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The occurrence of priority pesticides in the soil and groundwater of Peshawar

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Abstract

Priority pesticides imidacloprid (IMD), glyphosate (GLYP), pendimethalin (PND) were monitored in soil and water samples collected from different areas of Peshawar. Sampling locations were grouped into four regions based on agricultural activities. Priority pesticides were extracted from the soil and water samples and analyzed by HPLC. The results of the soil samples showed that IMD was in the range of up to 0.10 mgKg^{-1} and was detected in 24% of the region I samples. All the four regions' soil was found to be contaminated with PND, with the highest (0.18 mgKg^{-1}) was found in the region I samples. GLYP was only found in the region I samples. The analysis of the water sample showed that IMD was up to 11.40 µgL^{-1} 39% in region II while 64% in the region I samples. PND was not detected in region IV samples, however, a higher PND (3.21 µgL^{-1}) was present in the region I samples. Water samples of the region I (18%) were reported with higher GLYP concentration. It can be concluded that the priority pesticides have the potential to contaminate groundwater, therefore these pesticides should be considered in the environmental studies.

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Introduction

Pesticides are used to minimize and control the infestation of pests on fruits, vegetables, crops and other agricultural products. Pesticides are broadly utilized on crops at different stages. Pesticides are of various types and can be classified based on the target pest, chemical composition and structure, and sometimes on their physical state. Several classes of pesticides consist of herbicides, fungicides, insecticides, rodenticides, bio-pesticides and weedicides (Ata *et al.,* 2013*).* The use of chemical pesticides has fetched advantages, for example, the growth of agricultural production, soil efficiency and foodstuffs, health and sanitation. Nonetheless, due to only 10 percent of applied pesticides stretch to the intended organisms, a great percentage is dumped on unintended areas (soil and water) and may influence non-target organisms such as microbes, besides affecting public health (Shahgholi and Ahangar, 2014).

In contrast to natural and biological control practices which work over a more extended timeframe, pesticides have the benefits of speed of control in circumstances of massive pest flare-ups. The loss to the yield because of insect pests is 35-40% and occasionally it can be as high as 60-70% (Oerke, 2006). The use of pesticides is the major source to minimize crop losses as a result of pest attack. Over-dependence on these synthetic compounds, however, leads to serious environmental, ecological and natural problems.

In agricultural areas, the contamination of the environment by organic pollutants may occur by direct input, transport, or precipitation processes (Kördel *et al.,* 1997). Many of the pollutants of concern were found to be toxic and their application was restricted particularly when potentially destructive impacts on human health were reported. Nevertheless, the consequences of unselective and careless pesticide usage are contamination of food and food commodities by residues of these chemical substances. The behavior of pesticides in the agricultural produce is of great significance, the persistence, or partial degradations of these compounds decide its potential impact on our environment. Sometimes these build-ups make food commodities unsafe and present health threats to the consumers. The economy of the country is affected equally due to export refusal because of residues of pesticides.

A wide variety of pesticides are available in the market and are applied either to control a specific target pest or in broad-spectrum, use to control a wide and diverse range of pests. After application, pesticides undergo a variety of different chemical and biochemical reactions including interaction with organic matter and minerals to differing degrees, converting them into a variety of Transformation Products (TPs). The chemicals formed by transformation are referred to by a variety of terms including TPs, pesticide degradation products, pesticide residues and metabolic products, or simply metabolites. Some pesticides are easily degraded; however, several pesticides remain intact and not easily degraded in prevailing circumstances (Gavrilescu, 2004). These chemicals remain in different compartments of the environment and sometimes enter the food chain or water table. Once in the groundwater, these synthetic compounds can be present in drinking water, hence leads to health issues. Pesticides used in agriculture are mostly absorbed and degraded in the topsoil, whereas the pattern of use of some persistent pesticides combine with environmental conditions could involve a risk of leaching leads to a greater risk of groundwater contaminations (Felding, 1992). Once contaminated, an aquifer/spring may hold these pollutants for quite a long time.

Pesticide can either leach down to groundwater or absorbed into soil particles or it may be degraded by microorganisms. The transports of pesticides in the soil greatly rely on soil texture (percent sand, silt, and clay) and structure. Sandy soils exceptionally enable water to travel through them rapidly, provide less adsorption to pesticides and other organic matters, and for the most part do not contain a huge

population of soil microorganisms in respect to other soil types. Soils that contain more clay and organic matter will effectively slow water movement, favors pesticides attachment, and mostly these pesticides are then utilized by the soil microorganisms (Baishya and Sarma, 2015).

The present study was aimed to monitor the priority of pesticides in the soil and water samples of the district Peshawar, Pakistan. The priority list was based on the pesticide usage data of district Peshawar for the year 2016-17. It was also studied whether or not the priority of pesticides.

Material and methods

Collection of water and soil samples for pesticide analysis
Soil samples collected from 28 different locations of Peshawar district were analyzed for the residual behavior of the pesticides selected from the priority list. For sampling purposes, Peshawar district was divided into four regions.

Region-I comprised of Chamkani, Jhagra, Sardar garhi, Tarnab, Nasir pura, Akbar pura, Taru Jaba, Qasim kalay, Urmarh.
Region-II consists of Machani, Palosai, Sang e sufaid, Pajaggi, Shahi Bala, Darmangi. Malakandher, Molazai.
Region-III included Bahadar kalay, Matani, Badaber, Bazidkhel,
Region-IV included Hayatabad I-III, Speena warai, Nasir bagh, Regi, danish abad, Achini, Tajabad,

Extraction of pesticides from soil and water samples
Imidacloprid
Liquid extraction was used for the extraction of IMD from soil samples while solid-phase extraction was employed to extract IMD from water samples. A solution of acetonitrile and water (80:20; v/v) was used to extract IMD from the soil samples. A 20 g soil sample was added to the above solution. The mixture was shaken and cleaned with a glass pipette containing wool at the bottom. By using a rotary evaporator the extract was dried. The dried samples

were re-dissolved in 1 mL of ACN: H_2O (20:80, v/v) for HPLC analysis. A solid-phase extraction method was used for IMD extraction from aqueous samples. Isolate C_{18} cartridge was precondition with methanol and deionized water. After sample loading, the analytical elution was carried out in acetonitrile that was dried and the extract was reconstituted in acetonitrile and water (20:80, v/v) for HPLC analysis (Baskaran *et al.*, 1997).

4-Chloro-2-MethylPhenoxyacetic Acid
Extraction of MCPA was carried out from soil and water samples using a slightly modified method (Pozo *et al.*, 2001). Briefly, after homogenizing the air-dried soil samples 1.25g sub-samples were shifted to 50 ml centrifuge tubes. After mixing with 25mL of 0.5 M KOH, the mixture was shaken for one hour at 120 oscillations/min and then centrifuged for 15 min at 3000 rpm. After transferring the supernatant to a tube, it was neutralized to a pH between 2 to 3 using formic acid. Then by the use of centrifuge at 3000rpm for 15 min, humus material was removed.

The SPE 500 mg C18 cartridges were with 5ml of each of the following three solvents: methanol, acetone and 0.1% aqueous formic acid. Using a flow-rate of approximately 5mL/min, the acidified extract was passed through the pre-conditioned cartridge. The cartridge was dried for 30 minutes using air after flushing with 5ml of 0.1% aqueous formic acid. Formerly, the cartridge was shifted over a calibrated tube having acetonitrile and 0.1% aqueous formic acid in 40:60 v/v. 3mL of acetone was percolated through the tube using minor over-pressure and collected in the tube. The acetone fraction was evaporated by the water bath. Finally, the volume was adjusted to 1 mL by the addition of 0.1% aqueous formic acid.

Extraction of PND
PND from the soil samples was extracted by shaking the samples in methanol for an hour. The mixture was then subjected to centrifugation for 5-10 min at 2000-3000 rpm. Supernatant collected in a pre-cleaned and sterilized bottle. The sample was treated with an excess of solvent and re-centrifuged to get

maximum recoveries. The dried extracts were re-dissolved in 1mL of mobile phase before HPLC analysis.

PND was extracted from the water samples by SPE using Isolate C_{18} cartridges (UK). Pre-conditioning of the SPE was done by 5mL of each of methanol followed by deionized distilled water. Under high vacuum using vacuum manifold loading of the sample at 4 mL min^{-1} was done. To remove salt and ions etc. the washing of the cartridge was done using 5 mL of distilled. The excess water was dried under a high vacuum for 15 min. Analytical elution was done by 5mL of methanol: dichloromethane (9:1 v/v) and the extract was then dried.

Extraction of GLYP
GLYP was extracted from water samples by solid-phase extraction explained elsewhere (Suleman and Keely, 2019). Briefly, 5 mL each of methanol and deionized water (0.1 % formic acid) were used to precondition the Oasis HLB cartridges and finally analytical elution was carried out with 9 mL methanol. GLYP was extracted from the soil by the method of *(*Landr*y et al.,* 2005). A subsample of 20 g of the soil was shaken in deionized water (100 mL) for 10 h. After centrifugation, the supernatant was derivatised with FMOC-Cl for HPLC analysis (Hanke *et al.,* 2008).

Analysis of Pesticides by HPLC
PND
For routine analysis of PND in soil and water samples, Agilent LC1200 with isocratic pump and UV-Vis detector was used. A reversed-phase column Waters Xterra C_{18} (dimensions; 150 cm × 4.60 mm × 5 μg) was used for chromatographic separation with the help of mobile phase MeOH: water in (80:20 v/v). The sample was manually injected and PND was detected at wavelength λ_{max} 240nm.

GLYP
Chromatographic partitioning was accomplished by using the Agilent Zorbax C_8 column (250 × 4.6 mm; 5μm). The LC mobile phase gradient employed 10

mM ammonium acetate (A) and acetonitrile (B). The gradient program was started with 10% B (0 min), increasing gradually to 90% B (15 min) and reverting to the initial composition at 20 min. The injection volume used was 10 μL and the flow rate was kept 0.7 mL min^{-1}.

IMD
The dried samples were dissolved in 1 mL of acetonitrile-water (20:80, v/v) for HPLC analysis by a method of (Baskaran *et al.,* 1997). The method was slightly modified and conditions were optimized for the analysis of IMD in water as well as soil samples. Chromatographic separation was achieved by the Agilent C_8 column (250mm x 4.6mm x 5μm) with UV detection at λ 270 nm. The mobile phase has consisted of acetonitrile: water (20:80) at a flow rate of 1mL min^{-1}. The retention time of IMD was 9.2 min and the total analysis time was set to 15 min.

MCPA analysis
A modified HPLC method (Hu *et al.*, 2012) was used for the analysis of MCPA in soil and water samples. Agilent LC1200 system equipped with a UV detector and isocratic pump was used. A reversed-phase HPLC Waters Xterra C_{18} column (dimensions; 150 x 4.6 x mm x 5 μm) was used. The mobile phase used was methanol/water with pH 2.8 (70:30: v/v and pH were adjusted with formic acid) with a flow rate of 1.0 mL/min. The injection volume was 20 μL, and the UV was set to λ 230 nm.

Statistical analysis
All the soil and water sampling were done in triplicate. The concentrations of pesticides were represented as means of triplicates. Principle Component Analysis (PCA) was carried out using PAST 318 (Hammer *et al.*, 2001) and data was arranged in bi-plot for the measurement of correlation among pesticides and their occurrence in different areas of Peshawar's soil and water samples.

Results and discussion
Analysis of soil samples
Analysis of soil samples revealed that IMD was

present in samples collected from different areas of Peshawar (Table 1). Soil samples collected from region-I contained higher concentrations of IMD as compared to other regions. The range of the pesticide was ND-0.10 mgKg^{-1} of soil with a mean concentration of 0.07 mgKg^{-1} of soil. IMD residues were detected in 24% of all the soil samples collected from region-I. Region-I mainly consists of areas that have greater agricultural activities and different crops and fruits and vegetables are cultivated in these areas. Region-II was also found to be contaminated by pesticide residues. Due to agricultural activities, large volumes of pesticides are usually used in these areas to protect the crops from different pest infestations.

Table 1. Detection of IMD in soil samples collected from different areas of Peshawar district during March 2016-March 2017 (n= 28×3).

Sample location	Detection (Mean) Soil (mgKg^{-1})	Conc. Range (lowest-highest) Soil (mgKg^{-1})	Detection (%) Soil
Region- I	0.07	ND-0.10	24
Region-II	0.023	ND-0.09	17
Region-III	0.042	ND-0.083	5
Region-IV	ND	ND	ND

ND: not detected or below the limit of detection.

The larger the K_{oc} value the higher the tendency of the pesticides to adsorb to soil particles. The movement of pesticide in the soil or runoff from soil surface largely depends on K_{oc} of the pesticide. A low K_{oc} pesticide with high water solubility moves in the dissolved form, however, a high K_{oc} of pesticide favors the adsorption process with soil particles. Sorption of IMD is greater on the organic content of the soil rather than on the clay, which reveals that the soil organic matter influences the adsorption of IMD to soil particles (Liu *et al.,* 2006). Nevertheless, IMD is highly soluble in water; however, a high amount of organic matter in the soil can greatly affect the mobility of IMD in the soil. Nonetheless, IMD is mobile in soil, its metabolite IMD guanidine sorption varies in different soil (Cox *et al.,* 1997). IMD has low DT_{50}, on the other hand, it has been found stable in certain cases where it persisted intact for 2 years after application to soil (Baskaran *et al.*, 1997). Likewise other pesticides, IMD degradation depends on the pH of the (Zheng and Liu, 1999) soil or water environment. It was reported that acidic and neutral soils provide a favorable condition for the sorption of IMD, thus, its degradation is slow in these conditions as compared to alkaline pH condition where IMD is largely converted into its TP imidazolidone (Zheng and Liu, 1999) furthermore, it was found persistent below surface soil (Fossen, 2006). Due to variations in soil pH and their organic matter content, IMD was detected in soil samples of different regions of Peshawar. However higher concentrations were present in region-I and II.

As these two regions are actively involved in agricultural activities, hence the incidence of pesticide contaminations can be predicted in these areas.

Table 2. Detection of MCPA in soil samples collected from different areas of Peshawar district during March 2016-March 2017 (n= 28×3).

Sample location	Detection (Mean) Soil (mgKg^{-1})	Conc. Range (lowest-highest) Soil (mgKg^{-1})	Detection (%) Soil
Region- I	0.02	ND-0.08	29
Region-II	0.07	ND-0.12	19
Region-III	ND	ND	ND
Region-IV	0.065	ND-0.08	24

ND: not detected or below the limit of detection; detection (%): numbers of samples contaminated.

Soil analysis shows that MCPA is present in soil samples collected from different regions of Peshawar (Table 2). The highest detected concentration was found for two regions i.e., Region-I and IV in the range of ND-0.08 mgKg^{-1} of soil with a mean concentration of 0.02 and 0.065 respectively. MCPA residues were detected in 29% & 24% of all the soil samples collected from Region-I & IV respectively.

Table 3. Detection of PND in soil samples collected from different areas of Peshawar district during March 2016-March 2017 (n= 28×3).

Sample location	Detection (Mean) Soil (mgKg^{-1})	Conc. Range (lowest-highest) Soil (mgKg^{-1})	Detection (%) Soil
Region- I	0.11	ND-0.18	36
Region-II	0.09	ND-0.13	28
Region-III	0.07	ND-0.10	14
Region-IV	0.03	ND-0.07	11

ND: not detected or below the limit of detection; detection (%): numbers of samples contaminated.

In general K_d, K_{oc} and DT_{50} are the major parameters that may select the nature of MCPA in environmental samples. Leaching experiments of the soil columns showed that MCPA behaves differently in regosol and chernitsa, being more mobile in the former with 16.44% of the applied MCPA recovered from the former and 1.12% from the later one. The DT_{50} values showed that the breakdown of MCPA was almost six times faster in chernitsa (DT_{50}= 11.7) than in regosol (DT_{50}= 2.2 days) (Hiller *et al.,* 2010).

The DT_{50} of MCPA in fields as well as in labs are very small which shows the transformation into its TPs like MCPB and MCPA-thioethyl. Soil organic carbon content and soil pH play a vital role in the mobility of acidic herbicides such as phenoxy acidic herbicides in soils (Hiller *et al.,* 2006). MCPA sorption may be higher in region-I & IV than others following the higher organic carbon content of the former soil than the latter. Major processes i.e., Sorption, desorption and degradation may variably influence the herbicides to leach down to the groundwater. Both the texture and properties of the soils and the chemical structure of the herbicides may affect the sorption-desorption (Boivin *et al.,* 2005).

Though region-IV has very low agricultural practices, however, the presence of MCPA reveals its usage in lawns and parks as well as in different horticultural landscape activities for beautification purposes.

Table 4. Detection of GLYP in soil samples collected from different areas of Peshawar district during March 2016-March 2017 (n= 28×3).

Sample location	Detection (Mean) Soil (mgKg^{-1})	Conc. Range (lowest-highest) Soil (mgKg^{-1})	Detection (%) Soil
Region- I	0.07	ND-0.12	14
Region-II	ND	ND	ND
Region-III	0.04	ND-0.04	3
Region-IV	ND	ND	ND

ND: not detected or below limit of detection; detection (%): numbers of samples contaminated.

PND residues were detected in soil samples collected from different regions of Peshawar (Table 3). The highest concentration of PND was present in region-I in the range of ND-0.18 mgKg^{-1} of soil, followed by region-II i.e., ND-0.13 mgKg^{-1} of soil with % detection 36 and 28 of the soil samples being contaminated.

PND is usually used as a pre-emergence in crops and residential lawns and plants. Extensive and widespread application of PND might be one of its main reasons to be reported as a contaminant in soil, ground and surface water (Larson et al., 1999).

Being less soluble in water (0.33 mg/l) and with a high K_{oc} value (17,581), PND has a low tendency for leaching. Nevertheless, PND has a very low GUS index (0.59), it can be leached down to groundwater in a concentration that exceeds the EU limit value (Kjær et al., 2011). PND has been grouped along with the bio-accumulative pesticides that are usually persistent by the US EPA (Roca et al., 2009). The present study mainly found that herbicide usage is almost detected in all the regions of Peshawar even including the non-agricultural and residential areas like Hayatabad etc.

Table 5. Detection of IMD in water samples collected from different areas of Peshawar district during March 2016-March 2017 (n= 28×3).

Sample location	Detection (Mean) water (μgL^{-1})	Conc. Range (lowest-highest) water (μgL^{-1})	Detection (%) Water samples
Region- I	4.62	ND-9.12	64
Region-II	5.7	ND-11.40	39
Region-III	3.8	ND-7.72	21
Region-IV	4.0	ND-5.4	7

ND: not detected or below the limit of detection.

Soil sample analysis shows that GLYP was present in samples collected from different areas of Peshawar (Table 4). A soil sample collected from Region-I contained the highest concentration of GLYP followed by Region-III, the range of Pesticide was ND-0.12 and ND-0.04 respectively with 14% and 3% of the soil samples having residues of GLYP. (Newton et al., 1994) detected GLYP at a concentration of 5.0 mg kg^{-1} soon after the application on the same day in forest litter of Oregon Coast Range, however, after the rainfall on the following day the concentration of GLYP was almost two-fold then the first day. It was also reported that the level of GLYP declining rapidly to 0.2 mg kg^{-1} by day 55. High K_{oc}/Kf_{oc} (strong adsorption) of GLYP suggests its movement by associating itself with soil particles.

Table 6. Detection of MCPA in water samples collected from different areas of Peshawar district during March 2016-March 2017 (n= 28×3).

Sample location	Detection (Mean) water (μgL^{-1})	Conc. Range (lowest-highest) water (μgL^{-1})	Detection (%) Water samples
Region- I	2.34	ND-5.40	28
Region-II	2.95	ND-6.31	32
Region-III	2.45	ND-5.74	28
Region-IV	ND	ND	ND

ND: not detected or below the limit of detection; detection (%): numbers of samples contaminated.

Nevertheless, GLYP is considered a low leaching herbicide, however, soil properties and organic matter greatly influence the mobility of GLYP. AMPA is the main TP/degrade/metabolite of GLYP. The slow degradation of AMPA than its parent compound maybe because of its high sorption onto soil particles (USDA, 1984). A study by (Horner, 1990) examined dissemination, movement and degradation of GLYP in the soil of a forest. The study revealed that usage of GLYP according to labeled directions under normal

forest growing practices; 5ppm is the collective maximum residual level of both GLYP and AMPA. It is also determined that under high rainfall, GLYP and AMPA are strongly bound to soil and do not move vertically in the soil profile.

Principle component analysis shows (Fig. 1) that the PC1 and PC2 represented the maximum variations and provides maximum data representations over the x and y-axis. The bi-plot of PC1 and PC2 shows the distribution of pesticides in the four regions. It shows that region-I has a higher incidence of soil contamination with three of the selected pesticides however IMD and PND are the major pesticides detected in the soil samples of region-I. A small fraction of GLYP was also present in the soil samples of the region-I. Region-II soil samples were found to be loaded with MCPA and PND residues.

All these four regions' soil samples had significant differences in their pesticide residues. GLYP and MCPA are strongly negatively correlated in region-II and region-III. Region-IV soil was found to be less contaminated with these pesticides.

Table 7. Detection of PND in water samples collected from different areas of Peshawar district during March 2016-March 2017 (n= 28×3).

Sample location	Detection (Mean) water (μgL^{-1})	Conc. Range (lowest-highest) water (μgL^{-1})	Detection (%) Water samples
Region- I	1.88	ND-3.21	32
Region-II	1.02	ND-2.78	7
Region-III	1.10	ND-1.55	10
Region-IV	ND	ND	ND

ND: not detected or below the limit of detection; detection (%): numbers of samples contaminated.

Analysis of water samples

Analysis of water samples showed that IMD was present in samples collected from different regions of Peshawar (Table 5). Water samples collected from region-II were found to contain higher concentrations of IMD. The range of pesticide was ND-11.40 μgL^{-1} of water with a mean concentration of 5.7μgL^{-1} of water and only 39 % of the samples collected from this region were found to be contaminated.

Though region-I was found to be more contaminated with 64% detection residual range was ND-9.12 μgL^{-1} of water with a mean concentration of 4.62μgL^{-1} of water.

Table 8. Detection of GLYP in water samples collected from different areas of Peshawar district during March 2016-March 2017 (n= 28×3).

Sample location	Detection (Mean) water (μgL^{-1})	Conc. Range (lowest-highest) water (μgL^{-1})	Detection (%) water samples
Region- I	2.65	ND-4.32	18
Region-II	1.87	ND-3.68	10
Region-III	ND	ND	ND
Region-IV	ND	ND	ND

ND: not detected or below the limit of detection; detection (%): numbers of samples contaminated.

IMD is a very active insecticide against various pests including plant hoppers, crane flies, fleas, ants, aphids, crickets, termites and Colorado beetle. It is extensively used in nearly all the farming and sometimes in non-agricultural i.e., domestic areas.

Pesticides while on their way from soil towards groundwater pass through different hydrological zones and the soil properties and organic content of the respective zones may affect their transport. Region-I and II may have a water table closer to the

soil surface. Potential leaching of IMD may be because of low soil organic content. Irrigation is one of the lands uses related to groundwater contamination by pesticides (Andrade and Stigter, 2009). IMD is classified as a high potential leaching pesticide because of 3.76 GUS (Bonmatin *et al.,* 2015). The fate of IMD in water can lead to primarily four degradation products or TPs resulting from aqueous photolysis of IMD namely IMD urea, chloronicotinic aldehyde, 6-chloro-N-methylnicotinacidamide and 6-chloro-3-pyridyl-

methylethylenediamine as reported by (Moza *et al.,* 1998).

Examination of water samples showed that three regions were contaminated by residues of MCPA from the samples collected from Peshawar (Table 6). The highest detected residues were reported in region-II with a concentration range of ND-6.31µgL^{-1} of water with a mean of 2.95 µgL^{-1} and 32% of all the samples were contaminated, followed by region-III & I respectively.
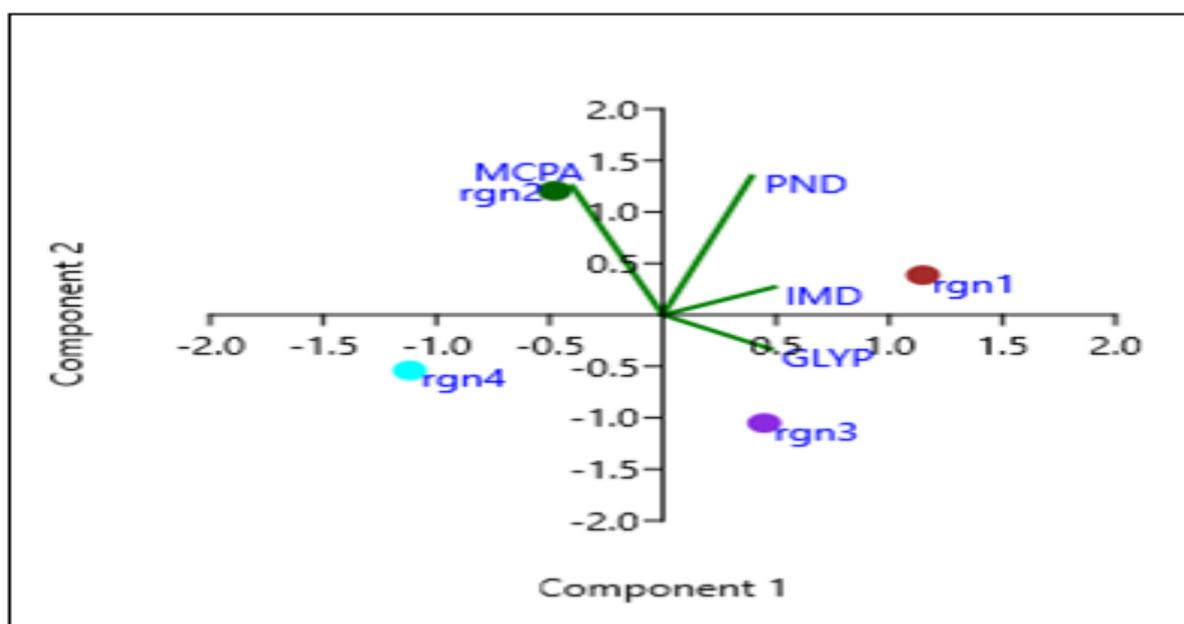
Fig. 1. Principal component analysis of soil samples collected from Peshawar regions.

The three main factors contributing towards leaching are high water solubility potential, low octanol-water partition coefficient and 2.94 GUS leaching potential index. Degradation of MCPA in soil DT_{50}1-16 weeks via 4-chloro-2-methylphenol to eventually non-hazardous form is being reported by several authors (CrespÍn *et al.,* 2001). It has been revealed that MCPA is weakly retained by the soil and migrates easily through soil columns (Helweg, 1987). Different ecological and soil situations may also contribute to the leaching of herbicides. Rainfall and water table positively affect the leaching of MCPA soon after its application. Water sample analysis collected from different regions of Peshawar showed that PND was contaminated in three regions (Table 7). The region-I being 32% contaminated was having a range of ND-

3.21 µgL^{-1} of water with a mean of 1.88 µgL^{-1}.

The application rate of PND, type of irrigation, high rain rainfall just after pesticide application can enhance the leaching of PND as reported by (Walker *et al.,* 1989). The samples of region-II and III were less contaminated with PND. Low water solubility, high octanol-water partition coefficient (K_{ow}) at pH 7, 20°C and low GUS index and other factors reviewed supported the results of the present study. (Chopra *et al.,* 2010) has reported similar kind of results, however, a lower leaching tendency (0.4 % of the applied) of PND was found. Pesticide monitoring from water samples collected from 28 different locations grouped under four different regions contamination of water sample by GLYP is not very

significant (Table 8). Region-I has the highest % detection of 18, with a concentration range ND-4.32 μgL⁻¹ and mean detection of 2.65 μgL⁻¹, followed by region-II which has only 10% of all the samples collected being contaminated by residues of GLYP in the range of ND-3.68 μgL⁻¹ and mean detection 1.87 μgL⁻¹. The results of the present study are in line with the literature review. Though GLYP has high water solubility coefficient its calculated GUS LPI of -0.25 confirms its low leaching capability as compared to its

TP AMPA. It can be rightly hypothesized that AMPA's persistent is much more than its parent compound as studied by (Simonsen *et al.,* 2008) revealed that DT_{50} for GLYP is 9 days while on the other hand DT_{50} of its major TP is reported to be 32 days but again the clayey soil may reduce degradation of GLYP and organic soil content may amplify the degradation of AMPA. Different soil systems and soil conditions, however, may have different effects on the mobility or leaching of these herbicides.
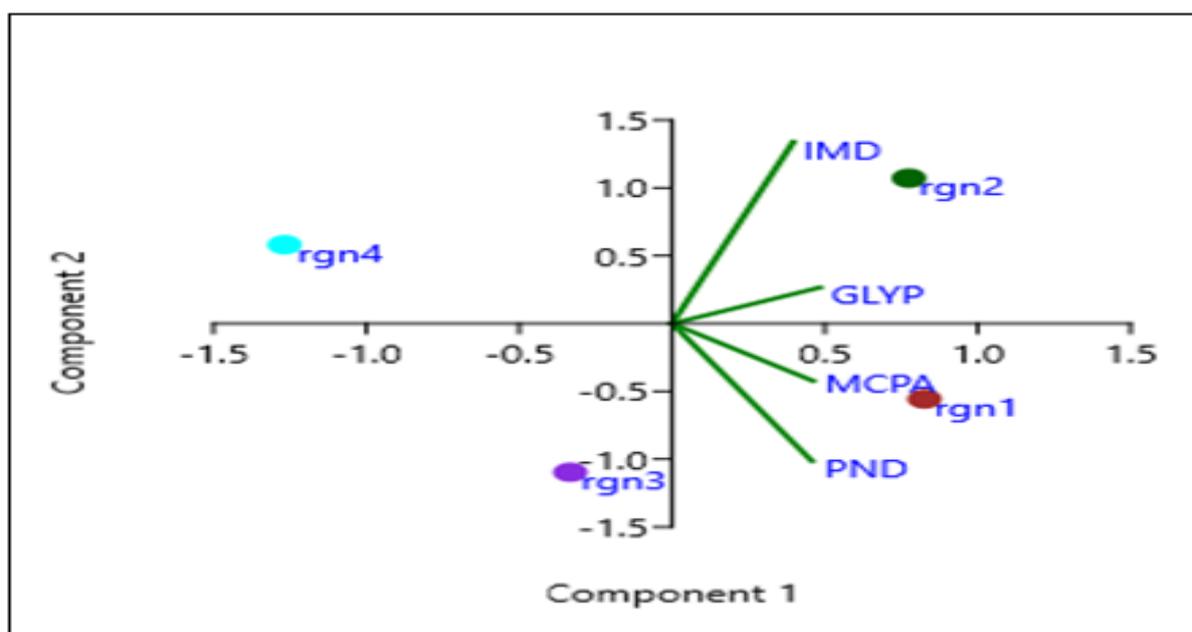
Fig. 2. Principle component analysis of water samples collected from Peshawar regions.

The PC1 and PC2 showed (Fig. 2) the maximum variability in the data. It was found that the water samples of region-I and II were contaminated largely with IMD, GLYP and PND. However, water samples from region-III and region-IV were found to be less contaminated with the priority of pesticides.

Conclusion

The assessment of the exposure of pesticides and their monitoring in the environment should be carried out systematically.

The priority pesticides provide useful information about their residual behavior in different environmental compartments. IMD, GLYP, PND and MCPA were detected in the soil as well as water samples and can impose a potential threat to

groundwater and raise environmental safety concerns.

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