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# REPORTING PESTICIDE RESIDUES IN SOIL OF LODHRAN DISTRICT, PUNJAB, PAKISTAN

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**ABSTRACT**

Pesticide residues of organophosphate (OP) and organochlorine (OC) are reported in soil samples collected from the cotton growing areas of District Lodhran, Punjab, Pakistan. All the 12 soil samples presently analyzed were found contaminated with tested pesticides (i.e. dichlorvos, mevinphos, dimethoate, methyl parathion, fenitrothion, chlorpyriphos endosulfan and profenofos). Most of the soil samplewere found contaminated with pesticide residues at different levels. The most widely detected pesticide were fenitrothion and endosulfan found in all samples with mean concentration of 0.433 and 0.198 mg. $Kg^{-1}$, respectively. The other most often detected pesticides investigated in eight samples with the mean concentration of were mevinphos (0.484), dimethoate (0.056), chlorpyriphos (0.226) and profenofos (0.153 mg. $Kg^{-1}$). Dichlorvos was the third most detected pesticide in four samples with mean concentration of 0.132 mg. $Kg^{-1}$. Methyl parathion was not detected in any soil sample. The mean value of total pesticides was found to be 1.679 ± 0.877 mg. $Kg^{-1}$ at 95% confidence level in soil samples collected with highest value of 3.180 mg. $Kg^{-1}$ in sample KL-2 followed by 2.837 mg. $Kg^{-1}$ in KL-4, while all other samples (66%) were found contaminated usually at concentration less than 2 mg $Kg^{-1}$.

**KEYWORDS:** Residual pesticides, Pesticide, Gas chromatography (GC), Soil, Punjab, Pakistan.

## INTRODUCTION

In Pakistan few efforts have been made to solve the challenges of dry lands (Rashid *et al*., 2004). Similarly the impact of soil on vegetation (Awan, 1992), reclamation and management studies on alkaline soil (Gupta and Zia, 2002). The other parameters like moisture conservation in soil (Salim *et al*., 2000) have been reported in the last decade. Whereas, Baig (1985) and Hussain *et al*., (1988) reported DDT residues in the agricultural soil of Punjab & Khyber Pukhtunkhwa and paddy ecosystem in Balochistan. Jabbar *et al*., (1993) reported the monocrotophos, cyhalothrin, dimethoate, fenvalerate, cypermethrin and profenofos in the top foot soil of Samudari, a cotton growing area. Recently Anwar *et al.*, (2012) reported the chlorpyriphos as the most widely detected pesticide with mean concentration of 0.486 mg $Kg^{-1}$ in soil samples collected from the agricultural areas of Nawabshah District, Sindh..Tahir *et al*., (1999) analyzed the fortified soil samples recoveries on GC-ECD. It was found that percent recoveries of methyl parathion were 100%, 67% and 94% at spiking level of 0.17, 1.7 and 8.7 µg $L^{-1}$. The data showed the evidence that capillary column GC-ECD could be used reliably and advantageously for pesticide analysis. Wang and Zhang (2006) extracted 13 organochlorine insecticides in soil with an ordinary pressure Microwave with Assisted Extraction (MAE) system and determined by GC. Detection limits for different substances were0.033-0.853 ng $g^{-1}$. The pesticides accumulated in the soil for relatively longer period of time and then passed into various parts of the plant grown on the contaminated soil as recently reported by Malhat *et al*., (2012) about the dissipation of new insecticide (chlorantraniliprole) to understand the residue and persistence behavior in tomato and soil. Fate of pesticides in sandy loam soil of Pakistan at different water table depth was reported by Tariq *et al*., (2010). Reported the chlorinated pesticide in the soil samples collected from the obsolete pesticide stores from three provinces (Punjab, Sindh and KPK) of Pakistan were reported by Ahad *et al.*, (2010). A number of reviews has been published on the occurrence of organochlorine pesticides in different environmental compartments of Pakistan (Ali *et al*., 2012), in agricultural commodities including water and soil (Ahmad *et al*., 2013) and pesticide residues and its pathological symptoms in occupational and non-occupation groups in Pakistan recently been reviewed by Anwar *et al*., (2013). The earlier investigations were carried out to monitor the residues of chlorinated pesticides in agricultural soil. The present investigation was carried out to monitor the different classes of pesticides in soil to determine the fate in the soil and their persistency to develop the strategy to prevent adverse effects on public health and farmers' community as pointed out by Khan *et al*., (2010).

## MATERIALS AND METHODS

**Sampling:** All the samples were collected randomly from the selected cotton growing areas of Lodhran District, Punjab, Pakistan. The field study was limited to manageable geographical areas where farmers and female cotton pickers were living and have a great potential to be exposed to pesticides. Twelve (12) soil samples were collected from different agricultural fields of Moza Lodhran (ML), Kallowala (KL) and Basti Bahowala (BB) and analyzed for the residues of dichlorvos, mevinphos, dimethoate, methyl parathion, fenitrothion, chlorpyriphos, endosulfan and profenofos. The soil samples were collected in plastic bags and transported to laboratory for analysis. The method reported by Tahir *et al*.,

(1999) was followed for the extraction of pesticide residues in soil. Fifty grams of soil sample were taken in a conical flask and then 150 ml of a mixture of acetone: hexane (1:1) was added. This was shaken for 1 hour with the help of mechanical shaker at a rate of about 300 Osc/minute. The mixture was filtered through a glass wool plug with Whattman filter paper No. 542 into a separating funnel. The extract was washed with distilled water (2×100 ml). The lower aqueous layer was discarded and a few grams of anhydrous sodium sulphate were added. Twenty ml of the aliquot was transferred to round bottom flask and evaporated to dryness at 40°C in a rotary evaporator. The contents of the flask were reconstituted in 6 ml ethylacetate and cyclohexane (1:1) mixture and then passed through high flow super cells. Two ml of this sample was applied on Gel Permeation Chromatograph (GPC) for further cleanup. After passing through GPC column, the samples were again dried under vacuum and reconstituted in 1ml ethylacetate for analysis on GC.

**Experimental**

**Apparatus:** Gas Chromatograph, Perkin-Elmer, Autosystem, Microprocessor fitted with Electron Capture Detector (ECD-$Ni^{63}$) and Nitrogen Phosphorous Detector (NPD). Nitrogen and Air Generator Peak Scientific. Hydrogen Generator, Peak Scientific, Gel Permeation Chromatograph (GPC), Mikrolab Arhus A/S, USA. Rotary Evaporator, made Buchi R-114/A, Switzerland. Food Blender, Germany. FlASK Shaker SF1, Sartatorius single pan analytical balance and Refrigerator/Freezer.

**Reagents:** The analytical grade standards of insecticides (dichlorvos, dimethoate, methyl parathion, fenitrothion, endosulfan,mevinphos,chlorpyriphos and profenofos were purchased form Riedel-d Haen AG Seelze, Germany or obtained from other institutes of Pakistan. Stock solutions and required working dilutions were prepared in ethlylacetate. All other solvents and reagents were of extra pure GC/HPLC grade. Acetone, Ethylacetate, anhydrous sodium sulphate, sodium hydroxide, potassium dichromate, sodium chloride, (Merk Company), cyclohexane and n-Hexane, high flow super cells, (British Drug House Company). Dichloromethane (Lock-light Ltd.), propane 1, 2-diol (Pharmacos Ltd., UK), bio-beads, SX3 200-400 (Reidel-de Haën) and Millipore distilled water.

**Instrumentations:** Multi residue method for analysis of soil was developed by using Gas Chromatograph (GC) equipped with Electron Capture Detector (ECD). All the pesticides could be determined simultaneously under the conditions. Retention time and calibration curve of each standard insecticide was prepared as mentioned in Anwar *et al*., (2012).

**RESULTS AND DISCUSSIONS**

The quantity of pesticide residues detected in the samples collected from different locations of Lodharn (Punjab) is reported in Table 1. A total of 12 samples were collected from different location of Moza Lodhran (ML), Kallwala (KL) and Basti Bahowala (BB) and analyzed for the residues of dichlorvos, mevinphos, dimethoate, methyl parathion, fenitrothion, chlorpyriphos, endosulfan and profenofos.

The average values of pesticide residues in soil sample ML-1 were mevinphos (0.915), dimethoate (0.024) and endosulfan (0.355 mg. $kg^{-1}$). However, residues quantified in sample ML-2 as dimethoate (0.033), fenitrothion (0.853) and chlorpyriphos (0.874), endosulfan (0.255) and profenofos (0.043 mg. $kg^{-1}$). In soil sample ML-3 the residues of dichlorvos (0.003), dimethoate (0.340), fenitrothion (0.630), chlorpyriphos (0.535), endosulfan (0.530) and profenofos (0.001 mg. $kg^{-1}$). In soil sample ML-4 the residues of dimethoate, fenitrothion, chlorpyriphos, endosulfan and profenofos were found in quantity of 0.142, 0.032, 0.070, 0.628 and 0.0.622 mg. $kg^{-1}$, respectively.

The average values of pesticide residues determined in soil sample KL-1 were mevinphos (0.926), fenitrothion (0.002), endosulfan (0.025) and profenofos (0.002 mg. $kg^{-1}$). However, residues quantified in sample KL-2 as dichlorvos (0.965), mevinphos (1.259), fenitrothion (0.953), endosulfan (0.005) and profenofos (0.001 mg. $kg^{-1}$). In soil sample KL-3 the residues of mevinphos (0.850), fenitrothion (0.436) endosulfan (0.041) and profenofos (0.626 mg. $kg^{-1}$). In soil sample KL-4 the residues of mevinphos, fenitrothion, endosulfan and profenofos were found in quantity of 1.650, 0.013, 0.639 and 0.535 mg. $kg^{-1}$, respectively.

The average values of pesticide residues determined in soil sample BB-1 weremevinphos (0.001), dimethoate (0.040), fenitrothion (0.560), Chlorpyriphos (0.060) and endosulfan (0.028 mg. $kg^{-1}$). However, residues quantified in sample BB-2 as dichlorvos (0.001), mevinphos (0.001), dimethoate (0.050), fenitrothion (0.633), chlorpyriphos (0.400) and endosulfan (0.035 mg. $kg^{-1}$). In soil sample BB-3the residues of dichlorvos (0.615), dimethoate (0.030), fenitrothion (0.075), Chlorpyriphos (0.0.035), endosulfan (0.0.56) and profenofos (0.001 mg. $kg^{-1}$). In soil sample BB-4 the residues of mevinphos, dimethoate, fenitrothion, chlorpyriphos and endosulfan were found in the quantity of 0.200, 0.010, 0.053, 0.250 and 0.250 mg $kg^{-1}$, respectively.

Most of the soil samples were found contaminated with pesticide residues at different levels. The most widely detected pesticide were fenitrothion and endosulfan found in all samples with mean concentration of 0.433 and 0.198 mg. $Kg^{-1}$ respectively. The other most often detected pesticides investigated in eight samples with the mean concentration of were mevinphos (0.484), dimethoate (0.056), chlorpyriphos (0.226) and profenofos (0.153 mg. $Kg^{-1}$). Dichlorvos was the third most detected pesticide in four samples with mean concentration of 0.132 mg $Kg^{-1}$. Methyl parathion was not detected in any soil sample. The mean value of all pesticides was found to be 1.679 ± 0.877 mg. $Kg^{-1}$ at 95% confidence level in soil samples collected with highest value of 3.180 mg $Kg^{-1}$ in sampleKL-2 followed by 2.837 mg. $Kg^{-1}$ in KL-4, while, other samples (66%) were found contaminated usually at concentration less than 2 mg, $Kg^{-1}$.

Presently the pesticides used are mostly synthetic organic compounds. The sediments might act as an important sink for persistent organic pollutants including many pesticides used presently or in the past. They are relatively insoluble in water and are retained strongly by the soil. Soil acts as filter buffer and degradation of pollutants with respect to storage of pollutants with the help of soil organic carbon (Burauel and Bassmann, 2005). Soil acts as a pathway of pesticide transport to contaminate water, plants, food and effect on human via runoff, leaching, transfer of mineral nutrients and pesticides from soil into the plants and animals that constitute human food chain (Abraham, 2002). Persistent pesticides slowly break down into the soil and lead to contamination which is closely correlated to human activities like industrial discharge, agricultural applications and deforestation which leads to soil erosion (Bhattacharya *et al*., 2003).

Soil samples analyzed were collected from the major cotton growing areas of Bahawalpur district Punjab. Most of the soil samples collected from these areas was contaminated with pesticides. The most widely detected pesticides which are currently or have been used heavily in the past included mevinphos, endosulfan and fenitrothion in 92%, 83% and 58% respectively, followed by 50% soil samples were found contaminated with dimethoate and dichlorvos (Anwar, 2009). On the other handin the present study fenitrothion and endosulfan were detected in twelve samples collected from the Lodhran. These results from cotton growing areas were in good agreement with data from the previous investigations. Endosulfan an OC pesticide was reported as pesticide of the particular concern in sediments from Queensland irrigation areas above the environmental guidelines (0.01 µg. $L^{-1}$) (Simpson, 1998). The sediments collected from the eleven areas in Queensland regions dominated by cotton cultivation were found contaminated with pesticides used presently and in the past. The most often detected pesticide was endosulfan which was detected in 78 samples out of 103 (Muller *et al*., 2000). Endosulfan due to its persistency and commonly used feature on crop was frequently found when applied in the past in the sediments. Pesticides such as endosulfan appeared widely distributed in soil from three locations of cotton growing areas of Pakistan. The pesticides retained for a longer period of time in the soil, pass into various parts of plants grown on the contaminated soil (Anwar, 2009 and 2011).

Several studies (Singh *et al*., 2005 and Gao *et al*., 2005) have reported the detection of pesticides in soil and the most frequent pesticides detected were of OC group which is more persistent and stay in the sediment, decomposed very slowly and may persist for several years as they are insoluble in water and are retained by the soils. DDT (long banned insecticide) was detected in most of the soil samples. Baig (1985) reported DDT in organic soil of Punjab and NWFP while the most applied DDT was retained on top 5 cm layer in sandy loam soil (Hussain *et al*., 1988 and Jabbar *et al*., 1993). Similarly in the present study the endosulfan, an organochlorine pesticides was detected in all samples with an average value of 0.190 ± 0.233 mg. $Kg^{-1}$.

In Pakistan the presence of pesticide residues was reported by several researchers (Baig, 1985; Hussain *et al*., 1988; Bano and Siddiqui, 1991; Jabbar *et al*., 1993; FAO, 2001; Sanpera *et al*., 2002 and Tariq *et al*., 2006, Anwar, 2009, Anwar *et al*., 2011 and Anwar *et al*., 2012). Jabbar *et al*., (1993) analyzed the soil of Samundari area of Faisalabad district in Punjab, Pakistan for pesticide residues. All the studied soil samples were found contaminated with varying amount of different pesticide residues, while the monochrotophos, dimethoate and profenofos were found at one foot depth. Tariq *et al*., (2004 and 2006) studied the hydrophobicity and persistence of pesticides that controlled the accumulation in different soil series of Pakistan. Some pesticides like organochlorine decompose very slowly and may persist for years and are retained by soil due to their insolubility in water. In the present study the detection of pesticides in soil from different locations demonstrated the difference in pesticide residues that could be related to the cultivation of crop with different time intervals. Pesticide usage like dichlorvos were detected only in four soil samples collected from Lodhran as compared to 6 soil samples from Nawabshah district (Anwar *et al*., 2012) and 9 soil sample from Bahawalpur district (Anwar, 2009). It is concluded that in order to prevent adverse effects on public health the dissipation studies on pesticides must be carried out in different climatic zone of agriculture in Pakistan to calculate the half-life and pre-harvest interval especially in vegetables growing on pesticide contaminated soil.

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