



Article Pesticide Contamination of Potable Water and Its Correlation with Water Quality in Different Regions of Punjab, Pakistan

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Abstract: The widespread use of pesticides leads to the contamination of groundwater, which harms environment and threatens life. The goal of the current study was to determine the degree of pesticide contamination of groundwater in agricultural regions with varying degrees of pesticide use. In 15 districts of the Punjab province of Pakistan, chemical residues of major pesticide groups including, neonicotinoids, organophosphates, carbamates and pyrethroids were detected in the water samples. Two most commonly used herbicides, isoproturan and diuron, were also tested but not detected in any of the water samples. Five districts in the southern Punjab/core area had highly contaminated groundwater due to the presence of residues from all major insecticide groups. Although less severe than in the core area, a different set of five districts in central Punjab also had significant water contamination issues. The districts located in marginal area had the lowest amount of insecticide residues. The highest levels of imidacloprid residues were identified in the core area throughout the winter season. Thiacloprid, fipronil, and acetamiprid were detected in nearly all water samples, with non-significant differences in concentrations throughout the summer and winter seasons, as well as in non-core and marginal areas. Different water quality parameters including, pH, electrical conductivity and temperature had varying degree of correlations with pesticide residues in water samples. Overall, it is concerning that significant insecticides are widely contaminating groundwater. This issue should be managed through integrated pest management, non-chemical pest control strategies, and judicious chemical use practices.

Keywords: pesticides; agro-chemicals; insecticides; water contamination; pollution

1. Introduction

The groundwater reserves of the Earth are recharged via the infiltration and percolation of surface water. Problems arise when the surface water to be filtered or percolated contains excessive amounts of pollutants. These pollutants contaminate the groundwater and reduce its quality. A large amount of infiltration takes place from agricultural fields. This water is loaded with multiple agricultural residues, especially pesticides. Globally, herbicides account for 49% of total pesticide applications, whereas fungicides accounts for 27% and insecticides account for 19% [1]. Pesticides are widely used in all the farming systems of Pakistan [2]. Pakistan imported pesticides worth USD 220 million in the 2019–2020 financial year [3]. Several studies have reported on the high mobility of some pesticides, with the infiltration and percolation of water from agricultural fields in Pakistan [4,5]. This might be due to the low organic matter contents of soils with variable texture, mineralogy, and low cation exchange capacities [6–10], and the use of pesticides with long half-lives [11] which may increase the mobility of pesticides into the groundwater. In addition, safe and judicious application methods are also not always followed due to various challenges associated with small landholding and the lack of mechanization in Pakistan.



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With increasing awareness about environmental issues associated with agrochemicals, researchers have started looking into this aspect and a few studies have already reported pesticide contamination in groundwater. For instance, pesticide residues were detected in groundwater from areas of intensive agriculture, especially in the cotton (Gossypium hirsutum L.) belt of Pakistan [12,13]. In another study, several pesticide chemicals, including monocrotophos, endrin, and cyhalothrin, were detected in the groundwater from the Faisalabad district, which lies in the mixed cropping area of Punjab province [14]. However, the concentrations of these pesticides were lower than the maximum residue limits. On the other hand, Tariq et al. [4] reported higher concentrations of monocrotophos, methyl parathion, and endosulfan in the groundwater of cotton-growing areas of Pakistan, where such chemicals have been and continue to be used heavily. Hence, the quality of groundwater is deteriorating over time due to pesticide contamination. This affects the groundwater used for drinking by the human population and makes them vulnerable to the harmful effects of pesticides. It may also affect other lifeforms, including livestock and wildlife, and the productivity of susceptible crops [15]. Herbicides, insecticides, and other chemicals are not found in isolation in nature, but rather in combination with other atoms in compounds. Overall, based on their acute toxicity, chlorpyrifos and cypermethrin are categorized as highly harmful (Class II). Since restrictions were implemented on the use of organochlorine pesticides such as dichlorodiphenyltrichloroethane, organophosphorus pesticides have been employed as insecticides. All the pesticides described above have negative effects on ecosystems, particularly on aquatic life and ground water reservoirs [16,17]. These pesticides have been outlawed in some parts of the world due to the hazardous effects of these toxins [18,19], but these policy frameworks are not strong enough in developing countries.

Unchecked usage has a negative impact on biodiversity, the environment, and human health by dispersing chemical pollutants from pesticide into soil, water, and food. Therefore, a straightforward, sensitive, focused, and fast sensor assay is needed in order to address the difficulties involved in the early detection of pesticides [13,20]. For accurate and effective detection, aptamer sensors represent a compelling option in the management of biowaste. Aptamer sensors have recently attracted the attention of researchers and technologists as the preferred method for detecting small molecules because they satisfy a number of requirements, providing less expensive, faster, simpler, easier, and more sensitive detection [21–25]. Other methods include fluorescence-based and label-free noncanonical G4-quadruplex-like DNA biosensors, DNA aptameric sensors, and aptameric fluorescent biosensors, which are all used to detect and treat toxic compounds released into water and food from pesticides [26–28].

Small, localized studies have explored this important issue as described above, but the extent of pesticide contamination of groundwater is unclear on large scale in the largest agricultural province of Pakistan, Punjab. Therefore, in the present study, we evaluated the presence of pesticide residues in the groundwater of 15 districts the Punjab province, belonging to areas with different cropping systems and historical pesticide use patterns. The objective was to explore the full extent of pesticide contamination in different areas and evaluate how contamination was correlated with the water quality parameters. The results of the current study will provide crucial information to farmers and policymakers about the scale of the pesticide contamination problem and emphasize the need for better integrated pest management practices.

2. Materials and Methods

2.1. Selection of the Study Area

The study area was selected after a public survey. It comprised a questionnaire including questions related to the use of pesticides, the type of pesticides used, pesticide application methods, the awareness of farmers about the hazards of pesticides, the use of safety measures, water used for drinking, and the epidemiological data of people facing pesticide-related health issues. As pesticide use in cotton crops accounted for 70% of total pesticides used in Pakistan, the survey area comprised cotton growing areas of Punjab

province, Pakistan. It contained 15 districts, divided into 3 regions: core area, non-core area, and marginal area, based on the relative acreage of cotton in those areas. The core area included the districts of Vehari, Bahawalpur, Bahawalnagar, Khanewal, and Multan. The non-core area included the districts of Jhang, Faisalabad, Sahiwal, Chiniot, and Toba Tek Singh. The marginal area included the districts of Rawalpindi, Sargodha, Sheikhupura, Gujranwala, and Lahore (Figure 1).



Figure 1. A map showing the sampling sites in different districts across the three major areas/regions selected for the study. Fifteen major districts were selected for the sampling of groundwater for the analysis of pesticide residues.

The weather patterns varied across the different districts. Total annual rainfall for the year 2018 and the mean temperature during the sampling moths of January and July in that year are presented in Figure 2. The average evaporation did not vary much during January (winter), falling in a narrow range between 3.5 and 3.8 mm per day across all 15 districts. However, the daily average evaporation during July (summer) varied in a wider range, between 6.8 and 11.4 mm per day.

A total of 900 water samples were collected from 10 collection sites in each of the 15 districts in two seasons (winter and summer) of the year 2018. Three replicate samples were obtained from each site in both seasons. Sampling sites included both farming areas and residential areas within farming lands. The locations of sampling sites were recorded with a global positioning system. The samples were taken from taps, hand pumps, and roadside tube wells in all districts. All these outlets extracted water from the groundwater table at depths of 30 to 60 m. The samples were taken within a 10 km radius of the nearest major town and the distance from sample to sample was 2 km each. Plastic bottles of 1 L in volume were used for the collection of samples. The bottles were prepared for sampling via



repeated rinsing with distilled water and drying in an oven. Water was filled to the top of the bottle to minimize the headspace. Then, the bottles were screwed, sealed, and labeled.

Figure 2. Total annual precipitation (whole year) and mean monthly temperature (during the sampling months of January and July) in 2018 across the 15 districts of Punjab.

2.2. Determination of Water Quality Parameters

Water quality parameters of the water samples were measured on the sites using a portable device (Hanna HI 9811-5, Hanna Instruments, Adelaide, Australia) [29]. These parameters included pH, temperature, electrical conductivity (EC), and total dissolved salts. After the determination of quality parameters on the sites, the samples were safely transported to the laboratory at the Department of Environmental Sciences, Government College University, Faisalabad. The samples were stored in the refrigerator at 4 °C to prevent any type of microbial growth and retained for the analysis of pesticide residues.

2.3. Extraction of Pesticide Residues from Samples

The method described by Asi et al. [30] was used, along with some modifications for the extraction of pesticide residues from water samples (Table 1). One liter of each water sample was used for pesticide extraction using the solid-phase extraction method. Solidphase extractor cartridges (Lichrolute C18 silica cartridge, Merck, Darmstadt, Germany) were pre-conditioned with different organic solvents, viz., acetone, ethyl acetate, methanol, ethyl ether, and acetonitrile (3 mL each) at a flow rate of 1 mL/min and a pressure of 10 mm/Hg. The cartridges were dried in a vacuum and then the 1 L volume of each sample was passed through the cartridges under a vacuum (flow rate: 1 mL per min; pressure: 10 mm per Hg). Cartridges were dried for one hour under a vacuum at a pressure of 30 mm per Hg. Pesticide residues were eluted from cartridges using organic solvents, including acetone, ethyl acetate, methanol, and acetonitrile (5 mL each). The cumulative volume of elution was obtained for further analyses.

2.4. Evaporation of Water Extract

A rotary evaporation apparatus (RE 400) was used for the concentration of the cumulative volume of each water sample extract. The extract of each sample was poured into round-bottom flasks at a temperature of 40 °C–60 °C up to dryness. The dried extract was dissolved in organic solvent (2 mL volume for each sample). The solvent in the vial was evaporated to dryness using a nitrogen stream.

Pesticide	Analysis Methodology
Neonicotinoids	The mobile phase of acetonitrile, water, and phosphoric acid (30:70:0.5%) at a flow rate of 1.5 mL per minute, a wavelength of 246 nm, and a pressure of 96 kgf cm ^{-2} were used
Chlorpyrifos	The mobile phase of acetonitrile and water (80:20) at a flow rate of 1.0 mL per minute, a wavelength of 208 nm, and a pressure of 68 kgf cm ^{-2} were used
Profenofos	The mobile phase of acetonitrile and water (55:45) at a flow rate of 1.0 mL per minute, a wavelength of 235 nm, and a pressure of 75 kgf cm ^{-2} were used
Triazophos	The mobile phase of acetonitrile and water (375:225) at a flow rate of 1.0 mL per minute, a wavelength of 235 nm, and a pressure of 93 kgf cm ^{-2} were used
Pyrethroids	The mobile phase of acetonitrile and water (75:25) at a flow rate of 1.0 mL per minute, a wavelength of 225 nm, and a pressure of 78 kgf cm ^{-2} were used
Carbamates	The mobile phase of acetonitrile and water (2:1) at a flow rate of 1.0 mL per minute, a wavelength of 220 nm, and a pressure of 75 kgf cm ^{-2} were used

Table 1. List of pesticide groups studied and the methodology used for their analysis.

Notes: Adapted from Lari et al. [25]. Herbicides are not included as they were not detected in the samples.

2.5. Analyses of Pesticide Residues via High-Performance Liquid Chromatography (HPLC)

High-performance chromatography (Buchii) was used with a UV-visible detector and an octadecylsilane C18 column ($250 \times 4.6 \text{ mm}$, 5 µm), an oven temperature of 30 °C, an injection loop of 20 µL, isocratic conditions, and reverse-phase chromatography. For these analyses, 20 µL of each sample was injected with a microsyringe into the HPLC injection loop.

2.6. Sample and Standard Preparation

Dried extracts of each water sample were dissolved in the respective mobile phase specified for the determination of each pesticide. Vortexing (6937) was used to ensure the complete dissolution of extracts in the mobile phase. Standard solutions of each pesticide were also prepared by dissolving it in a relevant solvent (0.5 mL for each pesticide).

2.7. Preparation of Mobile Phase

The mobile phase was prepared after filtration through 0.45 μ m filter paper with a filtration assembly. The mobile phase was sonicated for 5 min for the complete removal of air bubbles and dissolved oxygen.

2.8. Analyses of Samples

Analyses of samples were carried out for 7 groups of pesticides, including neonicotinoids (thiamethoxam, imidacloprid, thiacloprid, fipronil, and acetamiprid), chlorpyrifos (an organophosphate), profenofos (an organophosphate), triazophos (an organophosphate), pyrethroids (cypermethrin and cyhalothrin), carbamates (carbofuran, carbaryl, and carbendazim), and herbicides (isoproturan and diuron).

2.9. Statistical Analyses

The loads of different pesticides in groundwater from different regions of the Punjab province was determined after the statistical analysis of the data obtained from samples. Standard statistical procedures were followed for this purpose, including analysis of variance, comparison of means, and Duncan's multiple range test. The correlation of the physical parameters of water with the pesticide residues was also established. These analyses were conducted using the Minitab Package (Data analysis, statistical process improvement tool). Principal component analysis was mapped using XLSTAT-2019 [6].

3. Results and Discussion

3.1. Water Quality Parameters (pH, EC, and Temperature) during the Summer and Winter Season

Water quality parameters (pH, temperature, and EC) were significantly affected by the sampling area and season. The pH was found to be nearly neutral for all samples from all areas; however, there was a marginally significant change in the pH levels between the two seasons, with the winter season having a higher pH (Table 2). There was no significant difference (p > 0.05) in the pH of water across various districts, from all three regions (core area, non-core area, and marginal area) (Table 2). The salinity, as measured in the form of EC (μ S), was also significantly different between the two seasons (p < 0.01) but did not differ significantly across the different regions of Punjab (Table 3).

Table 2. The pH values of water samples collected from different regions of Punjab province during the two seasons of the study.

	p	Н	
	Summer	Winter	Mean
Core area	7.32 ± 0.01	7.44 ± 0.01	$7.38\pm0.01~\mathrm{A}$
Non-core area	7.32 ± 0.03	7.40 ± 0.03	$7.36\pm0.02~\mathrm{A}$
Marginal area	7.30 ± 0.03	7.40 ± 0.04	$7.35\pm0.03~\mathrm{A}$
Mean	$7.31\pm0.01~\text{B}$	$7.41\pm0.02~\mathrm{A}$	

Notes: The values represent mean \pm SE. Means sharing different letters in a row or in a column are significantly different (p < 0.05).

Table 3. The electrical	conductivity (EC	C) of water sam	ples collected	l from differen	t regions of	Punjab
province during the t	wo seasons of the	study.				

Area	EC (
	Winter	Summer	Mean
Core area	1333.4 ± 85.8	1149.9 ± 29.90	$1241.7\pm47.8~\mathrm{A}$
Non-core area	1645.1 ± 203.1	1143.2 ± 120.84	$1394.1 \pm 125.1 \; \mathrm{A}$
Marginal area	1358.3 ± 216.2	926.1 ± 107.43	$1142.2 \pm 125.2 \; \text{A}$
Mean	$1445.6\pm102.8~\mathrm{A}$	$1073.0\pm55.8~\mathrm{B}$	

Notes: The values represent mean \pm SE. Means sharing different letters in a row or in a column are significantly different (p < 0.05).

Over the whole Punjab province, the pH and salinity of groundwater initially seemed to vary only very slightly. However, when traveling from the core region to the margins and with season-to-season variance, there was significant variation among the values of all these factors. The temperature of the water samples was significantly affected by season, sampling region/area, and the interaction between season and area (Table S1). Overall, the highest temperature was observed for the samples from core area during the summer season (Table 4).

Table 4. The temperatures of water samples collected from different regions of Punjab province during the two seasons of the study.

Area	Temperature (°C)			
	Summer	Winter	Mean	
Core area	$23.8 \pm 0.11 \text{ a}$	$15.5\pm0.02~\mathrm{c}$	$19.7\pm0.77~\mathrm{A}$	
Non-core area	$23.3\pm0.11~\mathrm{b}$	$15.5\pm0.03~\mathrm{c}$	$19.4\pm0.72~\mathrm{B}$	
Marginal area	$23.3\pm0.11~\text{b}$	$15.5\pm0.05~\mathrm{c}$	$19.4\pm0.73~\mathrm{B}$	
Mean	$23.5\pm0.07~\mathrm{A}$	$15.3\pm0.02~\mathrm{B}$		

Notes: The values represent mean \pm SE. Means sharing different letters in a row or in a column are significantly different (p < 0.05). Small letters represent comparisons among interaction means and capital letters are used for main treatment effect means.

Pakistan's geographical position, with dry and semi-arid environments, makes its agriculture especially sensitive to climate variability [31,32]. Previous studies from Pakistan have shown that harvest and yield fluctuations are common in response to temperature and precipitation [33,34]. These differences in water quality parameters are vital, as pesticide persistence depends upon these parameters and environmental factors [35]. This has been elaborated further in the final section of this study, where we provided the correlation among pesticide residue amounts and these water quality parameters.

3.2. Screening of Water for Pesticide Residues

Neither the insecticides cyalohatherin, carbofuran, and carbendazim nor the herbicides isoproturon and diuron were detected in any of the water samples. The remaining chemicals listed in the Materials and Methods were detected in various samples at different concentrations. Pakistan is an agricultural country, exhibiting the high utilization of all types of pesticides in fields and for household purposes, with pesticides reaching the nearby tributaries, canals, and other types of surface water and finding their way into groundwater, with research showing that 45% of the applied pesticides may find their way into groundwater, causing pollution [13]. This trend is similar to those of many other countries where pesticides are in common use. For example, in a study from Thailand, chlorpyrifos, profenofos, ethion, and dicrotofos residues were reported to be present in high concentrations in potable water [24].

3.3. Pesticide Residues of Selected Pesticides in Water from Different Regions of Punjab

All the pesticides analyzed were observed in all regions. Pesticide concentrations varied significantly across the three areas (p < 0.01) (Tables S2 and S3; Figure 3). The maximum concentrations of all pesticides were found in the core area (Figure 3), where the majority of cotton is grown and sprayed. These findings are in agreement with those of Lari et al. [25]. The high levels of pesticide contamination found in core area are associated with repeated insecticide applications in this area. It is important to note that the differences in the quantities of pesticide residues across the three major areas (core, non-core, and marginal) align well with the pesticide consumption/sales trends in those areas.

In the core area, typically, large quantities of insecticides are sprayed on cotton (from pre-emergence until harvest) in Pakistan as compared to other agronomic and horticultural crops. This is mainly due to the high pest pressure on this crop in the country.

In addition, a large number of farmers still grow local varieties which are more susceptible to a variety of insect pests as compared with Bt cotton. Increased adoption of Bt cotton may significantly reduce the usage of multiple insecticides and therefore, may help in reducing the water contamination. The pesticide market is not well regulated or structured in Pakistan, which makes it difficult to obtain reliable data on actual pesticide consumption/sales trends and their effects on environmental indicators.

3.3.1. Neonicotinoids (Thiamethoxam, Imidacloprid, Thiacloprid, Fipronil, Acetamiprid) Pesticide Residues in Water

Neonicotinoids are considered neurotoxic pesticides as they cause inhibition at the presynaptic ends of neurons and nerves, thus causing various interruptions in neurotransmission and diseases. The highest residual level of thiamethoxam (5812 ng L^{-1}) was found in core area during the winter season, followed by 2926 ng L^{-1} in core area during the summer season (Figure 4).

Water samples from Bahawalpur exhibited the highest residual level of thiamethoxam, followed by Bahawalnager, Khanewal, Vehari, Jhang, and Multan, with highly significant differences. The remaining districts exhibited non-significant differences for the residues of this pesticide. These findings are in agreement with those of Schwartz et al. [36]. Cotton-growing regions were also the most affected areas in the Sindh and Punjab provinces in Pakistan [4,14].



Figure 3. Comparison of different pesticide residues in water samples collected from different regions of Punjab province. Bars present means \pm standard errors. The bars sharing the same letters in each chart did not differ significantly. Thiamethoxam = TM, imidacloprid = IC, thiacloprid = TC, acetamiprid = AM, fipronil = FN, triazophos = TA, profenofos = PF, chlorpyrifos = CP, carbyl = CL, cypermethrin = CM.



Figure 4. The quantities of (**A**) thiamethoxam, (**B**) imidacloprid, and (**C**) thiacloprid residues in water from different regions of Punjab during the summer and winter seasons. Bars represent means \pm standard errors. Bars sharing the same letters in each chart do not differ significantly.

Regarding imidacloprid residues, we observed a non-significant (p > 0.05) difference between the winter and summer seasons, as well as between non-core area and marginal area (Figure 4B), whereas the maximum residues of imidacloprid were found in core area during the winter season (Figure 4B). Similar results were reported by Dimitra et al. [37]. The maximum concentration of imidacloprid and thiacloprid were found to be accumulated in water samples from Rawalpindi. The areas surrounding Rawalpindi contain vegetable fields, where pesticides are sprayed in large quantities. Historically, mass-fish-killing events have occurred in the Rawal lake of Rawalpindi, where pesticides were found to be four times higher than recommended limits due to the intentional addition of pesticides into the lake to catch fish [38]. These results are in agreement with the results of Baig et al. [39], who found a high concentration of imidacloprid in different regions of Punjab.

Thiacloprid, fipronil, and acetamiprid were found in nearly all water samples. Their concentrations showed non-significant differences during the summer and winter seasons,

as well as in non-core area and marginal area (Figures 4C and 5A–C). In the case of both pesticides, the concentrations of pesticides were higher in winter as compared to summer, with highly significant differences. Because of the high rainfall in the summer season, pesticides are diluted in the summer season as compared to the winter season and degradation during summer due to high temperatures is another factor related to their reduced concentrations [40]. Neonicotinoides are well known for the blockage of neurotransmission and the inhibition of liver enzymes, as well as causing other diseases. Pesticide workers from Karachi, Lahore, and Multan have been found to show the deleterious effects of neonicotinoides in their liver enzymes in different studies [41].



Figure 5. The quantities of (**A**) acetamiprid, (**B**) fipronil, and (**C**) triazophos residues in water from different regions of Punjab during the summer and winter seasons. Bars represent means \pm standard errors. Bars sharing the same letters in each chart do not differ significantly.

Pesticide concentrations are dependent upon discharge during winter because of low temperature, spills, leaching, and surface runoff [42,43]. These pesticides reach water bodies

after their application because of leaching and surface runoff. Acetamiprid was found to have the maximum accumulations in water samples from Rawalpindi, similarly to other neonicotinoids, followed by Bahawalpur and Bahawalnagar, which were in turn followed by Vehari and Khanewal and then Multan, with significant differences (Figure 5A). These findings were related to those of Schwartz et al. [36], who explained that high residues levels of pesticides do not mean that there is a high application of pesticides, as sometimes loamyclay soils adsorb pesticides before they enter water bodies and seasons with high rainfall lead to dilution factors and enhanced degradation after application [40]. As compared to other neonicotinoids, the maximum concentration of fipronil was found in water samples from Bahawalnagar (960 ng L⁻¹), whereas the minimum concentration of this pesticide was estimated in water samples from Rawalpindi (13.70 ng L⁻¹) (Figure 5B). The findings of this study are in agreement with those of Musa et al. [44].

3.3.2. Organophosphates (Triazophos, Profenofos, Chlorpyrifos) Pesticide Residues in Water

Organophosphates, considered to be neurotoxic chemicals, are commonly used as treatments against bollworms and whitefly in cotton. Among all the organophosphates, profenofos showed the maximum accumulation in water sources, especially in core area during the winter season, at 5665 ng L^{-1} (Figure 6A).



Figure 6. The quantities of (**A**) profenofos, (**B**) chlorpyrifos, (**C**) carbaryl, and (**D**) cypermethrin residues in water from different regions of Punjab during the summer and winter seasons. Bars represent means \pm standard errors. Bars sharing the same letters in each chart do not differ significantly.

This concentration of profenofos was above the maximum residue limits of pesticides. These findings are in agreement with those of Dalvie et al. [45], who found that profenofos was accumulated in water samples and exceeded the maximum residue limit (100 ng L^{-1}). Triazophos showed a low accumulation rate, as a minimal concentration of triazophos was

found in the water samples. The lowest residue level of triazophos was observed during the summer season in non-core area (Figure 5C). These findings are in agreement with the findings of Schwartz et al. [36]. Triazophos is used on cotton crops, and chlorpyrifos is also used for the control of termites and other insects for indoor purposes. Organophosphates exhibit higher solubility and the potential for leaching, so the concentration of organophosphates increased [24,46]. In various areas the levels of chlorpyrifos exceeded the maximum residue limit [45].

3.3.3. Carbamates (Carbaryl, Carbofuran, and Carbendazim) Pesticide Residues in Water

The carbamate group consists of many chemical compounds, but the most commonly used ones are carbaryl, carbofuran, and carbendazim. Carbaryl is mainly sprayed on cotton, whereas carbofuran is commonly used on maize (*Zea mays* L.) and carbendazim is sprayed on vegetables as a fungicide. Carbamates are also reversible inhibitors of neural functions. In the current study, only carbaryl was detected in all water samples (Figure 6C). In contrast with all other pesticides, the maximum carbaryl level was detected in the marginal area as compared to core area and non-core area, with non-significant differences at *p* < 0.05 (Figure 6C). In the marginal area, a highly significant difference (*p* < 0.01) was observed during the winter and summer season, whereas in core and non-core areas we observed a non-significant difference (*p* > 0.05) in both seasons (Figure 6C). Carbofuran and carbendazim were not observed in any water sample. These findings are different to those reported by Xu et al. [47].

3.3.4. Pyrethroids (Cypermethrin, Cyalohathrin) Pesticide Residues in Water

There were no significant differences (p < 0.05) among all districts regarding the accumulation of cypermethrin in winter and summer (Figure 6D). The maximum concentration of cypermethrin was found in winter as compared to summer. These findings are related to those of Dimitra et al. [37]. Farmers generally use high concentrations of pyrethroids to control whitefly and bollworms in cotton; as a result, the use of pesticides such as cypermethrin has increased 19–725-fold [13]. In core area, the maximum concentration (1589 ng L⁻¹) of cypermethrin was found in the winter season as compared to the summer season (Figure 6D). The seasonal and geographic variability of this group of pesticides also depend upon the soil structure, as loamy clay soils adsorb substances and make the leaching process difficult [48–51], whereas pesticide retention in the soil profile can vary depending upon rainfall and temperature [40].

Overall, pyrethroids are considered to be less toxic compared to neonicotinoids, organophosphates, and carbamates, as they are considered naturally occurring. However, they can still affect the brain and other organs by blocking Mg channels and Na–K channels in membranes. In a previous study, cypermethrin was detected at a high level in the blood of cotton-picking women from the Khairpur district in Sindh province of Pakistan, causing endocrine disruption [52]. Cypermethrin results in an increased level of reproductive hormones such as estrogen, progesterone, follicle-stimulating hormone, and luteinizing hormone, along with hepatitis and altered levels of liver enzymes [53].

3.4. Correlations of Different Pesticide Residues with Water Quality Parameters

There were various correlations between the total burden of all pesticides and water quality parameters. A positive but non-significant correlation was observed between pH and EC in all regions (Figure 7; Table 5). In an overall comparison of the correlations of pesticides and water quality parameters in all districts and regions, pH was positively correlated with the majority of pesticides but temperature was negatively correlated with pesticide residues (Figure 7; Table 6). EC was positively correlated with the majority of pesticides but temperature was negatively correlated with pesticide residues (Figure 7). The correlation of pH was positive with thiamethoxam, fipronil, prfenofos, chlorpyrifos, carbaryl, and cypermethrin residues in both seasons (winter and summer) (Table 7). EC was also positively correlated with thiamethoxam, fipronil, triazophos, chlorpyrifos, profenofos, and cypermethrin during both seasons (Table 7). In

both seasons, the temperature was negatively and significantly correlated (p < 0.05) with imidacloprid, thiacloprid, and acetamiprid, whereas the correlation of temperature with other pesticides was non-significant (Table 7).



Figure 7. A principal component analysis plot presenting the correlations among different study parameters in different regions.

Thaimethoxam was positively and non-significantly correlated with pH in core area, whereas there was a highly significant and positive correlation (p < 0.01) between pH and this pesticide in non-core area (Figure 7; Table 5). Imidacloprid, thiacloprid, triazophos, chlorpyrifos, carbaryl, and cypermethrin were all positively and significantly correlated (p < 0.05) with pH in core area, whereas profenofos and acetmiprid had a highly significant (p < 0.05) positive correlation with pH in core area (Figure 7; Table 5).

The pH was positively correlated with EC but was negatively correlated with temperature (Table 6). Previously, Musa et al. [44] and Lari et al. [25] also reported that pH and EC were positively correlated with pesticide residues and that temperature had a negative correlation with pesticides. Jesußek et al. [54] demonstrated that the suitability of groundwater for drinking and for use as process water can be compromised at temperatures of 25 °C and higher. The type of gradient across which mixing takes place, such as a redox gradient, chloride gradient, pH gradient, or contamination gradient, will determine the predicted effect of mixing [55]. Consequently, the biochemical parameters, such as pH, may be somewhat altered due to slight changes in temperature. Although pesticides are targeted at pests, they affect other non-target organisms, including humans. Various studies have established the movement of pesticide residues across food chains, with major risks to humans from contaminated water, resulting in major health issues [56,57]. These findings are similar to those reported by Lari et al. [25], where pH and salinity were positively correlated, and temperature was negatively correlated with pesticide residues. Overall, the abundance of pesticide residues can be expressed in the following order: profenofos > imidacloprid > thiamethoxam > chlorpyrifos > carbaryl > thiacloprid > acetamiprid > fipronil > triazophos.

		Core Area			Non-Core Area	a	Ν	Marginal Are	a
	pН	EC	Temp	pН	EC	Temp	pН	EC	Temp
pH	1.000			1.000			1.000		
ĒC	0.205	1.000		0.293	1.000		0.160	1.000	
	0.277			0.117			0.399		
Temp	-0.798 **	-0.358	1.000	-0.318	-0.377 *	1.000	-0.279	-0.320	1.000
•	0.000	0.052		0.087	0.040		0.136	0.085	
Thiamethoxam	0.351	0.897 **	-0.526 **	0.480 **	-0.108	-0.189	-0.387 *	-0.350	-0.368 *
	0.057	0.000	0.003	0.007	0.569	0.318	0.035	0.058	0.046
Imidacloprid	0.436 *	0.849 **	-0.624 **	0.623 **	0.004	-0.324	-0.425 *	-0.361	-0.077
1	0.016	0.000	0.000	0.000	0.985	0.081	0.019	0.050	0.685
Thiacloprid	0.375 *	0.812 **	-0.564 **	0.191	-0.091	-0.452 *	-0.768 **	-0.128	-0.166
-	0.041	0.000	0.001	0.312	0.631	0.012	0.000	0.501	0.382
Acetamiprid	0.520 **	0.817 **	-0.733 **	0.653 **	0.341	-0.671 **	-0.426 *	-0.379 *	-0.094
*	0.003	0.000	0.000	0.000	0.065	0.000	0.019	0.039	0.622
Fipronil	0.261	0.768 **	-0.411 *	0.548 **	0.553 **	-0.591 **	0.033	0.761 **	-0.275
	0.164	0.000	0.024	0.002	0.002	0.001	0.862	0.000	0.141
Triazophos	0.448 *	0.687 **	-0.510 **	0.577 **	0.207	-0.743 **	-0.405 *	0.113	-0.253
-	0.013	0.000	0.004	0.001	0.272	0.000	0.026	0.552	0.177
Profenofos	0.556 **	0.792 **	-0.756 **	0.533 **	0.155	-0.734 **	0.075	0.658 **	-0.395 *
	0.001	0.000	0.000	0.002	0.413	0.000	0.692	0.000	0.031
Chlorpyrifos	0.459 *	0.759 **	-0.554 **	0.369 *	0.164	-0.604 **	0.015	0.916 **	-0.123
	0.011	0.000	0.002	0.045	0.386	0.000	0.937	0.000	0.516
Carbaryl	0.389 *	0.801 **	-0.507 **	0.508 **	0.243	-0.852 **	0.527 **	0.526 **	-0.475 **
-	0.034	0.000	0.004	0.004	0.195	0.000	0.003	0.003	0.008
Cypermethrin	0.438 *	0.800 **	-0.565 **	0.557 **	-0.029	-0.424 *	0.378 *	0.771 **	-0.419 *
	0.015	0.000	0.001	0.001	0.879	0.020	0.040	0.000	0.021

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Table 5. Correlations among water quality parameters and different pesticide residues in the three study areas of Punjab province.

Notes: Upper values indicate Pearson's correlation coefficients; lower values indicate levels of significance at 5% probability. * = significant (p < 0.05); ** = highly significant (p < 0.01).

Table 6. Correlations among different pesticide residues and water quality parameters across all the study areas of Punjab province.

	pH	EC	Temp
pН	1.000		
ĒC	0.214 *	1.000	
	0.043		
Temp	-0.385 **	-0.320 **	1.000
-	0.000	0.002	
Thiamethoxam	0.156	0.121	-0.171
	0.141	0.258	0.108
Imidacloprid	-0.052	-0.107	-0.199
-	0.627	0.314	0.059
Thiacloprid	-0.236 *	-0.022	-0.275 **
	0.025	0.835	0.009
Acetamiprid	-0.130	-0.184	-0.175
-	0.221	0.082	0.100
Fipronil	0.145	0.152	-0.157
	0.174	0.154	0.140
Triazophos	0.143	0.124	-0.251 *
-	0.179	0.243	0.017
Profenofos	0.259 *	0.201	-0.360 **
	0.014	0.058	0.000
Chlorpyrifos	0.180	0.127	-0.196
	0.089	0.233	0.064
Carbaryl	0.220 *	0.133	-0.215 *
-	0.037	0.212	0.042
Cypermethrin	0.186	0.116	-0.192
	0.078	0.275	0.069

Notes: Upper values indicate Pearson's correlation coefficients; lower values indicate levels of significance at 5% probability. * = significant (p < 0.05); ** = highly significant (p < 0.01).

		Summer			Winter	
	pН	EC	Temp	pН	EC	Temp
pН	1.000			1.000		
ĒC	0.131	1.000		0.086	1.000	
	0.390			0.573		
Temp	0.082	-0.031	1.000	0.535 **	0.079	1.000
-	0.592	0.840		0.000	0.607	
Thiamethoxam	0.010	0.159	0.609 **	0.121	0.036	0.056
	0.948	0.298	0.000	0.429	0.813	0.716
Imidacloprid	-0.260	-0.161	0.285	-0.096	-0.198	-0.271
-	0.085	0.290	0.057	0.532	0.192	0.072
Thiacloprid	-0.471 **	-0.050	0.167	-0.348 *	-0.153	-0.430 **
	0.001	0.747	0.274	0.019	0.317	0.003
Acetamiprid	-0.287	-0.198	0.205	-0.190	-0.283	-0.327 *
-	0.056	0.192	0.178	0.212	0.059	0.028
Fipronil	0.005	0.199	0.547 **	0.116	0.067	0.091
	0.974	0.189	0.000	0.447	0.663	0.554
Triazophos	-0.122	0.118	0.477 **	0.113	0.016	0.040
	0.424	0.439	0.001	0.458	0.916	0.795
Profenofos	0.037	0.251	0.514 **	0.164	0.053	0.119
	0.808	0.096	0.000	0.282	0.731	0.436
Chlorpyrifos	0.019	0.197	0.555 **	0.139	0.026	0.120
	0.900	0.196	0.000	0.362	0.864	0.432
Carbaryl	0.158	-0.038	-0.208	0.151	0.111	0.030
	0.300	0.805	0.170	0.321	0.466	0.844
Cypermethrin	0.018	0.183	0.559 **	0.153	0.015	0.113
	0.906	0.228	0.000	0.317	0.923	0.458

Table 7. Correlations among different pesticide residues and water quality parameters during the two sampling seasons (summer and winter).

Notes: Upper values indicate Pearson's correlation coefficients; lower values indicate levels of significance at 5% probability. * = significant (p < 0.05); ** = highly significant (p < 0.01).

The bioavailability of pesticides is a factor with equal importance to that of other environmental factors, and their higher bioavailability can lead to higher risks of death and illness. Therefore, the high use of several major pesticide groups has resulted in easier adulteration of the groundwater in Pakistan, causing serious health problems [58–63]. Our study shows the extent of this problem, which is linked with historic pesticide use in the major agricultural districts of Punjab province. It is important to devise stringent plans and adopt strong policy measures to tackle this problem.

4. Conclusions

The majority of the tested pesticides were found to be present in around 90% of the water samples. The level of contamination varied, however, being highest in the samples from districts in the core area, followed by samples from the non-core area, and lowest in those from the marginal area. This geographical variation can be broadly attributed to the historical use patterns of various pesticides, with long-term, heavy use in the cotton belt/core area. On the other hand, non-core and marginal districts belonged to mixed cropping zones and mainly rice/wheat cropping zones, respectively, where pesticide use has been relatively lower, but it is gradually increasing. The most and least prevalent compounds in the samples from all the districts in both seasons, respectively, were profenofos and triazophos. Temperature was negatively correlated with the majority of the pesticide residues, whereas the water quality indicators of pH and EC were positively correlated with pesticide residues.

Clearly, in most agricultural areas, water penetration and percolation has led to considerable pesticide mobility belowground. Due to the many constraints connected with small landholding and the lack of automation in Pakistan, safe and prudent application procedures must be followed for the proper control of contamination caused by pesticides. Future studies should focus on the regular monitoring of pesticide contamination across the food chain. It is also recommended that the concerned authorities establish a resourceful detection, monitoring, and evaluation program, which can not only assess the levels of pesticide contamination in environmental settings but can also track pesticide consumption/sales trends, as well as enforcing the safe-use thresholds on a regular basis.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15030543/s1; see attached Tables S1–S3.

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Abbreviations

Electrical conductivity = EC, high-performance liquid chromatography = HPLC, thiamethoxam = TM, imidacloprid = IC, thiacloprid = TC, acetamiprid = AM, fipronil = FN, triazophos = TA, profenofos = PF, chlorpyrifos = CP, carbyl = CL, cypermethrin = CM.

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