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Occurrence of Selected Pesticides and PCPs in Surface Water Receiving Untreated Discharge in Pakistan

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Abstract

This study investigated the presence of four pesticides (carbaryl, methomyl, carbofuran and chlorpyrifos) and two personal care products (PCPs) i.e., triclosan (TCS) and caffeine in River Kabul, upper River Indus and Kalpani stream receiving untreated wastewater from major towns in northern Pakistan. PCPs were also examined in domestic wastewater in Mardan district, Pakistan with untreated sewage disposal as common elsewhere in the country. Analysis were performed using liquid chromatography with a triple quadrupole tandem mass spectrometry (LC-MS/MS). All the target pesticides were detected in surface water bodies and in domestic sewage in various concentrations. Methomyl in River Kabul at maximum concentration of 8.3 µg/L was found above its reported LC_{50} for water fleas. PCPs level in sewage were comparable to other countries but in the absence of any treatment practice, environmental discharge to water bodies was higher by many orders of magnitude compared to treated effluent. Eco-toxicological risk assessment revealed a risk quotient (RQ) of >1 for methomyl, chlorpyrifos and carbofuran for water fleas and fish in River Kabul, River Indus and Kalpani stream and TCS for algae in Kalpani indicating a serious toxicity risk to aquatic organisms in these rivers.

Keywords: Emerging contaminants; Pesticides; Personal care products; Endocrine disrupting chemicals; Environmental risk; Untreated water

Introduction

Water bodies receive wastewater from different sources in treated and untreated form that contain a variety of physicochemical and biological constituents. In recent years, the presence of trace organic contaminants in surface water has gained increased attention due to their harmful effects in very small concentrations. A broad group of organic chemicals in personal care products (PCPs) and pesticides are amongst the prominent of these emerging micro-pollutants due to their wide ranging eco-toxicological effects and endocrine disrupting potential in living organisms [1]. Recent studies have shown that organic compounds of pesticides and PCPs origin have been frequently detected in aquatic environments around the world such as in the United States, China, Taiwan, Japan, Spain, Netherland, Germany and Canada [2-7]. In Pakistan, PCPs and pesticides are extensively used in domestic, industrial and agricultural sectors. Wastewater from these sources is discharged without proper treatment, allowing these chemicals to enter into water channels and streams and leach into soil or groundwater [8]. The contaminated surface water is further used for agricultural and domestic purposes posing a risk to human health and ecosystem while also entering the food chain. On the other hand, research on prevalence of such compounds in aquatic environment in Pakistan is limited. Few studies have reported the presence of pesticides such as dichloro diphenyl trichloroethane (DDT), cyclodiens, hexa chlorocylo hexane (HCHs) and poly chlorinated biphenyls (PCBs) in water bodies and in agriculture products such as dairy milk, vegetables and fruits [9-11]. Whereas, occurrence of many other pesticides and PCPs that are extensively used in Pakistan have received little attention.

This research investigated the presence of selected PCPs and pesticides in surface water (River Kabul, River Indus and Kalpani stream) and domestic sewage in Mardan city in the north-west Pakistan having similar wastewater disposal practices as other parts of the country. In Mardan, wastewater is discharged untreated into Kalpani stream that falls into River Kabul. River Kabul also receives untreated effluent from other major urban centres in the region and finally joins River Indus. The target compounds included two PCPs (triclosan and caffeine) and four pesticides (carbaryl, methomyl, carbofuran and chlorpyrifos). Triclosan is used as disinfectant in household products such as detergents, mouthwash, soaps, and cosmetics [12] whereas caffeine is a stimulant [13]. All these chemical species have known toxicity in aquatic environment while some are banned in developed countries such as carbofuran but still used in Pakistan. The objective of this study was to determine the level of these chemicals in the absence of sewage treatment and to assess any eco-toxicological risk to aquatic organisms in the rivers with these chemicals.

Materials and Methods

Chemicals and reagents

Standards for caffeine ($C_8H_{10}N_4O_2$) was acquired from Cerilliant (Round Rock, Texas), TCS ($C_{17}H_7Cl_3O_2$) from AVONCHEM, and Carbaryl ($C_{12}H_{11}NO_2$), methomyl ($C_5H_{10}N_2O_2S$), carbofuran ($C_{12}H_{15}NO_3$) and chlorpyrifos ($C_9H_{11}C_{l3}NO_3PS$) from Dr. Ehrenstorfer GmbtH (Ausburg, Germany). HPLC-grade methanol, formic acid and acetonitrile required for mobile phase were acquired from Merck (Germany). For individual compounds, stock solutions were prepared

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in methanol as 1000 mg/mL and stored at -18°C. Working standards for calibration were prepared from the stock solution by serial dilution in methanol.

Study area and sampling

Mardan district is situated at 34°12'0"N 72°2'24"E in Khyber Pakhtunkhwa (KP) Province, Pakistan with a total area of 1632 km^2 [14] (Figure 1). Untreated wastewater from the Mardan city is discharged into five major sewage drains falling into the perennial Kalpani stream. Besides, the stream collects agricultural drainage from a catchment area of 1023 km^2 up to Mardan and finally joins River Kabul at Nowshera District to the South. River Kabul originates in Paghman mountains in Afghanistan and enter Pakistan at Khyber Agency in the northwest [15]. It collects drainage (with wastewater discharges) from the densely populated areas of KP Province before finally merging with River Indus (Figure 1). River Indus originates in the Himalaya region and flows through the entire stretch of the country for a total length of 3000 km to the Arabian Sea [16]. Composite samples (at two hour interval) during the day were collected at two points each from River Kabul, River Indus and Kalpani stream and from the five sewage drains in Mardan (Figure 1). Sampling was carried out on dry days in the month of October when there was no rainfall event for at least 48 hours [17]. Samples were collected in 1 litre ultraclean amber-glass bottles pre-rinsed three times with the sample before collection [18]. Samples were immediately taken to the laboratory, stored in refrigerator at 4°C to avoid any degradation and analysed within 48 hours of sample collection [19]. Prior to sample collection, contact with detergent, soap, fragrance and sunscreen was avoided to prevent any interference from constituents in personal care products [17].

Sample preparation and analysis

The targeted compounds were analysed using liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis with Agilent triple quadrupole 6410 paired with Agilent 1200 series LC and C18 LC column [20]. Samples were first filtered through Whatman Glass fiber filters (GF/F 0.7 µm) followed by solid phase extraction (SPE) of the filtered samples (100 ml) using Oasis HLB cartridges [3,19]. Before extraction, cartridges were conditioned with 4 ml methanol followed by addition of 6 ml deionized water at 5 ml/min keeping the sorbent wet. Samples were passed through cartridges at 10 ml/min. Target compounds were collected in test tubes by elution with 5 ml methanol [20]. Extracted samples were further concentrated to a final volume of 500 µl using a gentle nitrogen gas stream [3,20]. The test tubes were then vortex mixed to dissolve any target compounds on the walls of the tube. Samples were then transferred to a 2 ml vial for LC-MS/MS analysis. Nitrogen gas was used as carrier gas and regulated at uniform flow rate of 11.0 ml/min. Except TCS, the analysis was in positive (ESI+) mode for carbaryl, methomyl, carbofuran, chlorpyrifos and caffeine analytes (Table 1). Temperature of the column was kept at 35°C and the flow rate at 0.5 ml/min. The injected sample volume was 10 µL. For determination of compounds of interest, mobile phase A (0.1% formic acid in deionized water) and mobile phase B (0.1% formic acid in acetonitrile) were used. For the results, standard deviation was used to show the standard error. Data analysis was performed using GraphPad Prism software (GraphPad Software, Inc., San Diego, CA, USA)

Quality control

For quality control, blank and spiked samples (150 to 1,000 ng/L) were run with each extraction round of six samples. Relative recoveries were computed from these samples. Calculation for limits of quantification (LOQ) were made as 10X the standard deviation of the blank values or as signal-to-noise ratios of 10 in case where no significant blank signals were present for certain analytes [21].

Results and Discussion

Prevalence in sewage and Kalpani stream

In domestic wastewater, both PCPs (caffeine and TCS) were detected with caffeine in comparatively higher concentration of 92 ± 51 µg/L. Caffeine in sewage could be mainly sourced to tea consumption. In Pakistan, caffeine intake in tea is reported as 150 mg/person/day and of this, 3% is usually excreted in urine [22,23]. Caffeine levels found in sewage in this study were similar to those in other countries such as 7 to 73 µg/L in Switzerland and 33 µg/L in the U.S. [24,25]. However, caffeine discharged into water bodies could be much higher in the absence of any sewage treatment in Mardan. Sewage treatment plants have been reported to reduce caffeine concentration by 90% [26]. TCS in sewage was detected as 4 ± 1 ng/L which was lower compared to the levels usually found in

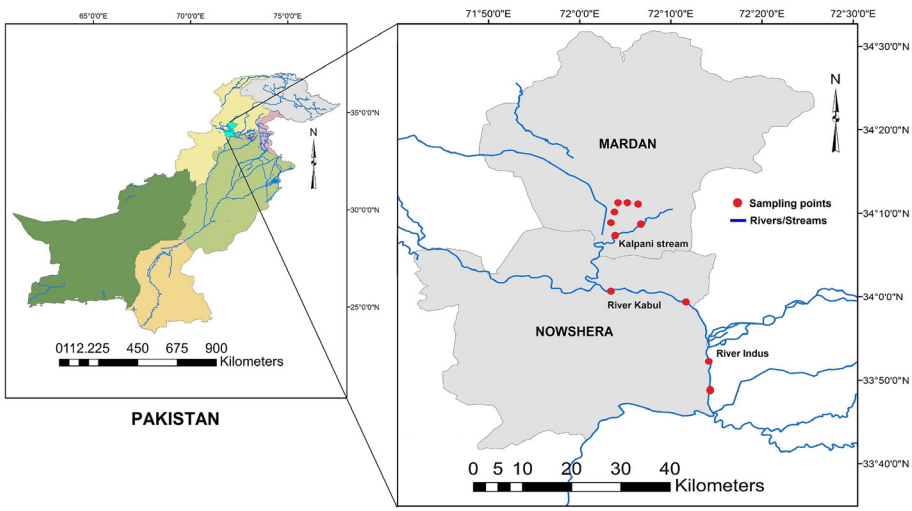

Figure 1: Study area and sampling points.

sewage in other countries, for instance 3.8 µg/L in U.S and 4.9 µg/L in Greece [25,27]. Meanwhile, the discharge of such effluent without treatment to surface water bodies and seepage from unlined and broken sewage drains into groundwater poses a serious concern. In the local Kalpani stream, the presence of caffeine and TCS at 8.4 ± 4.6 µg/L and 0.005 ± 0.001 µg/L respectively, seemed in conformity with the load received in domestic wastewater (Figure 2). Whereas among pesticides, methomyl was detected in higher concentration (5.5 ± 0.1 µg/L) compared to the other target pesticides that were present in nano gram range (Figure 2). Pesticides in Kalpani stream were mainly sourced from agriculture drainage received from the catchment area. In principal, levels of all the target compounds in Kalpani stream were below the respective toxicity threshold i.e., lethal concentration (LC_{50}) or effective concentration (EC_{50}) for fish, daphnia and algae [28-33]. Nevertheless, at these levels, potential eco-toxicological risks can be posed to aquatic life in the stream, which is discussed in Section 3.2. In addition, seepage of these compounds to groundwater from excessive field application and reuse of the stream's water for irrigation downstream is also a concern. In groundwater in the study area, presence of pesticides (chlorpyrifos, dichlorvos, endosulfan and methyl parathion) has been confirmed by Ahad et al. [34].

Pesticides in River Kabul and Indus

In principal, River Kabul had higher levels of target pesticides compared to River Indus. In both rivers, the occurrence of pesticides based on concentration was in the same order as found in Kalpani stream i.e., methomyl>chlorpyrifos>carbofuran>carbaryl. On one hand, this endorsed the intensive use of pesticides in the region and on the other, established the load received from local tributary streams. Compared to Kalpani stream, concentrations of methomyl, as well as caffeine and TCS increased in River Kabul, which shows the load received from other major towns in the region such Peshawar and Nowshera. The pesticide found in critical concentration was methomyl in River Kabul (max. 8.3 µg/L), which is reported to cause toxicity to water fleas at 7.6 µg/L [35]. For other pesticides, the values were below the respective LC_{50} or EC_{50} levels. Methomyl concentrations in both rivers was also found on the higher side compared to rivers in some other countries (Table 2). On the contrary, the other three pesticides had comparatively lower prevalence.

PCPs in River Kabul and Indus

Among the PCPs, caffeine in both rivers was found on the higher side of the reported levels in other countries (Table 2). As discussed earlier, caffeine concentration found in sewage was equivalent to those reported in literature for these countries; however, the increased difference in rivers indicated the role played by sewage treatment in reducing the caffeine concentrations disposed of into water bodies in these countries. TCS concentration on the other hand, in both rivers were mostly in agreement to those detected elsewhere e.g., Europe, America and China (Table 2). In comparison to LC_{50} or EC_{50} of caffeine and TCS for aquatic organisms, the levels observed in both River Kabul and Indus were lower [28,43].

Compound	Retention time (min)	Precursor Ion (m/z)	Product ions (m/z)	Fragmentor (V)	Collision Energy (e/v)	Ionization mode
Carbaryl	5.008	202 202	145 115	50	3 40	Positive
Methomyl	1.27	163 163	106 88	80	5 5	Positive
Carbofuran	4.82	222	123	120	15	Positive
Chlorpyrifos	7.34	352	296 200	125	12	Positive
Caffeine	0.59	195 195	138 110	110	15 25	Positive
TCS	6.80	289 287	37 35	75	5 5	Negative

Table 1: Optimized LC-MS/MS conditions for the target compounds.

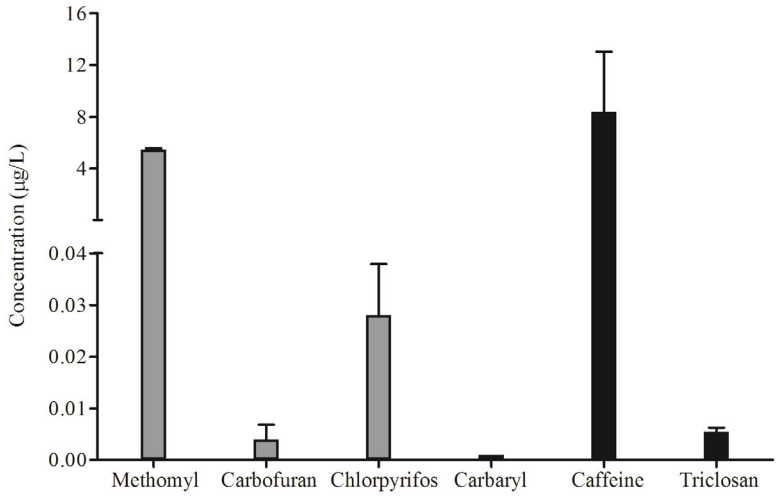

Figure 2: Pesticides and PCPs in Kalpani stream (µg/L ± SD).

Compounds	Concentration (µg/L)			Reference
	River Kabul	River Indus	Rivers in other countries	
Methomyl	5.50 ± 3.90	0.2 ± 0.03	<0.1 Croton River, USA	[36]
Carbaryl	0.001 ± 0.000	0.001 ± 0.001	<0.01 Shinano River, Japan	[37]
Chlorpyrifos	0.009 ± 0.003	0.007 ± 0.000	0.11 Lake Vistonis Basin, Greece	[38]
Carbofuran	0.003 ± 0.003	0.005 ± 0.001	0.025 Buenos Aires Souteast Basin, Argentina	[39]
Triclosan	0.002 ± 0.001	0.002 ± 0.001	0.001-0.034 Europe and America 0.012 Liuxi River, China	[19,40]
Caffeine	30.20 ± 28.30	8.0 ± 0.2	0.087 Danube River, Italy 0-0.038 Mississippi River, USA	[41,42]

Table 2: Comparison of levels detected in River Kabul and Indus to rivers in other countries.

Compounds	PNEC (LC_{50} or EC_{50}/1000) (µg/L)			References
	Water flea	Algae	Fish	
Methomyl	0.009	50	1.16	[30,46]
Carbaryl	0.0031	0.6	0.5	[31,47]
Chlorpyrifos	0.0009	0.33	0.001	[32,48]
Carbofuran	0.002	4.65	0.224	[33,49]
Triclosan	0.26	0.0007	0.4	[28,43]
Caffeine	182	>150	87	[29,50]

Table 3: PNEC of target compounds for water flea, algae and fish.

Compounds	RQ for River Kabul			RQ for River Indus			RQ for Kalpani stream		
	Water flea	Algae	Fish	Water flea	Algae	Fish	Water flea	Algae	Fish
Methomyl	629*	0.11	4.77*	23.01*	0.00	0.017	622*	0.11	4.72*
Carbaryl	0.38	0.00	0.002	0.149	0.00	0.001	0.38	0.00	0.00
Chlorpyrifos	9.72*	0.03	6.73*	7.500*	0.02	5.19*	30.6*	0.08	21.2*
Carbofuran	1.45*	0.00	0.013	2.750*	0.00	0.025	1.89*	0.00	0.02
Triclosan	0.01	3.33	0.006	0.006	2.38	0.004	0.02	7.61*	0.01
Caffeine	0.17	0.20	0.347	0.044	0.05	0.092	0.05	0.06	0.10

*RQ higher than 1

Table 4: Risk Quotient (MEC/PNEC) for River Kabul and River Indus.

Eco-toxicological risk assessment

Eco-toxicological risk associated with the presence of targeted compounds in both River Kabul and Indus as well as in Kalpani stream was evaluated by estimating the risk quotient (RQ). Whereas, RQ is the ratio between measured environmental concentration (MEC) in the rivers i.e., the concentrations (average) detected in this study and the predicted no-observed-effect concentration (PNEC) of the compounds from literature below which an unacceptable effect will unlikely occur [44]. PNEC values were based on LC_{50} or EC_{50} Values for water flea, algae and fish as reported in literature (Table 3). An assessment factor of 1000 (i.e., PNEC=LC_{50} or EC_{50}/1000) was applied to take into account toxicity to other more sensitive aquatic species [45]. A compound is judged to cause adverse effects if the RQ>1.

As shown in Table 4, except carbaryl and caffeine, a higher risk was associated with the presence of target compounds in the water bodies. Of concern were methomyl and chlorpyrifos having RQ>1 for fish and water fleas and carbofuran with RQ>1 for water flea in both rivers and Kalpani stream. The relative risk vulnerability for methomyl and chlorpyrifos was assessed as water flea>fish. For TCS, the risk characterization in Kalpani stream showed RQ>1 only for algae. A higher RQs with these compounds indicated a potential threat to the aquatic organisms in these aquatic bodies. The RQ values were relatively higher in Kalpani stream and River Kabul that showed a higher eco-toxicological risks in these two water bodies. In addition, parts of these chemicals can also accumulate in the sediments and hence the risk posed due to both aqueous and particulate phase could be more significant [46-50].

Conclusions

This study determined the presence of selected PCPs and pesticides in River Kabul, River Indus, Kalpani stream and domestic effluent in Mardan. Among the pesticides, methomyl was found in highest concentration in sewage and in rivers while caffeine and TCS were detected in all samples. The levels found in domestic wastewater were comparable to those in advanced countries but environmental discharge was considerably higher in the absence of sewage treatment. Concentrations of methomyl, caffeine and TCS increased in River Kabul compared to Kalpani distributary indicating a higher contribution from other towns. In Rive r Kabul, methomyl was detected above the reported LC_{50} for water flea. Caffeine, TCS, carbofuran, chlorpyrifos and carbaryl were also present in the rivers but below their LC_{50} levels.

From the environmental risk assessment, except for carbaryl and caffeine, RQ was>1 for methomyl, chlorpyrifos and carbofuran for water flea and fish in all three water bodies and in case of TCS for algae in Kalpani stream. The risk characterization indicated a serious eco-toxicological threat to aquatic organisms in both the rivers and Kalpani stream.

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