5.5 | 32 | 3.2 |
| **Cyclodiene** | | | | | **Amines** | | | | |
| Endosulfan | 60 | 2.75 | 95 | 1.6 | Trimethylamine | 28 | 5.6 | 53 | 3.2 |

GC/MS based systematic toxicological analysis requires a high level of expertise and experience for the evaluation of full-scan GC/MS data. The detection of analyte peaks in the total ion chromatogram (TIC) is a foremost challenge because they are often overlapped by intense matrix peaks. Deconvolution algorithms being able to extract pure compound peaks free of overlapping signals from complex TICs are the solution to this problem. Thus AMDIS (Automated mass spectral Deconvolution and identification system) is the freeware program that is based on this principle. It first deconvolutes pure spectra and related information from complex chromatogram and matches the obtained spectra with those of a reference library [21]. Fig. 2 shows AMDIS screen displaying identification of compounds in samples. The ions used for identification and quantification of detected compounds are listed in Table 3. Identified compounds are discussed below under different classes of compounds.


***Figure 2.*** **AMDIS screen showing identification of (a) diethyl toluamide (b) ibuprofen where first window shows full scan spectra of sample, second window shows identifying m/z ions with their relative abundance, third window reveals denconvoluted spectrum (white) juxtaposed with extracted spectrum and fourth window shows denconvoluted spectrum (white) juxtaposed with library spectrum of identified compounds**

*Table 3.* **m/z Ions selected for identification and quantification of screened compounds**

| Carboxylic acids & Esters | Identification Ions | Quantification Ion | Base Ion | Molecular Weight |
|---|---|---|---|---|
| Acetic acid ethenyl ester | 43, 86, 42, 44 | – | 43 | 86 |
| Vinyl butyrate | 43, 71, 41, 114 | – | 43 | 114 |
| 2-Propenoic acid, 2-methyl-, 1,2-ethanediyl ester | 69, 41, 113, 112 | – | 69 | 198 |
| Phthalic acid, 2-pentyl 2-propyl ester | 149, 209, 150, 167 | – | 149 | 209 |
| Benzoic acid, 2-ethylhexyl ester | 105, 70, 112, 77 | – | 105 | 234 |
| Isopropyl Myristate | 43, 102, 60, 57 | – | 43 | 270 |
| 1,2-Benzenedicarboxylic acid, butyl 2-methylpropyl ester | 149, 150, 223, 41 | – | 149 | 278 |
| 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester | 149, 167, 57, 71 | – | 149 | 278 |
| Sulfurous acid, 2-ethylhexyl hexyl ester | 57, 71, 43, 85 | – | 57 | 278 |
| Propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester | 71, 43, 56, 72 | – | 71 | 286 |
| 2-Ethylhexyl trans-4-methoxycinnamate | 178, 161, 179,134 | – | 178 | 290 |
| 2-Propenoic acid, 3-(4-methoxyphenyl)-, 2-ethylhexyl ester | 178, 161, 133, 134 | – | 178 | 290 |
| 9,12-Octadecadienoic acid (Z,Z)-, methyl ester | 41, 67, 55, 81 | – | 41 | 294 |
| p-Anisic acid, 3,4-dichlorophenyl ester | 135, 136, 77, 107 | – | 135 | 296 |
| 1,2-Benzenedicarboxylic acid, butyl cyclohexyl ester | 149, 150, 223, 205 | – | 149 | 304 |
| Pentanoic acid, 5-hydroxy-, 2,4-di-t-butylphenyl esters | 191, 206, 57, 192 | – | 191 | 306 |
| Phthalic acid, 4-fluoro-2-nitrophenyl methyl ester | 163, 164, 77, 140 | – | 163 | 319 |
| 1,2-Benzenedicarboxylic acid, dicyclohexyl ester | 149, 167, 55, 150 | – | 149 | 330 |
| Bis(2-ethylhexyl) maleate | 57, 117, 71, 41 | – | 57 | 340 |
| 2-Butenedioic acid (E)-, bis(2-ethylhexyl) ester | 112, 70, 57, 71 | – | 112 | 340 |
| Phthalic acid, di(3-methylphenyl) ester | 239, 240, 91, 65 | – | 239 | 346 |
| Phthalic acid, 6-ethyl-3-octyl butyl ester | 149, 150, 223, 205 | – | 149 | 362 |
| Phthalic acid, butyl 2-pentyl ester | 149, 58,45, 55 | – | 149 | 364 |
| Tetracosanoic acid, methyl ester | 74, 87, 382, 57 | – | 74 | 382 |
| Decanoic acid, methyl ester | 74, 87, 143, 155 | 74 | 74 | 186 |
| Dimethyl phthalate | 163, 77, 164, 76 | 163 | 163 | 194 |
| Diethyl phthalate | 149, 177, 150, 65 | 149 | 149 | 222 |
| Hexadecanoic acid, methyl ester | 74, 87, 43, 55 | 74 | 74 | 270 |
| Dibutyl phthalate | 149, 150, 41, 57 | 149 | 149 | 278 |
| Diisobutyl phthalate | 149, 57, 41, 223 | 149 | 149 | 278 |
| 9-Octadecenoic acid (Z)-, methyl ester | 55, 69, 74, 83 | 55 | 55 | 296 |
| Octadecanoic acid, methyl ester | 74, 87, 43, 55 | 74 | 74 | 298 |

| | | | | |
|---|---|---|---|---|
| Bis(2-ethylhexyl) phthalate | 149, 167, 57, 279 | 149 | 149 | 390 |
| Benzenepropanoic acid | 91, 104, 150, 105 | – | 91 | 150 |
| Benzoic acid, 4-(1-methylethyl)- | 149, 164, 105, 119 | – | 149 | 164 |
| Dodecanoic acid | 73, 60, 43, 57 | – | 73 | 200 |
| Ibuprofen | 163, 161, 91, 206 | – | 163 | 206 |
| Propanoic acid, 2-methyl-3-[4-t-butyl]phenyl- | 205, 220, 131, 147 | – | 205 | 220 |
| Tetradecanoic acid | 73, 60, 57, 55 | – | 73 | 228 |
| Mefenamic Acid | 223, 241, 208, 222 | – | 223 | 241 |
| n-Hexadecanoic acid | 43, 73, 60, 57 | – | 43 | 256 |
| 3,5-di-tert-Butyl-4-hydroxyphenylpropionic acid | 263, 278, 264, 57 | – | 263 | 278 |
| 1,2-Benzenedicarboxylic acid | 104, 76, 50, 148 | 104 | 104 | 166 |
| Benzoic acid, p-tert-butyl- | 163, 135, 91, 178 | 163 | 163 | 178 |
| Oleic Acid | 55, 69, 83, 97 | 55 | 55 | 282 |
| **Hydrocarbons and derivatives** | | | | |
| Undecane, 3,7-dimethyl- | 43, 57, 71, 85 | – | 43 | 184 |
| Tributyl phosphate | 99, 155, 41, 57 | – | 99 | 266 |
| Octacosane | 57, 43, 71, 85 | – | 57 | 294 |
| Tricosane | 57, 43, 71, 85 | – | 57 | 324 |
| Tetracosane | 57, 71, 85, 99 | – | 57 | 338 |
| Heptacosane | 57, 43, 71, 85 | – | 57 | 380 |
| 1-Tridecene | 43, 55, 41, 57 | – | 43 | 182 |
| 1,13-Tetradecadiene | 55, 41, 82, 81 | – | 55 | 194 |
| 3-Octadecene, (E)- | 69,57, 55, 83 | – | 69 | 252 |
| 3-Eicosene, (E)- | 57, 69, 55, 83 | – | 57 | 280 |
| 5-Eicosene, (E)- | 55, 57, 69, 83 | – | 55 | 280 |
| Squalene | 69, 81, 41, 136 | – | 69 | 410 |
| 1,3-Butadiyne | 50, 49, 48, 51 | – | 50 | 50 |
| Camphene | 93, 79, 91, 77 | – | 93 | 136 |
| Undecane | 57, 43, 71, 41 | 57 | 57 | 156 |
| Dodecane | 57, 43, 71, 85 | 57 | 57 | 170 |
| Tridecane | 57, 43, 71, 85 | 57 | 57 | 184 |
| Tetradecane | 57, 43, 71, 85 | 57 | 57 | 198 |
| Pentadecane | 57, 43, 71, 85 | 57 | 57 | 212 |
| Hexadecane | 57, 43, 71, 85 | 57 | 57 | 226 |

| | | | | |
|---|---|---|---|---|
| Heptadecane | 57, 43, 71, 85 | 57 | 57 | 240 |
| Octadecane | 57, 43, 71, 41 | 57 | 57 | 254 |
| 1-Nonadecene | 57, 83, 97, 55 | 57 | 57 | 266 |
| Pentadecane, 2,6,10,14-tetramethyl- | 57, 71, 43, 85 | 57 | 57 | 268 |
| Nonadecane | 57, 43, 71, 85 | 57 | 57 | 268 |
| Eicosane | 57, 43, 71, 85 | 57 | 27 | 282 |
| Heneicosane | 57, 71, 43, 85 | 57 | 57 | 296 |
| 1-Docosene | 57, 43, 97, 55 | 57 | 57 | 308 |
| **Imines, Amines, Amides** | | | | |
| Aziridine, 2-methyl- | 28, 56, 57, 30 | – | 28 | 57 |
| Acetamide | 59, 44, 43, 42 | – | 59 | 59 |
| 2-Propenamide | 44, 71, 55, 43 | – | 44 | 71 |
| N-Nitrosodimethylamine | 74, 42, 43, 75 | – | 74 | 74 |
| Formamide, N-formyl-N-methyl- | 30, 59, 42, 58 | – | 30 | 87 |
| 1,3,5-Triazine-2,4,6-triamine | 126, 43, 85, 42 | – | 126 | 126 |
| Diphenylamine | 169,168, 167, 51 | – | 169 | 169 |
| Benzamide, N,N-diethyl-4-methyl- | 119, 91, 190, 191 | – | 119 | 191 |
| Diethyltoluamide | 119, 91, 190, 65 | – | 119 | 191 |
| Trimethylamine | 58, 59, 30, 42 | 58 | 58 | 59 |
| **Alcohol derivatives** | | | | |
| 2-Propyn-1-ol | 55, 39, 53, 56 | – | 55 | 56 |
| Isopropyl Alcohol | 45, 43, 41, 59 | – | 45 | 60 |
| 2-Propanol, 2-methyl- | 59, 41, 43, 57 | – | 59 | 74 |
| Ethanol, 2-ethoxy- | 31, 59, 29, 72 | – | 31 | 90 |
| 1-Hexanol, 2-ethyl- | 57, 41, 43, 55 | – | 57 | 130 |
| 1-Propanol, 2-(2-hydroxypropoxy)- | 59, 31, 103, 45 | – | 59 | 134 |
| 3,7,11,15-Tetramethyl-2-hexadecen-1-ol | 81, 82, 95, 123 | – | 81 | 296 |
| 1-Undecanol | 55, 69, 41, 70 | 55 | 55 | 172 |
| 1-Dodecanol | 55, 43, 69, 56 | 55 | 55 | 186 |
| 1-Hexadecanol | 55, 69, 83, 97 | 55 | 55 | 242 |
| **Phenol Derivatives** | | | | |
| Resorcinol | 110, 82, 81, 55 | – | 110 | 110 |
| Eugenol | 164, 103,77, 149 | – | 164 | 164 |
| Phenol, 2-(1-phenylethyl)- | 183, 198, 165, 184 | – | 183 | 198 |
| Phenol, 2,4-bis(1,1-dimethylethyl)- | 191, 57, 41, 206 | – | 191 | 206 |
| Phenol, 3-methyl-5-(1-methylethyl)-, methylcarbamate | 135, 150, 91, 136 | – | 135 | 207 |

| | | | | |
|---|---|---|---|---|
| Butylated Hydroxytoluene | 205, 57, 220, 206 | – | 205 | 220 |
| à-Bisabolol | 93, 109, 204, 121 | – | 93 | 222 |
| Bisphenol A | 213, 228, 119, 214 | – | 213 | 228 |
| Cholesterol | 43, 55,81, 107 | – | 43 | 386 |
| Cholestan-3-ol, (3á,5á)- | 215, 233, 81, 107 | – | 215 | 388 |
| Phenol, p-tert-butyl- | 135, 107, 150, 95 | 135 | 135 | 150 |
| Phenol, m-tert-butyl- | 135, 107, 150, 95 | 135 | 135 | 150 |
| o-Hydroxybiphenyl | 170, 169, 141, 115 | – | 170 | 170 |
| **Heterocyclic aromatic compounds** | | | | |
| 1,3-Dioxolane | 73, 44, 45, 43 | – | 73 | 74 |
| Pyrrolidine, 1-nitroso- | 100, 41, 42, 43 | – | 100 | 100 |
| Quinoline | 129, 102, 128, 130 | – | 129 | 129 |
| 9H-Fluorene, 4-methyl- | 165, 180, 89, 179 | – | 165 | 180 |
| Dibenzothiophene | 184, 185, 139, 152 | – | 184 | 184 |
| Indole | 117, 90, 89, 63 | – | 117 | 117 |
| 1H-Indole, 3-methyl- | 130, 131, 77, 103 | – | 130 | 131 |
| Indoleacetic acid | 130, 175, 131, 103 | – | 130 | 175 |
| 2H-Indol-2-one, 1-(2,6-dichlorophenyl)-1,3-dihydro- | 214, 277, 242, 179 | – | 214 | 277 |
| Pyridine, 3-methyl-2,6-diphenyl- | 244, 245, 246, 115 | – | 244 | 245 |
| **Benzene derivatives** | | | | |
| Styrene | 104, 103, 78, 77 | – | 104 | 104 |
| Benzene, 1,2-diethyl- | 105, 119, 134, 91 | – | 105 | 134 |
| Benzene, 1-methyl-2-(1-methylethyl)- | 119, 91, 134, 117 | – | 119 | 134 |
| Benzene, 1,3-dimethyl-5-(1-methylethyl)- | 133, 148, 105, 91 | – | 133 | 148 |
| Benzene, (1-methyldodecyl)- | 105, 106, 91, 260 | – | 105 | 260 |
| Naphthalene, 2-methyl- | 142, 141, 115, 143 | – | 142 | 142 |
| Naphthalene, 1,2-dimethyl- | 156, 141, 155, 157 | – | 156 | 156 |
| 1-Naphthalenamine, N-phenyl- | 219, 218, 217, 220 | – | 219 | 219 |
| Indane | 117, 118, 115, 91 | – | 117 | 118 |
| 1H-Indene, 2,3-dihydro-5-methyl- | 117, 132, 131, 115 | – | 117 | 132 |
| **Ketone derivatives** | | | | |
| Methyl vinyl ketone | 55, 43, 27, 70 | – | 55 | 70 |
| Propiolactone | 42, 28, 43, 29 | – | 42 | 72 |
| Acetophenone, 2-chloro- | 139, 111, 141, 154 | – | 139 | 154 |
| Ethanone, 1-(4-hydroxy-3-methoxyphenyl)- | 151, 166, 123, 52 | – | 151 | 166 |
| 2(3H)-Furanone, 5-hexyldihydro- | 85, 29, 128, 43 | – | 85 | 170 |
| Benzophenone | 105, 77, 182, 51 | – | 105 | 182 |

| | | | | |
|---|---|---|---|---|
| 7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione | 57, 205, 55, 175 | – | 57 | 276 |
| **Cyclodienes** | | | | |
| Endosulfan | 241, 239, 195, 237 | 241 | 241 | 404 |
| **Azole derivatives** | | | | |
| 1-Methyl-1H-1,2,4-triazole | 83, 28, 56, 40 | – | 83 | 83 |
| 3-Amino-s-triazole | 84,28,57, 85 | – | 84 | 84 |
| 1H-Tetrazol-5-amine | 28, 57, 85, 42 | – | 28 | 85 |
| 3H-1,2,4-Triazol-3-one, 1,2-dihydro- | 85, 42, 57, 86 | – | 85 | 85 |
| Carbazole | 167, 166, 139, 140 | – | 167 | 167 |
| **Aldehyde derivatives** | | | | |
| Vanillin | 152, 151, 81, 109 | – | 152 | 152 |
| 3,5-di-tert-Butyl-4-hydroxybenzaldehyde | 219, 191, 234, 57 | – | 219 | 234 |
| **Diphenyl ether derivatives** | | | | |
| Diphenyl ether | 170, 51, 77, 141 | 170 | 170 | 170 |

*Table 4a.* **Phthalate esters identified and quantified in river Indus, Indus tributaries and wastewater samples (concentration is presented in ng/L).**

| Sampling Station | Dimethyl phthalate | | | | Diethyl phthalate | | | | Dibutyl phthalate | | | | Diisobutyl phthalate | | | | Bis(2-ethylhexyl) phthalate | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Year* | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | |
| *Month* | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun |
| Jamshoro | 2.4 | 2.2 | 2.5 | 1.9 | 4.2 | 5.1 | 4.7 | 8.8 | 223.9 | 229.8 | 263.0 | 1227.3 | 8.3 | 31.9 | 61.1 | 27.7 | 154.7 | 49.0 | 79.9 | 251.5 |
| K.B feeder "A" | 5.8 | 2.5 | 15.2 | 6.0 | 3.8 | 5.7 | 6.7 | 4.2 | 383.7 | 313.0 | 279.7 | 330.9 | 17.9 | 49.1 | 68.6 | 65.7 | 362.9 | 235.6 | 272.3 | 253.9 |
| Kotri drain | 11.3 | 18.9 | 372.6 | 23.2 | 42.3 | 68.6 | 142.9 | 196.3 | 622.1 | 673.0 | 50.4 | 1685.0 | 46.0 | 65.0 | 400.0 | 359.3 | 521.8 | 576.4 | 625.7 | 823.2 |
| K.B feeder "B" | 5.9 | 8.2 | 19.1 | 5.6 | 4.0 | 7.0 | 4.9 | 7.6 | 401.1 | 196.6 | 191.8 | 248.1 | 20.8 | 42.5 | 44.8 | 67.1 | 469.4 | 52.5 | 758.5 | 232.0 |
| Deplai town drain | 18.8 | 11.1 | 74.2 | 7.5 | 13.9 | 66.7 | 60.8 | 55.5 | 298.1 | 386.3 | 361.2 | 1215.9 | 13.8 | 57.5 | 75.7 | 583.7 | 44.8 | 488.8 | 1097.1 | 834.6 |
| Hoor camp drain | 18.9 | 16.4 | 54.9 | 99.7 | 14.0 | 26.7 | 32.7 | 39.7 | 253.9 | 290.1 | 222.8 | 1177.0 | 6.9 | 62.9 | 42.1 | 379.7 | 32.5 | 49.6 | 482.0 | 1965.4 |
| Kali mori drain | 17.3 | 15.5 | 36.5 | 82.4 | 30.5 | 31.0 | 53.2 | 21.8 | 496.4 | 401.4 | 446.8 | 367.0 | 59.5 | 229.1 | 43.4 | 135.7 | 111.4 | 536.7 | 341.3 | 980.3 |
| Main autobhan drain | 11.1 | 10.3 | 30.4 | 64.2 | 29.1 | 97.5 | 28.3 | 386.3 | 876.5 | 324.9 | 312.9 | 1219.4 | 27.3 | 72.4 | 15.8 | 276.1 | 40.1 | 94.2 | 225.1 | 245.7 |
| Khattar | 8.1 | 3.6 | 11.1 | 13.1 | 5.4 | 14.6 | 5.5 | 10.2 | 335.8 | 167.5 | 284.6 | 1490.5 | 55.6 | 36.9 | 48.8 | 326.0 | 345.0 | 58.9 | 144.0 | 292.4 |
| Tando.M.Khan | 4.4 | 3.1 | 2.5 | 15.3 | 4.0 | 8.9 | 8.7 | 5.4 | 573.3 | 181.0 | 207.7 | 1646.6 | 17.8 | 53.4 | 48.8 | 313.0 | 466.1 | 17.8 | 598.8 | 252.3 |
| Matli | 1.6 | 5.4 | 2.4 | 11.4 | 6.3 | 7.1 | 5.9 | 13.9 | 699.6 | 304.5 | 151.0 | 1103.6 | 26.4 | 156.2 | 31.3 | 245.2 | 733.7 | 43.4 | 62.8 | 264.0 |
| Mughal village | 2.4 | 5.7 | 3.2 | 14.1 | 8.8 | 8.0 | 5.2 | 5.0 | 26.1 | 145.4 | 159.5 | 561.0 | 16.7 | 62.8 | 24.2 | 140.4 | 38.7 | 103.4 | 126.0 | 119.7 |
| Badin | 3.1 | 2.7 | 3.4 | 15.6 | 4.3 | 8.9 | 6.1 | 7.3 | 697.4 | 327.2 | 75.9 | 1081.5 | 19.2 | 91.9 | 26.9 | 219.5 | 273.5 | 119.3 | 56.2 | 159.8 |

*Table 4b.* **Esters identified and quantified in river Indus, Indus tributaries and wastewater samples (concentration is presented in ng/L) (--- means contaminant not found).**

| Sampling Station | Decanoic acid, methyl ester | | | | Hexadecanoic acid, methyl ester | | | | Octadecanoic acid, methyl ester | | | | 9-Octadecenoic acid (Z)-, methyl ester | | | | Benzoic acid, p-tert-butyl- | | | | Oleic Acid | | | | 1,2-Benzenedicarboxylic acid | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Year* | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | |
| *Month* | *Jan* | *Jun* | *Jan* | *Jun* | *Jan* | *Jun* | *Jan* | *Jun* | *Jan* | *Jun* | *Jan* | *Jun* | *Jan* | *Jun* | *Jan* | *Jun* | *Jan* | *Jun* | *Jan* | *Jun* | *Jan* | *Jun* | *Jan* | *Jun* | *Jan* | *Jun* | *Jan* | *Jun* |
| Jamshoro | --- | --- | --- | --- | 16.7 | --- | --- | --- | --- | --- | --- | 18.0 | --- | --- | --- | --- | --- | --- | --- | --- | 75.0 | --- | --- | --- | --- | -- | --- | --- |
| K.B feeder "A" | 19.6 | 20.5 | 28.2 | 14.6 | 20.4 | 97.9 | --- | --- | 19.9 | 71.8 | --- | --- | 14.7 | 38.6 | --- | --- | --- | 23.0 | --- | --- | --- | --- | 424.1 | --- | --- | -- | --- | --- |
| Kotri drain | 79.3 | 65.6 | 112.3 | 88.3 | 53.5 | --- | 49.5 | --- | 53.5 | 14.1 | 14.7 | 36.4 | --- | --- | --- | 55.1 | 86.2 | 149.0 | 169.4 | 608.1 | --- | 749.9 | 360.3 | --- | 15.0 | --- | 16.9 | 21.3 |
| K.B feeder "B" | --- | --- | --- | 20.3 | --- | --- | 18.1 | --- | 14.1 | --- | 17.3 | 18.6 | --- | --- | 20.0 | --- | --- | --- | 4.0 | --- | --- | --- | 177.9 | --- | --- | -- | 6.9 | --- |
| Deplai town drain | --- | --- | --- | --- | --- | 34.7 | 53.5 | 38.2 | --- | --- | --- | 44.5 | --- | 46.9 | 81.0 | --- | 59.4 | 70.9 | 47.5 | 55.7 | --- | 881.6 | 1368.7 | 917.3 | 6.3 | 4.4 | 21.9 | --- |
| Hoor camp drain | 38.4 | | 48.1 | --- | 169.4 | --- | --- | 36.5 | --- | --- | --- | 64.7 | 105.0 | --- | 102.2 | 45.5 | 62.5 | 62.5 | 56.3 | 486.3 | --- | 372.0 | 2182.1 | | 4.4 | 3.1 | 13.4 | 1.3 |
| Kali mori drain | --- | --- | --- | --- | --- | 100.5 | --- | 34.9 | --- | --- | --- | 35.1 | --- | --- | 108.1 | 37.2 | 17.2 | 17.2 | 19.3 | 18.4 | --- | --- | 3117.5 | 214.5 | --- | -- | --- | --- |
| Main autobhan drain | 52.7 | 38.3 | 48.6 | 54.7 | --- | | --- | --- | --- | 14.3 | 18.9 | 36.3 | --- | --- | 35.4 | | 48.8 | 48.8 | 32.6 | 124.0 | --- | 722.2 | 336.8 | 2087.5 | 21.4 | 2.0 | 21.2 | 3.9 |
| Khattar | --- | --- | --- | --- | --- | 15.3 | --- | --- | 14.3 | --- | --- | --- | 14.8 | 14.2 | 15.4 | --- | --- | --- | --- | --- | --- | --- | 191.1 | 330.6 | --- | -- | --- | --- |
| Tando.M.Khan | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | 21.1 | --- | --- | --- | --- | --- | 3.4 | --- | 369.3 | --- | 63.3 | 101.5 | --- | -- | --- | 6.8 |
| Matli | --- | --- | --- | --- | 14.4 | --- | --- | --- | --- | --- | 15.9 | --- | 24.0 | --- | --- | --- | --- | --- | --- | --- | 457.3 | --- | --- | --- | --- | -- | --- | --- |
| Mughal village | --- | --- | --- | --- | --- | 26.0 | 15.4 | --- | --- | 17.9 | --- | 14.2 | 26.0 | --- | 14.9 | --- | --- | --- | 5.1 | --- | 750.0 | --- | --- | --- | --- | -- | --- | --- |
| Badin | 20.8 | 14.6 | 22.4 | 22.1 | --- | 52.8 | --- | 17.8 | 17.9 | 9.8 | --- | 19.8 | --- | 25.3 | --- | 15.1 | 10.2 | 15.2 | --- | 38.3 | 295.2 | 647.8 | --- | --- | 7.2 | 2.4 | 15.2 | 17.4 |

***Table 5.*** **Carboxylic acids and esters identified in river Indus, Indus tributaries and wastewater samples (√ shows presence of contaminant and □ shows its absence at sampling point).**

| Name of Compound | Jamshoro | K.B feeder A | Kotri drain | K.B feeder B | Deplai town drain | Hoor camp drain | Kali mori drain | Main autobhan drain | Khattar | Tando.M.Khan | Matli | Mughal Village | Badin |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Carboxylic acids and esters** | | | | | | | | | | | | | |
| Acetic acid ethenyl ester | √ | √ | | √ | | | √ | | | √ | √ | | |
| Vinyl butyrate | √ | √ | | √ | | | √ | √ | √ | | √ | | |
| 2-Propenoic acid, 2-methyl-, 1,2-ethanediyl ester | √ | | √ | √ | √ | | √ | | √ | √ | √ | √ | √ |
| Phthalic acid, 2-pentyl 2-propyl ester | √ | | √ | | | √ | √ | | √ | | | √ | √ |
| Benzoic acid, 2-ethylhexyl ester | √ | | | √ | √ | | | | √ | | √ | √ | |
| Isopropyl Myristate | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| 1,2-Benzenedicarboxylic acid, butyl 2-methylpropyl ester | √ | √ | | | √ | | √ | | | | √ | | √ |
| 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| Sulfurous acid, 2-ethylhexyl hexyl ester | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| Propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester | √ | √ | | √ | √ | | √ | √ | √ | √ | √ | √ | |
| 2-Ethylhexyl trans-4-methoxycinnamate | √ | | | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| 2-Propenoic acid, 3-(4-methoxyphenyl)-, 2-ethylhexyl ester | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| 9,12-Octadecadienoic acid (Z,Z)-, methyl ester | | √ | | √ | √ | | √ | | | | | | √ |
| p-Anisic acid, 3,4-dichlorophenyl ester | √ | √ | √ | √ | √ | | | √ | √ | √ | √ | √ | √ |
| 1,2-Benzenedicarboxylic acid, butyl cyclohexyl ester | √ | | | | | √ | √ | | | | | √ | |
| Pentanoic acid, 5-hydroxy-, 2,4-di-t-butylphenyl esters | | | √ | | √ | | √ | √ | √ | | √ | √ | |
| Phthalic acid, 4-fluoro-2-nitrophenyl methyl ester | | √ | | | | | | | √ | √ | | √ | |
| 1,2-Benzenedicarboxylic acid, dicyclohexyl ester | √ | √ | √ | √ | | | √ | √ | √ | √ | √ | | √ |
| Bis(2-ethylhexyl) maleate | | | √ | | | | | | √ | √ | √ | | √ |
| 2-Butenedioic acid (E)-, bis(2-ethylhexyl) ester | | | √ | √ | √ | | √ | | √ | √ | √ | | |
| Phthalic acid, di(3-methylphenyl) ester | √ | √ | √ | | | | | | √ | | | | |
| Phthalic acid, 6-ethyl-3-octyl butyl ester | | | √ | | √ | | | | | | √ | √ | √ |
| Phthalic acid, butyl 2-pentyl ester | √ | | √ | | | | | | | | √ | | |
| Tetracosanoic acid, methyl ester | | | | | √ | | √ | √ | | | | | |
| Benzenepropanoic acid | | | √ | √ | √ | | √ | √ | | √ | √ | √ | √ |
| Benzoic acid, 4-(1-methylethyl)- | | √ | | | | | √ | √ | √ | √ | √ | √ | √ |
| Dodecanoic acid | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| Ibuprofen | | | √ | | √ | √ | √ | √ | √ | | | | |
| Propanoic acid, 2-methyl-3-[4-t-butyl]phenyl- | | | | √ | √ | √ | √ | √ | | √ | | √ | |
| Tetradecanoic acid | | | | | | | | √ | | √ | √ | | |
| Mefenamic Acid | | | | | √ | √ | √ | √ | | √ | | | |
| n-Hexadecanoic acid | | | √ | √ | √ | | √ | | √ | √ | √ | √ | √ |
| 3,5-di-tert-Butyl-4-hydroxyphenylpropionic acid | | | | | | √ | √ | √ | √ | √ | √ | | √ |

### *Carboxylic acids and esters*

Data on identified and quantified carboxylic acid and esters in the studied samples are presented in Table 3. This set of identified compounds contains numerous phthalate esters that belong to the class of priority pollutants and are limited for further use. Among them dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), Diisobutyl phthalate and Bis (2-ethylhexyl) phthalate (DEHP) are prominent. Table 4a reveals that all of the sampling sites especially main sewerage drains are highly polluted with phthalate esters, which are due to their widespread use in a large variety of products. They are used in enteric coating of pharmaceutical pills, viscosity control agents of nutritional supplements, film formers, gelling agents, stabilizers, dispersants, lubricants, emulsifiers, binders and suspending agents. Their end products are adhesives, glues and binding materials, medical devices i.e. catheters, blood transfusion equipments and pharmaceuticals, detergents and surfactants, packaging, children's toys, waxes, paint, printing inks, food products, textiles, household accessories i.e. curtains, floor tiles, food containers and wrappers and cleaning agents, personal care products i.e. perfumes, eye shadow, moisturizer, nail paint, liquid soap and hair spray, etc. The most adverse effect of phthalates is the decline of reproductive function in human and wildlife populations over the last 40 years. Diesters of phthalic acid, commonly known as Phthalates are suspected to be responsible for this decline [22]. Swan et al. [23] studied the prenatal exposure of phthalates on male infants; according to them prenatal exposure to phthalates even at environmental levels can badly affect male reproductive development in humans. In another study, young girls with premature breast development were found with elevated levels of phthalates [24]. Evidences have been provided by different studies about the high exposure of phthalates to individuals of different areas and ages. The exposure of only Bis (2-ethylhexyl) phthalate to children is twice to the exposure to adults [25-28]. Rests of the other quantified esters are given in Table 4b. Apart from these esters 2-ethylhexyl trans-4-methoxycinnamate and 2-Propenoic acid, 3-(4-methoxyphenyl)-, 2-ethylhexyl ester are widespread in all samples (Table 5), they are the active ingredients in sunscreen personal care products and lip balms. Similarly, isopropyl myristate is another main component of skin creams, perfumes and mouth wash. The major source of these contaminants is direct runoff of household sewerage to the fresh water bodies. The production of tributyl phosphate, 1,2-Benzenedicarboxylic acid, dicyclohexyl ester's and their use as a plasticizer for nitrocellulose, ethyl cellulose, chlorinated rubber, polyvinyl acetate, polyvinyl chloride and other polymers results in their release to fresh water bodies through various waste streams. This can be witnessed in most of the samples analyzed (Table 4a and 5).

Benzenepropanoic acid is used as preservative, sweetener and flavoring agent in foods, tooth pastes and mouth washes. Due to its floral aroma, it is widely used in perfumes, liquid and powder detergents, bath gels, fabric softener and soaps etc. Ibuprofen (IBP) and mefenamic acid, the nonsteroidal anti-inflammatory drugs are found in most of the sewerage water samples (Table 5). They are prescribed for pain relief, swelling and fever reduction.

### *Hydrocarbons and derivatives*

The second class of identified compounds includes many hydrocarbons and their derivatives. Number of higher alkanes had been identified (Table 3) and some of them were quantified as well (Table 6a and b). Almost all the sampling sites are being contaminated with higher alkanes (Table 6a, b and 7). Among them the liquid alkanes (undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane, etc.) are widely used in fuel oils and as anti-corrosive agents in lubricating oils and solid alkanes (octadecane, nonadecane, eicosane, heneicosane, tricosane, tetracosane, heptacosane, octacosane, etc.) find their use in paraffin waxes of different kinds. Although higher alkanes are insoluble in water but spilling of oils directly to the sewerage as well as to the river water is the main cause of contamination. Furthermore squalene (Table 7) is found in all the samples, it is mainly used in skin moisturizing PCPIs as well as in conjunction with surfactants in certain adjuvant formulations. Camphene is used in preparation of fragrances and as a food additive, it is also found in all the samples (Table 7).

*Table 6a.* **Hydrocarbons identified and quantified in river Indus, Indus tributaries and wastewater samples (concentration is presented in ng/L) (--- means contaminant not found).**

| Sampling Station | Tridecane | | | | Tetradecane | | | | Pentadecane | | | | Hexadecane | | | | Heptadecane | | | | Octadecane | | | | Nonadecane | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Year* | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | |
| *Month* | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun |
| Jamshoro | 9.5 | 7.1 | 3.7 | 10.2 | 12.3 | 7.6 | --- | 25.6 | 4.8 | 8.6 | 10.2 | 63.0 | 22.0 | 7.4 | 23.7 | 14.2 | --- | --- | --- | 95.1 | 17.1 | 12.2 | 33.3 | 146.8 | 10.6 | 10.4 | 28.3 | 105.0 |
| K.B feeder "A" | 6.3 | 6.9 | 17.4 | 6.5 | 7.6 | 3.6 | 4.4 | --- | 8.3 | 6.5 | 15.2 | 27.3 | 8.6 | 13.7 | 39.1 | 9.0 | 11.7 | 4.8 | 46.8 | 163.1 | 19.9 | 14.1 | 53.1 | 77.1 | --- | 16.0 | 48.6 | 34.6 |
| Kotri drain | 11.1 | 5.3 | 36.3 | 62.7 | 49.2 | 61.2 | --- | 29.9 | 18.3 | 17.0 | 69.7 | 82.2 | 20.6 | 12.3 | 99.0 | 104.2 | 17.5 | 16.2 | 61.9 | 329.4 | 66.8 | 77.3 | 109.9 | 124.2 | 6.9 | 30.6 | --- | 211.8 |
| K.B feeder "B" | 6.6 | 9.0 | 4.3 | 15.6 | --- | 13.4 | 4.7 | 11.5 | --- | 30.3 | 9.7 | 20.2 | 8.4 | 23.6 | 8.6 | 36.3 | 43.8 | 17.9 | 17.3 | 105.9 | 42.0 | 28.8 | 29.5 | 19.5 | 39.5 | --- | 68.8 | 16.7 |
| Deplai town drain | 9.8 | 17.4 | 13.2 | 29.1 | --- | 70.5 | --- | 15.3 | 40.1 | 25.2 | --- | 29.6 | 17.4 | 18.0 | 12.7 | 16.5 | 16.9 | 15.6 | 54.8 | 1.4 | 23.9 | 24.6 | 216.7 | 325.7 | 12.2 | 49.4 | 152.0 | 79.7 |
| Hoor camp drain | 5.9 | 5.6 | 16.5 | 38.8 | --- | --- | --- | --- | 23.1 | 44.1 | --- | 17.5 | 12.9 | 12.1 | 17.2 | 46.2 | 14.1 | 24.7 | --- | --- | --- | --- | --- | --- | 62.1 | 19.2 | --- | 44.2 |
| Kali mori drain | 13.9 | 4.0 | 21.3 | 28.9 | --- | 26.6 | 37.6 | --- | 35.5 | 11.0 | --- | 25.1 | 15.8 | 12.1 | 49.7 | 33.2 | 43.3 | 23.5 | --- | --- | 53.3 | 25.0 | --- | --- | 23.9 | 15.4 | --- | 34.7 |
| Main autobhan drain | 21.8 | 12.1 | 7.0 | 46.2 | --- | 44.0 | --- | 45.8 | --- | --- | 12.1 | 129.1 | 6.8 | 10.1 | 15.0 | 131.4 | 57.8 | 31.6 | --- | 64.0 | --- | --- | --- | 317.7 | --- | --- | --- | 71.7 |
| Khattar | 11.7 | 7.8 | 5.5 | 9.1 | 7.1 | 30.0 | 4.2 | 15.3 | --- | 4.0 | 13.3 | 7.2 | 10.1 | 23.6 | 10.1 | 15.3 | 49.0 | 77.4 | 17.2 | 25.2 | 17.6 | 15.9 | 65.8 | 145.4 | 24.8 | --- | 53.0 | 166.1 |
| Tando.M.Khan | 5.2 | 11.4 | 8.1 | 17.1 | --- | --- | 6.7 | 14.4 | --- | | 12.7 | 12.3 | 13.4 | 9.1 | 22.0 | 16.9 | --- | --- | 96.7 | 32.9 | --- | --- | 49.6 | 255.1 | --- | --- | --- | 195.9 |
| Matli | 15.7 | 10.1 | 3.7 | 5.1 | 109.3 | --- | 18.5 | 13.2 | 7.1 | 12.7 | 28.8 | 19.3 | 10.6 | 13.4 | 13.4 | 36.8 | --- | --- | --- | --- | 18.8 | --- | 55.5 | 265.9 | 43.4 | 7.2 | 69.5 | 8.4 |
| Mughal village | 4.2 | 9.7 | 3.7 | 10.2 | --- | --- | --- | --- | 6.7 | --- | 7.3 | 23.5 | 10.1 | 10.6 | 30.3 | 86.2 | --- | --- | 19.4 | 38.1 | --- | --- | 28.1 | 67.5 | --- | --- | 29.6 | 52.7 |
| Badin | 12.5 | 18.3 | 4.6 | 14.3 | --- | 4.3 | --- | 14.6 | 12.7 | --- | 4.3 | 13.0 | 4.5 | 8.3 | 21.8 | 101.1 | --- | --- | --- | 84.5 | 14.3 | 13.6 | 27.3 | 187.8 | --- | --- | 11.5 | 132.8 |

*Table 6b.* **Hydrocarbons identified and quantified in river Indus, Indus tributaries and wastewater samples (concentration is presented in ng/L) (--- means contaminant not found).**

| Sampling Station | Dodecane | | | | Undecane | | | | Eicosane | | | | Heneicosane | | | | Pentadecane, 2,6,10,14-tetramethyl- | | | | 1-Nonadecene | | | | 1-Docosene | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Year* | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | |
| *Month* | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun |
| Jamshoro | 15.3 | 12.9 | 2.4 | 2.7 | 16.3 | 2.2 | 8.2 | 7.1 | 16.1 | 11.0 | 58.6 | 201.5 | 25.6 | 30.3 | 21.7 | 112.6 | --- | 9.6 | --- | 21.5 | 9.8 | 16.8 | 5.6 | 17.3 | 12.2 | 6.5 | 4.5 | --- |
| K.B feeder "A" | 26.6 | 15.6 | 5.4 | 27.9 | 5.0 | 3.5 | 5.2 | 7.3 | 7.3 | 18.0 | 129.6 | 28.6 | 27.9 | --- | 90.5 | 34.4 | 5.9 | --- | 24.2 | 26.3 | 12.2 | 8.2 | 11.0 | 13.4 | --- | --- | --- | --- |
| Kotri drain | 56.2 | 61.1 | 23.4 | 39.5 | 61.2 | 39.6 | 56.6 | 50.7 | 108.1 | 53.6 | 88.5 | 354.5 | 76.1 | 82.3 | 139.1 | 638.7 | 15.7 | 14.1 | 20.9 | 49.0 | 17.7 | 17.2 | 11.9 | 23.9 | --- | --- | --- | 241.5 |
| K.B feeder "B" | --- | 12.9 | --- | --- | --- | 3.0 | 6.1 | 7.6 | 12.9 | 11.5 | 70.6 | 32.7 | 1.0 | --- | --- | 18.6 | 9.6 | 9.8 | 4.9 | 33.7 | 15.6 | 12.2 | 10.1 | --- | --- | --- | --- | --- |
| Deplai town drain | --- | --- | --- | --- | --- | --- | --- | 31.8 | 10.3 | 83.6 | 299.3 | 284.9 | 8.4 | 32.1 | 208.2 | 321.3 | 5.0 | --- | 43.1 | 35.2 | --- | 17.9 | --- | --- | 17.9 | 12.3 | 9.6 | 77.9 |
| Hoor camp drain | 12.2 | 8.3 | --- | 28.2 | 7.0 | --- | --- | --- | 115.6 | 71.1 | 85.0 | 126.0 | --- | --- | --- | 237.6 | --- | 17.3 | --- | --- | 22.2 | --- | --- | 39.2 | 16.9 | 14.4 | 16.1 | 229.2 |
| Kali mori drain | --- | 45.8 | 36.7 | --- | 39.7 | 9.4 | 17.3 | --- | 55.0 | 57.9 | 201.6 | 55.5 | --- | --- | --- | 38.6 | --- | 11.7 | --- | --- | 1.4 | 9.9 | --- | --- | 16.5 | 17.9 | 9.5 | 22.5 |
| Main autobhan drain | --- | 7.3 | 23.2 | 12.3 | | 9.1 | --- | --- | 13.2 | 34.2 | 61.8 | 324.2 | --- | --- | --- | 248.5 | 15.0 | --- | --- | 21.1 | 16.9 | 17.6 | --- | 52.4 | --- | --- | --- | 153.3 |
| Khattar | --- | --- | --- | --- | --- | --- | --- | 15.0 | 14.3 | 46.0 | 42.0 | 226.3 | 17.9 | 38.2 | 28.4 | 117.9 | 8.6 | --- | 4.8 | 24.0 | 12.5 | --- | 5.8 | 40.8 | --- | --- | --- | --- |
| Tando.M.Khan | 3.1 | --- | --- | --- | --- | --- | 5.2 | 32.8 | 18.1 | 54.2 | 54.9 | 152.3 | 16.1 | 9.6 | 83.3 | 141.9 | --- | --- | 8.8 | --- | --- | --- | 4.4 | 45.4 | 9.5 | --- | --- | 16.8 |
| Matli | 15.3 | 14.1 | --- | 16.8 | 6.9 | 7.4 | 4.5 | 6.0 | 25.1 | 11.5 | 37.6 | 45.5 | 21.6 | 29.4 | 55.0 | 93.3 | --- | 7.0 | --- | 13.2 | --- | --- | 5.3 | 44.1 | --- | --- | --- | 11.1 |
| Mughal village | --- | --- | --- | 4.7 | --- | --- | 8.9 | 15.1 | 25.4 | 30.4 | 61.6 | 108.7 | --- | 17.5 | 42.9 | 128.6 | --- | --- | 8.3 | 51.9 | --- | --- | --- | 46.2 | --- | 11.4 | --- | --- |
| Badin | 22.0 | --- | 3.5 | --- | --- | 8.3 | 2.6 | 18.2 | 8.3 | 18.5 | 53.6 | 140.0 | 22.6 | 15.3 | 15.7 | 94.6 | 3.6 | 12.1 | --- | 13.5 | 12.2 | 12.4 | --- | --- | 11.7 | 12.4 | 7.2 | --- |

***Table 7.*** **Hydrocarbon, imines, amines, amides and alcohol derivatives identified in river Indus, Indus tributaries and wastewater samples (√ shows presence of contaminant and □ shows its absence at sampling point).**

| Name of Compound | Jamshoro | K.B feeder A | Kotri drain | K.B feeder B | Deplai town drain | Hoor camp drain | Kali mori drain | Main autobhan drain | Khattar | T.M.Khan | Matli | Mughal Village | Badin |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Hydrocarbons and derivatives** | | | | | | | | | | | | | |
| Undecane, 3,7-dimethyl- | √ | | | | | | | √ | | | √ | | |
| Tributyl phosphate | √ | √ | √ | √ | √ | √ | √ | √ | √ | | √ | √ | √ |
| Octacosane | | | √ | | | | | | √ | √ | | | |
| Tricosane | | | | √ | | | √ | √ | √ | √ | √ | | |
| Tetracosane | | | √ | √ | √ | √ | | √ | √ | | √ | | √ |
| Heptacosane | | | √ | √ | √ | | | √ | √ | √ | | √ | |
| 1-Tridecene | √ | | | √ | | | √ | | | √ | √ | √ | √ |
| 1,13-Tetradecadiene | | | | | | | | | √ | √ | √ | | |
| 3-Octadecene, (E)- | √ | √ | √ | | √ | | | | | √ | √ | | |
| 3-Eicosene, (E)- | √ | √ | √ | √ | | | √ | √ | √ | √ | | √ | |
| 5-Eicosene, (E)- | √ | | | | | | | | | | √ | √ | √ |
| Squalene | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| 1,3-Butadiyne | | | | | | | | | √ | √ | √ | √ | √ |
| Camphene | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| **Imines, Amines, Amides derivatives** | | | | | | | | | | | | | |
| Aziridine, 2-methyl- | √ | | √ | | √ | √ | √ | √ | √ | | √ | √ | √ |
| Acetamide | √ | √ | √ | √ | √ | | √ | √ | √ | √ | √ | √ | √ |
| 2-Propenamide | √ | | √ | √ | | √ | | √ | | √ | √ | | √ |
| N-Nitrosodimethylamine | √ | | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| Formamide, N-formyl-N-methyl- | √ | | √ | √ | √ | | √ | √ | √ | √ | √ | √ | √ |
| 1,3,5-Triazine-2,4,6-triamine | | | | | √ | | | √ | √ | | | √ | |
| Diphenylamine | √ | √ | √ | √ | √ | | √ | √ | √ | √ | | √ | |
| Benzamide, N,N-diethyl-4-methyl- | | | | √ | √ | √ | | | | | | | |
| Diethyltoluamide | | | | | | √ | √ | √ | | | | | |
| **Alcohol derivatives** | | | | | | | | | | | | | |
| 2-Propyn-1-ol | √ | | | | √ | √ | | √ | | | √ | √ | √ |
| Isopropyl Alcohol | √ | | √ | | √ | | | | | √ | √ | | |
| 2-Propanol, 2-methyl- | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| Ethanol, 2-ethoxy- | | | | | | √ | | | √ | √ | | | √ |
| 1-Hexanol, 2-ethyl- | √ | | | √ | | | | | | | | | √ |
| 1-Propanol, 2-(2-hydroxypropoxy)- | | | √ | | √ | | | √ | | | | √ | |
| 3,7,11,15-Tetramethyl-2-hexadecen-1-ol | | | √ | √ | | | | | | | | | √ |

***Imine, amine, amide derivatives***

Aziridine, 2-methyl- is an imine, which is widely spread in ten sampling stations out of thirteen (Table 7). It is suspected to be human carcinogen because of adequate evidences obtained from studies carried out in experimental mammals [29]. It is exclusively used as chemical intermediate and its derivatives are used in the paper, textile, rubber and pharmaceutical industries. Thus its extensive use in chief industries is responsible for contamination of sewerage as well fresh water bodies. Acetamide is used as plasticizer and industrial solvent where as 2-propenamide (acrylamide) is mainly used to manufacture variety of polymers. 2-propenamide additionally finds its applications as binding, thickening or flocculating agent in grout, cement, wastewater treatment, pesticide formulations, cosmetics, sugar manufacturing, soil erosion prevention, ore processing, food packaging and plastic products. Some evidences propose that male reproductive glands can be damaged by exposure to excessive amount of acetamide, the US government agencies have announced it a potential occupational carcinogen. *N*-Nitrosodimethylamine (NDMA) is water soluble and highly toxic compound. It has been detected in twelve out of thirteen sampling stations. It is used as an antioxidant, as an additive for lubricants, and as a softener of copolymers. It is a semi-volatile organic compound produced as by-product in many industrial processes. The chlorination of organic nitrogen containing wastewater can lead to the production of NDMA at potentially harmful levels and is a matter of utmost concern. Chronic exposure to NDMA can cause severe damage to liver, lower platelets count and is suspected human carcinogen [30,31]. 1,3,5-Triazine-2,4,6-triamine (melamine) is detected at four sampling sites, two of them are sewerage water sites and rest two are samples from canal. It is an organic base which is when mixed with resins has fire retardant properties; melamine resin is a strong thermosetting plastic used in Formica, melamine dinner ware and laminate flooring. In order to mislead protein content in food products, melamine is illegally added to them, it has been an adulterant for feedstock and milk in Mainland china for several years. Chronic toxicity of melamine may lead to reproductive damage or bladder or kidney stones that may result in to bladder cancer [32,33]. Diphenylamine is mainly released to the environment through chemical industry during production, formulation of heating oil, lubricant additive and plant protection product and processing. Consumption of fruits that are treated with storage aid containing diphenylamine can also cause its unintentional release to the environment [34]. Diethyltoluamide (DEET) is an insecticide that repels, but does not kill insects. It is an active ingredient in many insect repellent PCPIs; there are approximately 225 commercial insect repellent PCPIs that contain DEET [35]. One U.S. water survey detected DEET in 75% of streams tested in 30 states [36], however in our study we detected it in three main municipal sewerage drains and assume that the possible source of contamination is body wash runoff. Trimethylamine is found in the range of 7.25 to 285 ng/L at different sampling sites (Table 10). It is a good nucleophile, and this reaction is the base of its most applications.

***Alcohol derivatives***

2-propyn-1-ol is the simplest and stable organic alcohol, it is found in 7 sampling stations. It is used as a corrosion inhibitor, a solvent stabilizer, an electroplating brightener additive and an intermediate in organic synthesis. The above industrial uses of this compound give a clue that the direct disposal of industrial wastewater may cause contamination of fresh water bodies as well as sewerage waters with 2-propyn-1-ol. Isopropyl alcohol (IPA) is detected at some of the sampling stations, one of them is industrial effluent and another is municipal sewerage drain, rests of sampling points belonged to the fresh water resources (Table 7). It is used as a solvent and in making many commercial products. IPA is also used as a component of antifreeze; a solvent for gums, essential oils, creosote and resins; component of quick drying oils and ink; antiseptic for hand lotions, after shave lotions and other cosmetics [37]. 2-propanol, 2-methyl is another alcohol which is used in industry as a solvent, ethanol denaturant, paint remover ingredient, and gasoline octane booster and oxygenator.

*Table 8.* **Alcohol and phenol derivatives identified and quantified in river Indus, Indus tributaries and wastewater samples (concentration is presented in ng/L) (--- means contaminant not found).**

| Sampling Station | 1-Undecanol | | | | 1-Dodecanol | | | | 1-Hexadecanol | | | | Phenol, p-tert-butyl- | | | | Phenol, m-tert-butyl- | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Year* | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | |
| *Month* | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun |
| Jamshoro | 171.5 | 145.7 | 151.7 | 243.3 | 189.1 | 177.3 | 193.1 | 107.3 | 66.2 | 73.6 | 67.0 | 78.7 | --- | --- | --- | --- | -- | 3.2 | --- | --- |
| K.B feeder "A" | 39.0 | 39.5 | 31.2 | 296.2 | 125.2 | --- | --- | --- | 38.9 | 30.9 | 139.4 | 70.0 | --- | --- | --- | --- | -- | --- | --- | 5.1 |
| Kotri drain | 722.9 | 385.9 | 746.2 | 1183.0 | 106.1 | --- | 90.6 | 365.7 | 471.6 | 126.2 | 342.0 | 1424.3 | 1308.0 | 1307.7 | 1091.4 | 162.7 | -- | --- | 62.8 | 206.3 |
| K.B feeder "B" | 29.7 | 14.1 | 37.1 | 234.2 | --- | 57.6 | 41.9 | 45.1 | 209.5 | 28.5 | 157.1 | 105.2 | --- | --- | --- | --- | -- | 3.4 | --- | --- |
| Deplai town drain | 36.0 | 90.5 | 174.7 | 374.1 | --- | 89.4 | 383.2 | --- | 32.8 | 229.3 | 267.7 | 366.4 | 1438.1 | 708.1 | 1438.4 | 1276.4 | -- | 57.0 | 57.1 | --- |
| Hoor camp drain | 539.4 | 653.9 | 784.7 | 670.2 | 88.3 | 137.6 | --- | 239.1 | 51.3 | 363.4 | 331.9 | 300.4 | 1279.0 | 1438.4 | 163.0 | 370.4 | -- | 49.7 | --- | --- |
| Kali mori drain | 649.6 | 468.7 | 1481.1 | 356.3 | --- | --- | 450.7 | 66.4 | 110.7 | 62.3 | 383.5 | 277.9 | 1411.6 | 488.6 | 545.8 | 756.9 | -- | --- | --- | --- |
| Main autobhan drain | 69.7 | 81.2 | 67.8 | 199.2 | 88.1 | 101.0 | --- | 343.2 | 65.5 | 102.6 | 133.3 | 381.3 | 1438.7 | 1148.5 | 758.3 | 806.8 | -- | --- | --- | --- |
| Khattar | 63.4 | 82.2 | 89.4 | 157.8 | --- | --- | --- | --- | 56.6 | 26.9 | 182.8 | 89.3 | 15.3 | --- | --- | 162.5 | 7.0 | --- | --- | --- |
| Tando.M.Khan | 43.4 | 38.1 | 21.4 | 116.8 | --- | 175.3 | 228.1 | 126.2 | 55.4 | 40.7 | 199.2 | 297.2 | --- | --- | --- | --- | -- | --- | --- | --- |
| Matli | 255.7 | 244.3 | 314.2 | 434.9 | 16.7 | --- | --- | 171.6 | 16.8 | 34.0 | 134.3 | 176.1 | 24.5 | --- | --- | --- | 5.5 | 4.6 | --- | --- |
| Mughal village | 18.1 | 27.1 | 34.0 | 29.6 | --- | --- | 181.7 | 223.2 | 41.2 | 56.3 | 122.6 | 462.0 | --- | --- | 18.4 | --- | -- | --- | 18.3 | --- |
| Badin | 19.4 | 70.4 | 46.7 | 38.2 | 67.0 | 126.1 | 124.2 | 126.2 | 61.2 | 88.6 | 244.7 | 335.5 | --- | --- | --- | 27.0 | -- | --- | --- | --- |

Ethanol, 2-ethoxy- also known by the trademark “cellosolve” or “ethyl cellosolve” is also a solvent used widely in commercial and industrial applications. It has ability to dissolve chemically diverse compounds i.e. oils, resins, grease, waxes, nitrocellulose and lacquers. Ethanol, 2-ethoxy- is an ideal multi-purpose cleaner, and, therefore it is used in varnish removers and degreasing solutions. 1-hexanol, 2-ethyl is produced on a massive scale as a precursor to an endocrine disrupting plasticizer DEHP. 1-propanol, 2-(2-hydroxypropoxy)- also known as dipropylene glycol is used as a plasticizer, an intermediate in industrial chemical reactions, as a polymerization initiator or monomer, and as a solvent. It is also used in perfumes, skin and hair care products [38]. 3, 7, 11, 15-tetramethyl-2-hexadecen-1-ol also known as phytol finds its applications in PCPIs and cleaning agents. Its worldwide use has been estimated to be approximately 0.1-1.0 metric tons per year [39]. In our study it is mainly detected in industrial sewerage drain at Kotri district. 1-undecanol, 1-dodecanol and 1-hexadecanol are the alcohols that are quantified. Table 8 shows that 1-undecanol and 1-hexadecanol are consistently found at all sampling sites in all seasons, whereas 1-dodecanol is not detected at all sampling sites but most of the sites are contaminated with it. Although, 1-undecanol and 1-hexadecanol are insoluble in water and 1-dodecanol’s solubility is 0.004 g/L in water but they are detected in samples due to direct discharge of sewerage wastewater into river and canals. They are generally used in PCPIs, lubricants and as food additives.

### *Phenol derivatives*

Numerous phenol derivatives were detected while this screening study, among them resorcinol, eugenol and α-bisabolol are identified at number of sampling sites (Table 9). They have many applications in PCPIs, skin ointments and creams, synthesis of pharmaceuticals, antiseptics, anesthetics, azo dyes and plasticizers. Hence their extensive use in industry and presence in PCPIs; medicines etc is contaminating water bodies through municipal and industrial sewerage water. All the 52 samples were found contaminated with Phenol,2,4-bis(1,1-dimethylethyl)- (2,4-DTBP). It is used as a chemical intermediate for the synthesis of UV stabilizers or antioxidants. 2,4-DTBP is very toxic to aquatic organisms. Phenol, 3-methyl-5-(1-methylethyl)-, methylcarbamate is an insecticide that belongs to phenyl methylcarbamate insecticides group. It is found in seven sampling stations out of which four stations belong to canal water. The possible source of contamination is agricultural runoff that goes directly to the canals. Butylated hydroxytoluene (BHT) is consistently found in all samples, it is used as an antioxidant additive in cosmetics, pharmaceutical, rubber and electrical transformer oil. BHT is also used in hydraulic fluids, turbine, gear oils and jet fuels. Some additive products contain BHT as their primary ingredient, while others contain it merely as a component of their formulation. BHT can promote tumor in some particular situations. The high exposure to BHT can result in worst reproductive effects by intimating female sex hormone estrogen [40,41]. Numbers of sites were found contaminated with Bisphenol A (BPA), it is mainly used as plasticizer and a key monomer in epoxy resins and polycarbonate plastic production. BPA is an endocrine disruptor, more specifically; it alters the tasks of estradiol, the hormone. It is capable of binding to and activating the estrogen receptor same as natural hormone. The prenatal exposure to BPA may lead to physical and neurological difficulties later [42,43].

o-hydroxybiphenyl is an agricultural fungicide, which is applied post harvest. It is a surface disinfectant and can also be used in the manufacture of other fungicides, dyestuffs, resins and rubber chemicals.

### *Heterocyclic aromatic compounds*

Pyrrolidine, 1-nitroso- (NPYR) is an important hepatocellular carcinogen frequently present in the environment [44], it is found at six sampling sites most of which are sewerage drains (Table 9). Indole is frequently used as component of fragrances and precursor to many pharmaceuticals. 1H-indole, 3-methyl- commonly known as skatole is present in feces; this may be the reason of its presence in sewerage waters.

*Table 9.* **Phenol, heterocyclic aromatic, benzene and ketone derivatives in river Indus, Indus tributaries and wastewater samples (√ shows presence of contaminant and □ shows its absence at sampling point).**

| Name of Compound | Jamshoro | K.B feeder A | Kotri drain | K.B feeder B | Deplai town drain | Hoor camp drain | Kali mori drain | Main autobhan drain | Khattar | T.M.Khan | Matli | Mughal Village | Badin |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Phenol Derivatives** | | | | | | | | | | | | | |
| Resorcinol | | | √ | √ | √ | √ | √ | | √ | | | | √ |
| Eugenol | | | | | | | √ | √ | √ | | | | |
| Phenol, 2-(1-phenylethyl)- | √ | | √ | √ | √ | √ | √ | √ | √ | | | √ | √ |
| Phenol, 2,4-bis(1,1-dimethylethyl)- | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| Phenol, 3-methyl-5-(1-methylethyl)-, methylcarbamate | | √ | | | √ | | √ | √ | | √ | | √ | √ |
| Butylated Hydroxytoluene | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| à-Bisabolol | √ | | | √ | | | √ | √ | √ | √ | √ | √ | √ |
| Bisphenol A | | | √ | √ | | | √ | √ | | | | | √ |
| Cholesterol | √ | √ | √ | | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| Cholestan-3-ol, (3á,5á)- | | | √ | √ | √ | √ | √ | √ | | | | | |
| o-Hydroxybiphenyl | | | | | | | | √ | | | √ | | √ |
| **Heterocyclic aromatic compounds** | | | | | | | | | | | | | |
| 1,3-Dioxolane | | | | | √ | | √ | | √ | | | √ | √ |
| Pyrrolidine, 1-nitroso- | | | | √ | √ | | √ | √ | √ | √ | | | |
| Quinoline | | | √ | | √ | | √ | √ | | | √ | √ | √ |
| 9H-Fluorene, 4-methyl- | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| Dibenzothiophene | | √ | | | | | | | | √ | | | √ |
| Indole | | | √ | √ | | | √ | √ | | √ | | | |
| 1H-Indole, 3-methyl- | | | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| Indoleacetic acid | | | | | √ | | √ | | √ | | | | |
| 2H-Indol-2-one, 1-(2,6-dichlorophenyl)-1,3-dihydro- | | | √ | | √ | | | | √ | | | √ | |
| Pyridine, 3-methyl-2,6-diphenyl- | | | | √ | √ | | √ | √ | | | | | |
| **Benzene derivatives** | | | | | | | | | | | | | |
| Styrene | | | | | √ | | √ | | | | | | √ |
| Benzene, 1,2-diethyl- | √ | √ | | √ | | | | | √ | | | √ | |
| Benzene, 1-methyl-2-(1-methylethyl)- | √ | | | √ | | | | | √ | √ | √ | | √ |
| Benzene, 1,3-dimethyl-5-(1-methylethyl)- | | √ | √ | | √ | | √ | √ | | √ | √ | | √ |
| Benzene, (1-methyldodecyl)- | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| Naphthalene, 2-methyl- | √ | | √ | √ | √ | | √ | √ | √ | √ | | | √ |
| Naphthalene, 1,2-dimethyl- | √ | | | | | | | | | | √ | | √ |
| 1-Naphthalenamine, N-phenyl- | | | | √ | | √ | | | √ | √ | | | |
| Indane | | | √ | | √ | √ | √ | √ | | | | | |
| 1H-Indene, 2,3-dihydro-5-methyl- | | | | √ | | √ | | √ | | √ | √ | √ | |
| **Ketone derivatives** | | | | | | | | | | | | | |
| Methyl vinyl ketone | | | √ | √ | | | √ | | | | | | √ |
| Propiolactone | √ | | | | √ | | | √ | | √ | | | |
| Acetophenone, 2-chloro- | √ | √ | | √ | √ | | √ | √ | √ | √ | √ | √ | √ |
| Ethanone, 1-(4-hydroxy-3-methoxyphenyl)- | √ | | | √ | | | √ | | | √ | | | √ |
| 2(3H)-Furanone, 5-hexyldihydro- | | | | | √ | | | √ | √ | √ | | √ | |
| Benzophenone | | | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| 7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione | √ | √ | √ | √ | √ | √ | √ | √ | √ | | | √ | √ |

### *Benzene derivatives*

Industrial uses of styrene include production of polystyrene plastics and resins. Acute toxicology to styrene causes mucous membrane irritation, eye irritation and gastrointestinal effects whereas chronic exposure adversely affects central nervous system in humans [47]. Benzene, 1,2-diethyl- is found in fuel oil, gasoline and kerosene and is released to environment through various waste streams. Naphthalene, 2-methyl is a natural component of crude oil and coal, and is found in pyrolysis and combustion products such as coal tar residues, used oils, etc. It is utilized in the formation of alkyl-naphthalenesulfonates, chlorinated naphthalenes and hydronaphthalenes. Naphthalene, 2-methyl is also a key component for the manufacture of vitamin K and insecticide Carbaryl. The toxicological studies of naphthalene, 2-methyl in humans are not available yet [45]. 1-naphthalenamine, N-phenyl- commonly known as PANA is used in turbine oils and miscellaneous lubricants and greases. Several studies reveal that PANA is toxic to aquatic environment.

### *Ketone derivatives*

Methyl vinyl ketone (MVK) is one of the key components in making plastics, resins, vitamin A and steroids. Exposure to MVK leads to nausea, vomiting, headache, fatigue, weakness, tremors, dizziness, loss of coordination and passing out. Propiolactone is logically expected to be a human carcinogen since it has shown to cause skin and stomach cancers in animals. It is mainly used to sterilize blood plasma, vaccines, tissue grafts, surgical instruments and enzymes; to inactivate viruses for use in vaccines for animals and humans; and in organic synthesis [48]. Benzophenone is one of the components of PCPIs and pharmaceuticals that frequently occur in surface, drinking and sewerage water. It is used as an additive for plastics, coatings and adhesive formulations and as a flavor ingredient. It is also a component in the manufacture of insecticides, agricultural chemicals hypnotic drugs, etc [49]. 7,9-di-ter-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione has been detected at most of the sampling stations, it is known as a breakdown product of one of the phenolic antioxidants, used in plastics and engine oils. There are no U.S. EPA primary health standards, secondary standards or health advisory levels established for this compound [50].

### *Cyclodienes*

This class of compound holds one of the most toxic and organochlorine pesticide endosulfan. It is found consistently in three sampling sites and they belonged to canals (Table 10). Thus the agricultural runoff is responsible to this contamination. Its acute toxicology can result in permanent neurological impairment; typical clinical signs include seizures, nausea, vomiting, abdominal discomfort, hyperesthesia of the mouth, face and tongue, headaches, agitation, hyperactivity, confusion, dizziness, etc [46]. According to Stockholm Convention definition, endosulfan is a “persistent organic pollutant” (POP), bioaccumulative, demonstrates long range environmental transport, and causes adverse effects to human health and the environment.

### *Azole derivatives*

3-amino-s-triazole (3-AT) is a nonselective systemic triazole herbicide used on nonfood croplands to control annual grasses, broadleaf and aquatic weeds. It has carcinogenic properties and agricultural runoff that directly falls into the river and canals is major source of contamination. Carbozole which is an active ingredient for the production of pigment violet 23 is detected at 9 sampling sites (Table 11).

### *Aldehyde derivatives*

Vanillin is largely used for flavoring sweet foods, ice cream and chocolate industrially. It is a chemical intermediate in the production of pharmaceuticals.

### *Diphenyl ether derivatives*

Diphenyl ether is used as a chemical intermediate in the production of polyesters, surface active agents and high temperature lubricants.

***Table 10.*** **Diphenyl ether, endosulfan and trimethylamine identified and quantified in river Indus, Indus tributaries and wastewater samples (concentration is presented in ng/L) (--- means contaminant not found).**

| Sampling Station | Diphenyl ether | | | | Endosulfan | | | | Trimethylamine | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Year* | 2010 | | 2011 | | 2010 | | 2011 | | 2010 | | 2011 | |
| *Month* | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun | Jan | Jun |
| Jamshoro | 4.4 | 4.5 | 43.3 | - - - | - - - | - - - | - - - | - - - | 18.4 | 29.6 | 28.2 | 105.6 |
| K.B feeder "A" | - - | 4.2 | 15.6 | - - - | - - - | - - - | - - - | - - - | - - - | - - - | 34.7 | 21.3 |
| Kotri drain | 6.6 | - - - | 8.1 | 8.0 | - - - | - - - | - - - | 145.5 | - - - | 53.3 | 105.8 | 188.8 |
| K.B feeder "B" | 5.9 | 4.3 | 16.3 | - - - | - - - | - - - | - - - | - - - | 38.3 | - - - | 34.5 | 23.1 |
| Deplai town drain | - - | 10.6 | 17.1 | 22.8 | - - - | 8.1 | 9.6 | - - - | - - - | 33.2 | 76.4 | 285.5 |
| Hoor camp drain | - - | 9.0 | 19.1 | 8.2 | - - - | - - - | - - - | - - - | 129.5 | - - - | 46.8 | 183.9 |
| Kali mori drain | - - | 3.7 | 47.0 | - - - | - - - | 22.0 | 22.0 | - - - | - - - | - - - | 127.7 | 77.5 |
| Main autobhan drain | 6.8 | 17.9 | 28.7 | 41.9 | - - - | - - - | - - - | - - - | 35.0 | - - - | 86.7 | 108.8 |
| Khattar | 4.7 | 3.9 | 5.8 | - - - | 46.1 | 65.6 | 32.9 | 85.8 | 24.5 | 11.8 | 27.8 | 116.8 |
| Tando.M.Khan | - - | - - - | 12.5 | - - - | 60.5 | 57.9 | 166.9 | 93.8 | - - - | - - - | 24.4 | 132.2 |
| Matli | 4.4 | 4.1 | 5.8 | 7.4 | 85.5 | 56.7 | 61.4 | 149.4 | 24.4 | 7.3 | 13.9 | 101.9 |
| Mughal village | - - | - - - | 18.5 | - - - | - - - | - - - | - - - | - - - | 19.4 | - - - | 27.8 | 54.1 |
| Badin | 9.0 | 11.0 | 3.6 | - - - | - - - | - - - | - - - | - - - | 12.1 | - - - | 29.6 | 109.5 |

***Table 11.*** **Azole and aldehyde derivatives identified in river Indus, Indus tributaries and wastewater samples (√ shows presence of contaminant and □ shows its absence at sampling point).**

| Name of Compound | Jamshoro | K.B feeder A | Kotri drain | K.B feeder B | Deplai town drain | Hoor camp drain | Kali mori drain | Main autobhan drain | Khattar | T.M.Khan | Matli | Mughal Village | Badin |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Azole derivatives** | | | | | | | | | | | | | |
| 1-Methyl-1H-1,2,4-triazole | √ | --- | --- | --- | √ | --- | --- | √ | √ | √ | --- | --- | --- |
| 3-Amino-s-triazole | √ | | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | --- |
| 1H-Tetrazol-5-amine | --- | √ | √ | √ | √ | | √ | √ | √ | √ | --- | √ | --- |
| 3H-1,2,4-Triazol-3-one, 1,2-dihydro- | --- | --- | --- | √ | --- | --- | --- | √ | --- | √ | --- | --- | √ |
| Carbazole | √ | --- | √ | √ | √ | --- | √ | √ | √ | √ | --- | --- | √ |
| **Aldehyde derivatives** | | | | | | | | | | | | | |
| Vanillin | --- | --- | √ | √ | --- | --- | --- | --- | --- | --- | --- | --- | √ |
| 3,5-di-tert-Butyl-4-hydroxybenzaldehyde | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ | √ |

## Conclusion

GC/MS non-target screening analysis of samples collected from river Indus, its tributaries and main wastewater drains revealed detailed knowledge of contaminants in these water bodies. As expected, the highest level of contamination is associated with residential and industrial areas. Highly toxic POPs, EDCs, carcinogens and compounds that are rarely noticed or quite new pollutants have been identified. According to our knowledge there is little or no environmental information available for these uncommon compounds. Most of the identified compounds are toxic at very low concentrations and are capable of bioaccumulating through the food chain. Many of the POPs can retain for very long durations in soils, sediments, animals and human tissues. The elimination of these contaminants from the environment will take years even if their discharge is restricted in near future. Thus the continued discharge of injurious pollutants will only lead to more extensive and environmentally destructive contamination.

In order to protect river Indus, long-term solution based on reduced waste generation is needed. Clean-up of basin is required as well as industry, along with the bodies responsible for sewage treatment and water quality are required to take full legal and financial accountability to save this only source of fresh water in Sindh. If the current situation is not controlled, a vast decay of river Indus basin cannot be avoided.

**Acknowledgements**

Authors are thankful to the National Centre of Excellence in Analytical Chemistry, University of Sindh for providing financial support & research facilities for this work.

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