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Determination of Pesticide Residues in Sediments of River Ravi

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ABSTRACT

Sediments are socioeconomic, geomorphologic, and an important environmental resource. The purpose of this study was to determine the pesticide residues in the sediments of River Ravi. For analysis 12 sediment samples were collected along with River Ravi, reaching from Ravi Siphon to BS (Balloki Suleiman) link. River Ravi is enlisted as one of the most polluted rivers of Pakistan followed by extreme flow variations, i.e. 10 – 10,000 m^3/s. The concentration of pesticide residues in samples was detected by the High-pressure liquid chromatography (HPLC) technique. Noticeable concentrations of pesticides were detected in the majority of the samples which depicted high toxicity levels of pesticides in the sediments of River Ravi. High amounts of pesticides were observed in the right and left banks of Saggian (S4) i.e. 11.37 mg/kg and Khudpur (S6, S7) i.e. 12.116 mg/kg. A significant amount of Imidacloprid and Bifenthrin was detected in the majority of the sediment samples, i.e. 22.78 mg/kg and 15.82 mg/kg. Furthermore the detected concentration of pesticides in the right and left bank of Balloki head works (S10, S11) and Ravi Bridge (S3) was relatively less as compared to other sampling sites. All these sampling points receive irrigational runoff from nearby agricultural lands and urban wastewater, resulting in the accumulation of pesticides in the sediments. The following trend of pesticide contamination was observed in the sediment samples of River Ravi, Bifenthrin > Imidacloprid > Dimethomorph > Glyphosate.

INTRODUCTION

Sediments are socioeconomic, geomorphologic, and an important environmental resource. They play an important role in our ecosystems and are stated as a tool of nature (Silva et al., 2020). Pollution in sediments is caused by several points and non-point sources. Accumulation of resistant pollutants in the sediments imposes a serious threat to the quality of river water and causes contamination through desorption and other processes that make the contaminants mobile (Chahinian et al., 2012) Polluted sediments make rivers their sink of contamination. Accumulation of pesticides in sediments of a river is a major environmental concern because of their persistent nature and adverse effects on aquatic flora, fauna, and humans (Net et al., 2014). Pesticides by definition are agents that are primarily used in agriculture to kill harmful organisms in the field and to protect crops from various diseases. Since human development, environmental pollution caused by the use of a wide range of different compounds has increased to a large extent. In modern agriculture, the use of pesticides has become an important part of the system. Despite its usage complications, the use of pesticides is not under control, hence its becoming a major environmental contaminant (Radiovic et al., 2015, Eqani et al., 2011). Pakistan is consuming pesticides for the last 50 years in agricultural fields in large quantities to mainly control agricultural pests, insects, termites, etc. Pesticides are still being frequently used for different activities because of their low prices and high efficiency. The use of DDT was banned years ago because of its detrimental effects but unfortunately, it is still being used in many developing countries, including Pakistan (Eqani et al., 2011). In developing and developed countries variety of insecticides, fungicides, herbicides, and bactericides are being used. The usage pattern of

pesticides specifically depends upon locality, and climate user needs. The use of organochlorine insecticides is still observed in developing countries but according to some studies, the use of these insecticides is being replaced by organophosphate, carbamate, and pyrethroid insecticides (Edwards, 2013). The estimated usage of pesticides during the years (2017 – 2020) at the global level is approximately 2.7 kg/ha. The use of pesticides in a non-regulated manner has led to serious environmental and health issues. Immunity among pests is increasing due to over usage of pesticides. The Lethal nature of pesticides is difficult to reduce because they are more soluble in water, polar in nature, and have higher thermal stability. Organochlorines, which are considered least biodegradable, are used much in Pakistan; however, they are banned in several countries (Popp et al., 2013).

Lately, a study in Lahore was conducted to study the organochlorine pesticides from the sediments of River Chenab and this river is also linked with River Ravi. The results detected that HCH pesticide was most abundantly found i.e. 63% and DDD as 56%. High frequencies of DDT metabolites were found in winters followed by DDT isomers being more prevalent in the summer season (Eqani et al., 2011).

Despite some early research, still have limited understanding of the presence, distribution, and methods of detection, removal, and impacts of these persistent compounds i.e. different types of pesticides. A comprehensive understanding of these contaminants is the need of the hour so that appropriate policies can be regulated; hence this study aims to determine the pesticide residues in the surface sediments of River Ravi.

METHODS

Lahore is the largest city of the five major cities of Pakistan. Lahore a metropolitan city is situated at 31.5204 degrees north, and 74.3587 degrees east (Akhtar et al., 2014). The River Ravi enters Pakistan near Jassar and meets with the river Chenab and it has been serving Lahore for a very long time. River Ravi is enlisted as one of the most polluted rivers of Pakistan followed by extreme flow variations, i.e. 10 – 10,000 m^3/s. 12 sediment samples were collected along with River Ravi, reaching from Ravi Siphon to Balloki headworks at the selected reachable location.

Primary data was collected through field visits to the selected sites. 12 sediment samples were collected along with River Ravi, reaching from Ravi Siphon to Balloki headworks at the selected reachable location. All the samples were collected in plastic bags with proper labeling. The samples collected from the selected areas were a laboratory for the determination of physicochemical parameters, and pesticide residues. The analysis of pesticides was done by HPLC Technique.

Table 1. Sampling codes along with their locations

Sample Name	Sample Identity	Sampling Site
Sediment Sample	S1	Ravi Siphon Right Bank
Sediment Sample	S2	Ravi Siphon Left Bank
Sediment Sample	S3	Ravi Bridge
Sediment Sample	S4	Saggian Right Bank
Sediment Sample	S5	Saggian Left Bank
Sediment Sample	S6	Khudpur Right Bank
Sediment Sample	S7	Khudpur Left Bank
Sediment Sample	S8	Mallah da Dera Right Bank
Sediment Sample	S9	Mallah da Dera Left Bank
Sediment Sample	S10	Ravi Balloki Headworks Right Bank
Sediment Sample	S11	Ravi Balloki Headworks Left Bank
Sediment Sample	S12	BS link

Source: Sample coding (primary data)

The physiochemical properties of sediments samples were determined by using standard methods. Sediment pH and electrical conductivity (EC) were measured using the portable combined

meter (Eutech Instrument Pc 510). For precise results, the process was repeated thrice with sediment sample quantities as (5g, 10g, and 15g).

After the collection of samples, the sediment samples were sun-dried and impurities were removed from them for further analysis. 5 grams of each dried sample will be weighed separately in a beaker to prepare a solution by adding 5g of NaCl, 20ml of dichloromethane (DCM), 20ml of ethyl acetate, and 150ml of distilled water. After that in each solution, a magnet was placed and was stirred for at least 20 minutes with the help of a magnet stirrer then the solution was allowed to stand for 5 minutes and was filtered. 20ml of ethyl acetate and dichloromethane (DCM) was added again into the sample solution and then was allowed to separate by using a separating funnel. After some time two distinct layers were formed one of organic content and the other of aqueous content. The organic layer was separated and placed in a rotary evaporator. The rotary evaporator was pre-heated for at least 20 minutes before placing the rotary flask containing the sample. After that rotator and vacuum were set up. When the evaporation of the sample was completed then a vacuum was released and 10ml of methanol was added to the sample. It was shaken well and stored in the vial for further analysis on High Pressure Liquid Chromatography (HPLC). Standard solutions were prepared by adding 20ml of methanol into 10 grams of pesticide to be detected and stirred for 20 minutes. After stirring, the solution was filtered. The filtrate was placed in the vial and was allowed to run through High Pressure Liquid Chromatography.

RESULTS AND DISCUSSION

The importance of sediment quality has been enough emphasized in this article. Physiochemical analysis and the use of pesticides and fertilizers are important factors in determining the quality of sediments. pH of sediments represents the acidity and alkalinity of the soil. The levels of pH range from 0 to 14. The measured pH of all the collected sediment samples ranged from 7.25 to 8.59. Results of pH are shown in Table 2 of all the collected sediment samples, observed pH ranged from moderate to high, not all the pH values were within the permissible limits. pH controls various microbial activities within the sediments and they also determine the persistence of the settled contaminants.

Table 2. pH and electrical conductivity of sediment samples

Serial No.	Sample	pH	EC (μS/cm)
1.	S1	8.11	54.7
2.	S2	7.51	304.6
3.	S3	7.25	255
4.	S4	7.38	92.2
5.	S5	7.39	34
6.	S6	7.52	90
7.	S7	7.32	1103
8.	S8	7.35	98.6
9.	S9	7.48	81
10.	S10	7.43	80
11.	S11	8.59	45
12	S12	7.42	31

Source: Analyzed results of sediment samples (pH and electrical conductivity)

Electrical conductivity is the measure of the amount of electric current a substance can carry; conductivity is an intrinsic property of a material. In terms of sediments, according to the given guidelines, a good electrical conductivity level lies between 200μS/cm and 1200μS/cm. However, if the measured EC is below 200μS/cm it states that the soil doesn't have enough nutrients and the area is not fertile because of little microbial activity, and above 1200μS/cm can indicate that too many nutrients are present in the sediments, which might affect the overall growth activities. Table 2 explicates the measured EC values of all collected sediment samples and the values ranged from 31μS/cm to 1103μS/cm of 12 different samples, showing noticeable variation (Singare et al., 2011).

Quantitative Analysis

Quantitative analysis was done to determine the concentration of pesticides in sediment samples of River Ravi. Quantification of pesticide residues is important to evaluate human health risks. For quantitative analysis response factor was calculated using the following formula.

Calculation of response factor:

Response factor = Peak Area / Standard Amount

Whereas,

Peak Area = Peak area of standard

Standard Amount = Amount of standard used in solvent

Pesticides are agrochemical and they are widely used in agricultural fields for pest control and to protect plants and crops from various diseases. Many international organizations have set maximum residual limits for intake of a broad range of pesticides which in case of exceeding limits could pose serious health risks (Nicolopoulou et al., 2016). 12 sediment samples were collected along with River Ravi, reaching from Ravi Siphon to Balloki Headworks. They were analyzed in the laboratory and pesticide residues were detected in the majority of the sediment samples. Table 3 shows the concentration of pesticides in the sediment samples. According to the analyzed results, noticeable concentrations of pesticide residues were detected in the majority of the sediment samples.

Table 3: Concentration of pesticides in sediment samples

Sample Name/Code	Amount of Imidacloprid in samples (ppm)	Amount of Bifenthrin in samples (ppm)	Amount of Dimethomorph in samples (ppm)	Amount of Glyphosate in samples (ppm)
Sediment Sample/S1	X	8.33	2.41	X
Sediment Sample/S2	X	X	X	X
Sediment Sample /S3	X	2.78	X	X
Sediment Sample /S4	11.37	X	X	X
Sediment Sample /S5	X	X	X	X
Sediment Sample /S6	X	9.93	X	X
Sediment Sample /S7	X	X	0.866	1.32
Sediment Sample /S8	X	X	X	X
Sediment Sample /S9	X	X	X	X
Sediment Sample / S10	X	1.74	X	X
Sediment Sample / S11	1.92	X	4.87	X
Sediment Sample / S12	2.53	X	X	0.882

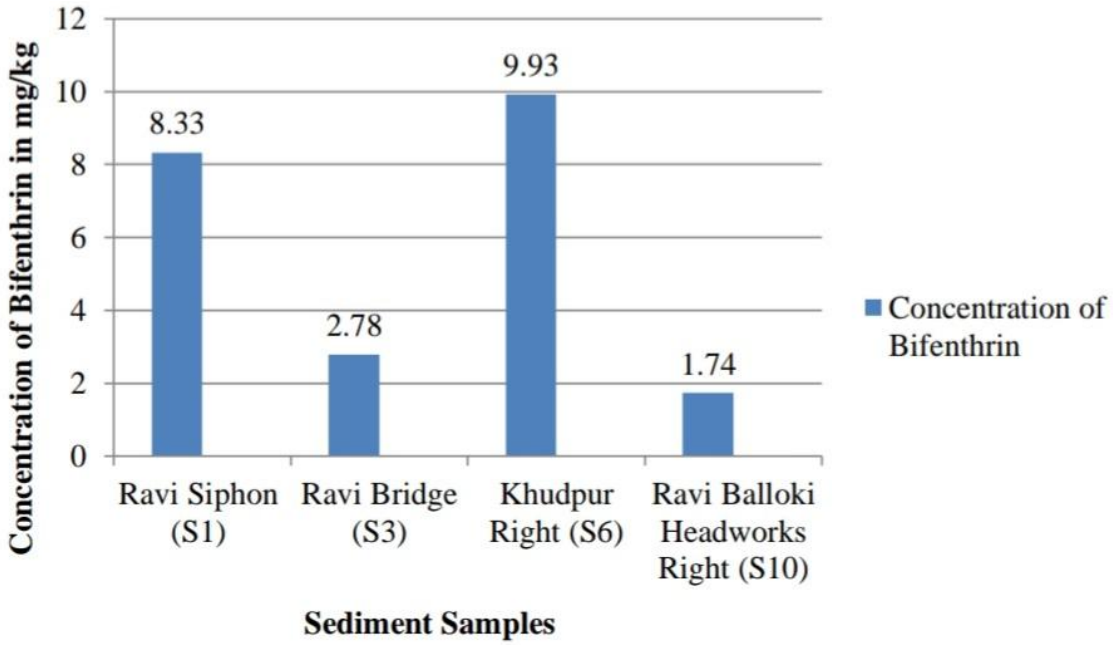
Source: Analyzed results of sediment samples (pesticide residues)

12 sediment samples were collected along with River Ravi, reaching from Ravi Siphon to Balloki Headworks. They were analyzed in the laboratory and pesticide residues were detected in the majority of the sediment samples. Table 3 shows the concentration of pesticides in the sediment samples. According to the analyzed results, noticeable concentrations of pesticide residues were detected in the majority of the sediment samples.

Graphical Representation of Pesticides Results

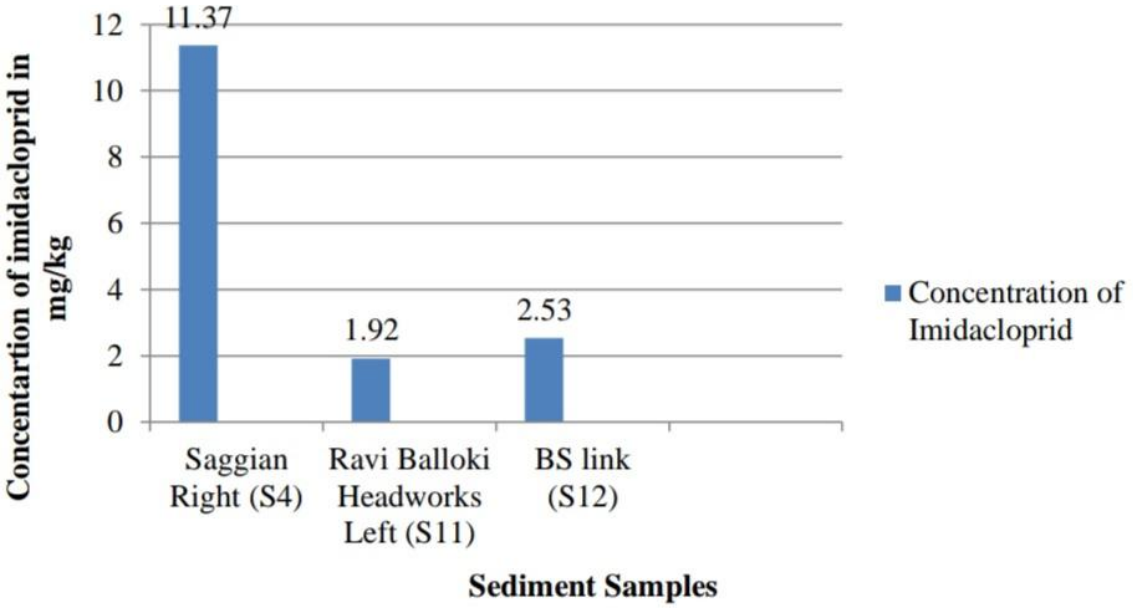
Following are the graphs showing the concentration of pesticides in sediment samples of River Ravi.

Figur 1. The concentration of Bifenthrin in mg/kg in sediment samples



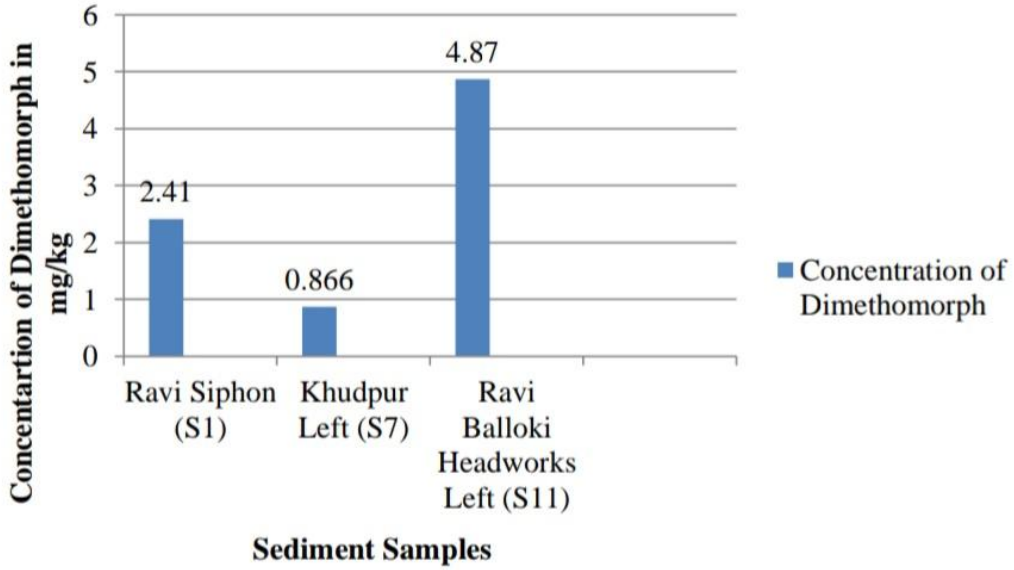
Residues of bifenthrin were found in 3 sediment samples, i.e. Ravi Siphon (S1) had 8.33 mg/kg, Ravi Bridge (S3) had 2.78 mg/kg and the right bank of Khudpur (S6) sediment sample had 9.93 mg/kg and right bank of Ravi Balloki headworks had 1.74 mg/kg of pesticide respectively.

Figure 2. The concentration of Imidacloprid in mg/kg in sediment samples



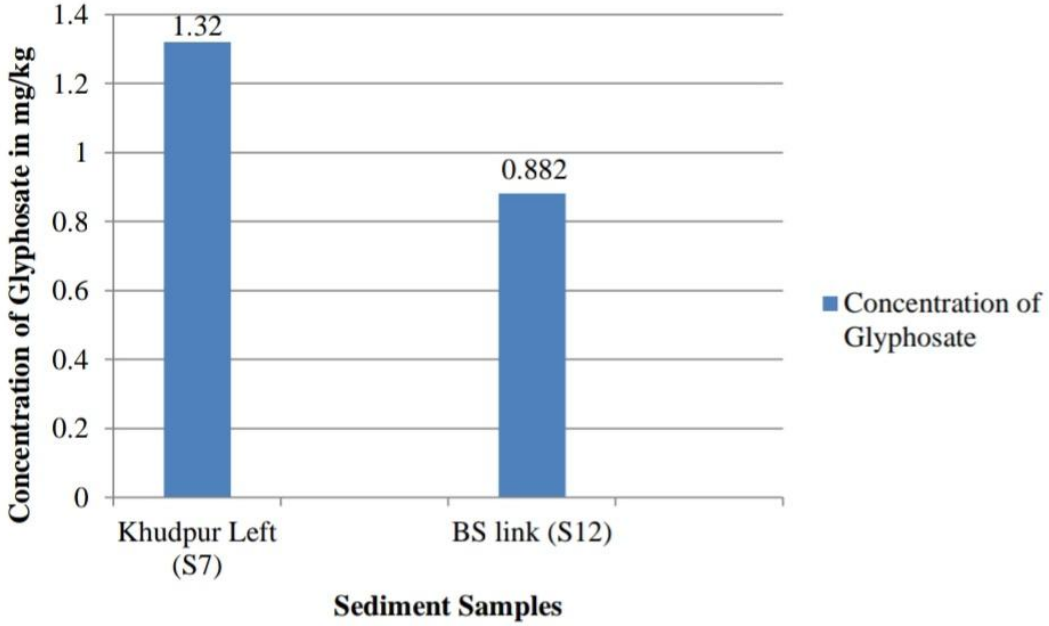
Imidacloprid concentrations were found in 3 sediment samples i.e. Right bank of the Saggian (S4) sample had 11.37 mg/kg, the left bank of Ravi Balloki Headworks had 1.92 mg/kg, and the BS link (S12) sediment sample had 2.53 mg/kg of the pesticide.

Figure 3. Concentration of Dimethomorph in mg/kg in Sediment Samples



Dimethomorph concentration was detected in 3 sediment samples i.e. Ravi Siphon (S1) had 2.41 mg/kg, the Left bank of Khudpur (S7) sample had 0.866 mg/kg, and the left bank of Ravi Balloki Headworks had 4.87 mg/kg of the pesticide respectively.

Figure 4. The concentration of Glyphosate in mg/kg in sediment samples



Glyphosate was detected in only 2 sediment samples i.e. left bank of Khudpur (S7) had 1.32 mg/kg and BS link (S12) had 0.882 mg/kg of the pesticide respectively. Imidacloprid is defined as a neonicotinoid insecticide and it is highly persistent in soil and sediments. It was detected in 3 different sediment samples i.e. 11.37 mg/kg in the right bank of Saggian (S4), 1.92 mg/kg was detected in the left bank of Ravi Balloki Headworks (S11) and 2.53 mg/kg in BS link (S12) sediment sample. Imidacloprid can leach into groundwater due to its mobility and solubility in water. It is used to control the population of pests, termites, and other sucking insects (Sardo, Soares, 2010). Dimethomorph is used as a fungicidal spray and is considered a toxic compound. The detected concentration of dimethomorph was 2.41 mg/kg in Ravi Siphon (S1), 0.866 mg/kg in the left bank of Khudpur (S7), and 4.887mg/kg concentration was observed in the left bank of Ravi Balloki Headworks (S11) sediment sample respectively. Dimethomorph does not hydrolyze and slowly photo degrades in water and

on surface sediments. It can easily enter into groundwater and surface water sources through the leaching process which can play role in widespread effects on humans and other terrestrial and aquatic species.

Bifenthrin is an insecticide and it is used in many agricultural activities. A noticeable concentration of this specific pesticide was observed in the collected sediment samples, Ravi Siphon (S1) had 8.33 mg/kg, 2.78 mg/kg was observed in Ravi Bridge (S3), the right bank of Khudpur (S6) had 9.93 mg/kg and right bank of Ravi Balloki Headworks (S10) had 1.74 mg/kg of the pesticide. Bifenthrin works by attacking the nervous system of the insects which results in the stunted production of ATPase enzyme hence causing the death of insects. Furthermore few studies reported that long-term exposure to this pesticide may cause nausea, sore throat, and irritation in the lungs among humans. Bifenthrin also has a high affinity for sediments and can be up taken by plants for a longer time (Ensiminger et al., 2013, Putt et al., 2005). Bifenthrin is hydrophobic and insoluble in water and can persist in sediments for about 8 to 17 months (Rogers et al., 2016). Glyphosate was only found in 2 sediment samples with concentrations of 1.32 mg/kg and 0.882 mg/kg in the left bank of Khudpur (S7) and BS (Balloki Suleiman) link (S12). Glyphosate is used to kill broadleaf plants and grasses. It may bind to the soil very strongly and can persist in sediments for up to 6 months depending on the climatic conditions (Peruzzo et al., 2008, Silva et al., 2020).

Pollution in the River Ravi, stretching from Ravi Siphon to BS link is mainly due to agricultural and urban activities in the nearby areas. Also, the River Ravi flows through densely populated and industrial cities. The river tributaries carry a huge burden of various industrial and municipal effluents. Degh and the Hudiara drain contribute a significant amount of untreated wastewater from textile mills, leather processing units, tanneries, etc (Syed et al., 2014). The River receives wastewater from various industries without any prior treatment (removal/breakdown of pollutants), hence causing pollution stress in the tributaries and sediments of River Ravi. Noticeable pesticide contamination was observed in the sediment samples due to the uncontrolled use of pesticides in nearby agricultural lands, irrigational run-offs, urban wastewater, and industrial effluents. A significant amount of pesticides were found on the right and left bank of Khudpur, until this site, the River receives municipal and industrial wastewater from the city, of Lahore. Right and left banks (S6, S7) of Khudpur are located near Hudiara drain outfall point and it receives wastewater from 6 major wastewater outfalls of Lahore city eventually all the pollutants are released into River Ravi. Similarly, noticeable concentrations of pesticides were observed in the sediment samples of Ravi siphon, Ravi Bridge, Saggian (S4), and Ravi Balloki headworks (S10, S11) all these sampling points receive irrigational runoff from nearby agricultural lands and urban wastewater, resulting in the accumulation of pesticides in the sediments. The following trend of pesticide contamination was observed in the sediment samples of River Ravi, Bifenthrin > Imidacloprid > Dimethomorph > Glyphosate.

In 2012 Akhtar *et al.* reported severe contamination in the sediments of river Ravi stretching from Shahdhara to Balloki Headworks. Sampling sites near Hudiara drain were found to be severely contaminated by pesticides (DDT, DDE, Endosulfan, and Carbofuran). Furthermore, the study concluded significant concentration of pesticides was observed due to high pollution stresses on river tributaries caused by agricultural runoff, industrial effluents, and seepage lagoons around these reservoir bodies. Negative effects on fish species were also discussed in this research as a varying amount of industrial effluents, pesticides tend to accumulate in fish, resulting in detrimental diseases (Akhtar et al., 2012). The presence of persistent pollutants in the sediments of River Ravi greatly affects the microbial activity and potentially affects the quality of river water too, making the aquatic environment unfit for the species by altering the pH and other physiochemical characteristics of water. Hence it is important to regularly monitor the quality of sediments. In the case of pesticides, Integrated Pest Management (IPM) is the best practice to control the use of all kinds of pesticides (Akhtar et al., 2012).

CONCLUSION

The study revealed the condition of the sediments of River Ravi. Pesticide contamination was observed in the majority of the collected samples. Noticeable concentrations of pesticides

were detected which depicted high toxicity level of pesticides in the sediments of River Ravi stretching from Ravi Siphon to BS (Balloki Suleiman) link. A significant amount of pesticides were found in the right and left bank of Khudpur, The detected concentration of dimethomorph was 0.866 mg/kg and 0.882 mg/kg of glyphosate pesticide in the left bank of Khudpur (S7), the right bank of Khudpur (S6) had 9.93 mg/kg of the Bifenthrin pesticide. The right and left banks (S6, S7) of Khudpur are located near Hudiara drain outfall point and it receives the wastewater from 6 major wastewater outfalls of Lahore city eventually all the pollutants are released into River Ravi. Similarly, noticeable concentrations of pesticides were observed in the sediment samples of Ravi siphon, i.e. 2.41 mg/kg of dimethomorph, and 8.33 mg/kg of bifenthrin. Saggian (S4) had 11.37 mg/kg of Imidacloprid. Furthermore, the detected concentration of pesticides in the right and the left bank of Balloki head works and Ravi Bridge was relatively less as compared to other sampling sites. All these sampling points receive irrigational runoff from nearby agricultural lands and urban wastewater, resulting in the accumulation of pesticides in the sediments. The following trend of pesticide contamination was observed in the sediment samples of River Ravi, Bifenthrin > Imidacloprid > Dimethomorph > Glyphosate.

REFERENCES

1. Akhtar M, Mahboob S, Sultana S, Sultana T. (2012). Assessment of pesticide residues in sediments collected from river Ravi and its tributaries between its stretches from Shahdara to Balloki headworks, Pakistan. *Journal of Biology, Agriculture and Healthcare*. (2):127-33.
2. Akhtar MM, Tang Z, Mohamadi B. (2014). Contamination potential assessment of potable groundwater in Lahore, Pakistan. *Polish Journal of Environmental Studies*. 23(6):1905-16.
3. Chahinian N, Bancon-Montigny C, Caro A, Got P, Perrin JL, Rosain D, Rodier C, Picot B, (2012). Tournoud MG. The role of river sediments in contamination storage downstream of a wastewater treatment plant in low flow conditions: organotins, faecal indicator bacteria and nutrients. *Estuarine, Coastal and Shelf Science*. 114:70-81.
4. Edwards CA, editor. (2013). *Environmental pollution by pesticides*. Springer Science & Business Media.
5. Ensminger MP, Budd R, Kelley KC, Goh KS. (2013). Pesticide occurrence and aquatic benchmark exceedances in urban surface waters and sediments in three urban areas of California, USA, 2008–2011. *Environmental monitoring and assessment*.185(5):3697-710.
6. Eqani SA, Malik RN, Mohammad A. (2011). The level and distribution of selected organochlorine pesticides in sediments from River Chenab, Pakistan. *Environmental Geochemistry and Health*. 33(1):33-47.
7. Net S, Dumoulin D, El-Osmani R, Rabodonirina S, Ouddane B. (2014). Case study of PAHs, Me-PAHs, PCBs, phthalates and pesticides contamination in the Somme River water, France. *International Journal of Environmental Research*. 8(4):1159-70.
8. Nicolopoulou-Stamati P, Maipas S, Kotampasi C, Stamatis P, Hens L. (2016). Chemical pesticides and human health: the urgent need for a new concept in agriculture. *Frontiers in public health*. (4):148.
9. Peruzzo PJ, Porta AA, Ronco AE. (2008). Levels of glyphosate in surface waters, sediments and soils associated with direct sowing soybean cultivation in north pampasic region of Argentina. *Environmental Pollution*. 156(1):61-6.
10. Popp J, Peto K, Nagy J. (2013). Pesticide productivity and food security. A review. *Agronomy for sustainable development*. 33(1):243-55.
11. Putt AE. (2005). Bifenthrin Toxicity to Midge (Chironomus tentans) During a 10-d Exposure. Report, Springborn Smithers Laboratory Study. (13656.6106).
12. Radovic T, Grujic S, Petkovic A, Dimkic M, Lausevic M. (2015). Determination of pharmaceuticals and pesticides in river sediments and corresponding surface and groundwater in the Danube River and tributaries in Serbia. *Environmental Monitoring and Assessment*. 187(1):4092.
13. Rogers HA, Schmidt TS, Dabney BL, Hladik ML, Mahler BJ, Van Metre PC. (2016).

Bifenthrin causes trophic cascade and altered insect emergence in mesocosms: implications for small streams. *Environmental science & technology*. 50(21):11974-83.

14. Sardo AM, Soares AM. (2010). Assessment of the effects of the pesticide imidacloprid on the behaviour of the aquatic oligochaete Lumbriculus variegatus. *Archives of environmental contamination and toxicology*. 58(3):648-56.
15. Silva V, Gonzalez-Pelayo O, Abrantes N, Keizer JJ, Mol H, Ritsema C, Geissen V. (2020). Pesticide residues in vineyard soils and water-eroded sediments-predictions versus observations. InEGU General Assembly Conference Abstracts (p. 10656).
16. Singare PU, Trivedi MP, Mishra RM, Dagli DV. (2011). Assessing the physico-chemical parameters of sediment ecosystem of Vasai Creek at Mumbai, India. *Marine Science*. 1(1):22-9.
17. Syed JH, Malik RN, Li J, Chaemfa C, Zhang G, Jones KC. (2014). Status, distribution and ecological risk of organochlorines (OCs) in the surface sediments from the Ravi River, Pakistan. *Science of the total environment*. (472):204-11.