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Residues of cypermethrin and endosulfan in soils of Swat valley

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Abstract

Swat Valley was studied for two widely used pesticides; cypermethrin and endosulfan. A total of 63 soil samples were collected from 27 villages selected for this purpose. The collected soil samples were extracted with n-hexane, pesticides were separated, identified and quantified by a GC-ECD system. Endosulfan was 0.24 - 1.51 mg kg^{-1} and 0.13 - 12.67 mg kg^{-1} in rainfed and irrigated areas, respectively. The residual level of cypermethrin was comparatively high with a level of 0.14 to 27.62 mg kg^{-1} and 0.05 to 73.75 mg kg^{-1} in rainfed and irrigated areas, respectively. For assessing the possible causes of pesticide residues in soil, 360 farmers were interviewed. It was found that both, cypermethrin and endosulfan, apart from agriculture were also widely misused for fishing in the entire stretch of River Swat and its tributaries. River Swat is used for irrigation in Swat Valley and this wide misuse of pesticides can also contribute to pesticide residue in soil.

Key words: Pesticides residue, gas chromatography, soil texture, off-season vegetable, different swat regions

Introduction

The trend of pesticide use in Pakistan in general and North West Frontier Province (NWFP) in particular is towards increase. On one hand it is contributing to increase crop protection while on the other hand has got negative impacts on flora and fauna (Nafees *et al*., 2008a). In Pakistan, pesticide use started during 1954 with limited number of insecticides, which presently has reached up to 108 types, apart from the introduction of a varieties of fungicides (30 types) and herbicides (39 types) (Tariq *et al*., 2007). During 1994-1995, 30 % crop used to be sprayed with a regular increase every year (Pesticides Action Network, 1995). During 1980-2002, a 100 time increase has been reported in which pesticides use increased from 665 MT in 1980 to 69897 MT in 2002 (Khan *et al*., 2002).

Pesticide has got a wide range of impacts on human and other living beings. The direct impacts are on soil microorganisms, which has got special role in various nutrient cycles (Jan *et al*., 2001; Cycon *et al*., 2006). Besides this, majority of pesticides, especially organochlorine pesticides, have got bio-accumulative capacity (Shokrzadeh and Ebadi, 2006). Its negative impact on flora and fauna can also be linked to the continuous direct exposures as for example cypermethrin, having a half life of 4 weeks and remains in soil for up to seven months (Class, 1992). While the direct spray, which remain affective for few days, can affect macro fauna (Ahmad *et al*., 2009)

US-EPA recommends that the level of endosulfan in lakes and rivers should not exceed 74 ppb (Araujo *et al*., 1999). Endosulfan concentration of 0.50 to 0.75 µg L^{-1} has negative impact on fish (Cengiz and Unlu, 2002). In soil, the half-life of endosulfan is short (one month at 20 ^{o}C at pH-7) but has potential hazards for fish as well as other micro flora and fauna (DeLorenzo *et al*., 2002). Besides, it also produces endo-sulfate, endosulfan diol, endosulfan ether and endosulfan lactone which is also hazardous and can stay several years (Callahan *et al*., 1979; Wan *et al*., 1995).

These pesticides, cypermethrin and endosulfan are extensively used in Swat Valley. According to a recent study, 75 % decrease has occurred so for in the natural honey (Honey prepared by wild honey bee) which is no more available in the market. Still the apicultural activities are ongoing and people are keeping honeybee, but pesticides are the main hurdles in this business, and thus it is adversely affecting the socio-economic activities of the people in the business (Nafees, 2008). Another study conducted during 2005-2006 on pesticides use in Swat Valley revealed that 75 (of total 205) people fell sick during spraying, out of which 50 people recovered after a few hours while 25 people recovered after being shifted to the hospital. Another bulk of 130 people experienced headaches and vomiting due to not adopting preventive measures during spraying. The recovery time was observed as about 30 minutes (Nafees *et al*., 2008a).

The main fruit plants in the study area are apple and peaches, both require heavy input of pesticides (cypermethrin and endosulfan). In Swat Valley, till 1990, apple was grown on 44.4% area mostly covering middle and upper Swat (Inam, 2000). In the late 90s, the trend shifted toward peaches. While in lower Swat persimmon is

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a common fruit crop. Among these, peaches need maximum use of pesticides, ranging from one spray in a month to two sprays (during flowering and fruit). On apple tree pesticide spray is needed during flowering and fruiting only while persimmon requires one or two sprays in a year. At present peaches are grown on 60 % area, while apple and persimmon are grown on 30 and 10 % area, respectively (Nafees, 2008).

The main crops of the area are wheat, maize and rice. These crops require insecticides and fungicides, at least once in a year. While for vegetables, heavy use of pesticides is practiced. Different vegetables are grown in the study area, which include pea, tomato, onion, brinjal (eggplant), okra (lady's finger), etc. The frequency of pesticides use is twice a month, and some times once a week. Among vegetables, okra and peas require maximum pesticides (1-2 spray per month) while in case of the remaining vegetables its use remains minimum.

This study was aimed to analyze soil samples for cypermethrin and endosulfan residue with the objective to compare the soil residue level of these pesticides in different regions of the Swat Valley.

Materials and Methods

Soil sampling

Prior to sample collection, from Kalam to Totakan (Figure 1), the whole area was visited twice. After identifying major land types, sampling points were decided. For representative sample, the criteria adopted for site selection included, maximum area coverage and accessibility.

A systematic composite soil sample of five sub-samples was collected from un-cultivated field, before sowing of crop, at a depth of 30 cm from a plot size of 25 m^2 (Shrestha, 2006). Samples were collected during the months of November and December 2005 (winter season). As Kalam area is not accessible in winter and was therefore, sampled in June (summer). The collective five sub-samples were mixed in a plastic basket, and packed in a plastic bag. The weight of sample was from 2 to 3 kg. Each sample after collection was properly labeled and transferred to the laboratory within 24 hours time for extraction and was analyzed immediately for different pesticides (Table 1). The concentration was calculated on air dry basis, for which samples were dried at room temperature (Agnihotri *et al*., 1996; Dechert *et al*., 2004). In case of expected delay the extracted sample was stored at 4 ^oC.

Extraction of pesticides

Pesticides from soil samples were extracted using standard solvent extraction method. For this purpose 50 g fresh soil sample (on air dry basis) was extracted with acetone followed by n-hexane. Each sample was allowed to soak in the solvent for 1 hour with intermittent shaking. The samples were then centrifuged and decanted into a separatory funnel containing sufficient de-ionized distilled water (100-150 mL) to facilitate partitioning of residues into hexane portion. The hexane was washed twice with de-ionized distilled water. After separation the organic portion was concentrated to appropriate volume (10 mL) using rotary evaporator. For clean up purpose the sample was then passed through a Florisil mini-column topped with anhydrous sodium sulfate, using 12 mL n-hexane followed by 12 mL of 1 % methanol in n-hexane. The extracts were stored in proper bottle in a refrigerator below 4 ^oC before analyses where required.

Pesticides determination and quantification

Pesticides residues were quantified by GC-14A gas chromatograph (Shimadzu, Japan) equipped with Electron Capture Detector (ECD). Chromatographic separations were performed with a 50 meter fused-silica capillary column with 0.53 id (Australia made). Pure nitrogen was used as a carrier gas at a flow rate of 3.0 mL min^{-1}. The temperature of the injection port was 240 °C, and that of the detector was 300 °C. The column oven temperature was programmed as follows: 80 °C for 2.0 min, then to 160 °C @ 20 °C min^{-1} and holding for 1.0 minute and was further increased to 250 °C @ 4 °C min^{-1} and holding for 5.0 minutes and finally increasing to 275 °C @ 10 °C min^{-1} and holding for 5.0 minutes (Jasmin *et al*., 2005). For calibration, chromatography grade pesticides were obtained from Toxicology Lab. of National Agriculture Research Council, Islamabad. The purity of cypermethrin and endosulfan was 99.60 % and 99.50 %, respectively. Remaining chemicals used were of chromatography grade purity from Merck and BDH. The retention time was observed as 12.901 and 19.308 minutes for endosulfan and cypermethrin, respectively.

The equipment was calibrated by using three standards, 1, 5, 10 and 15 ppm by using computer software CLASS-CR-10 developed by Shimadzu chemical Laboratory Analysis, software, Japan. For quantification, the "Post Run Module" of the said software was used.

Interview

To explore causes of pesticides residue in soil, 360 farmers were interviewed selected from 12 villages.

Study area

River Swat watershed also called Swat valley comprises three main districts of North West Frontier

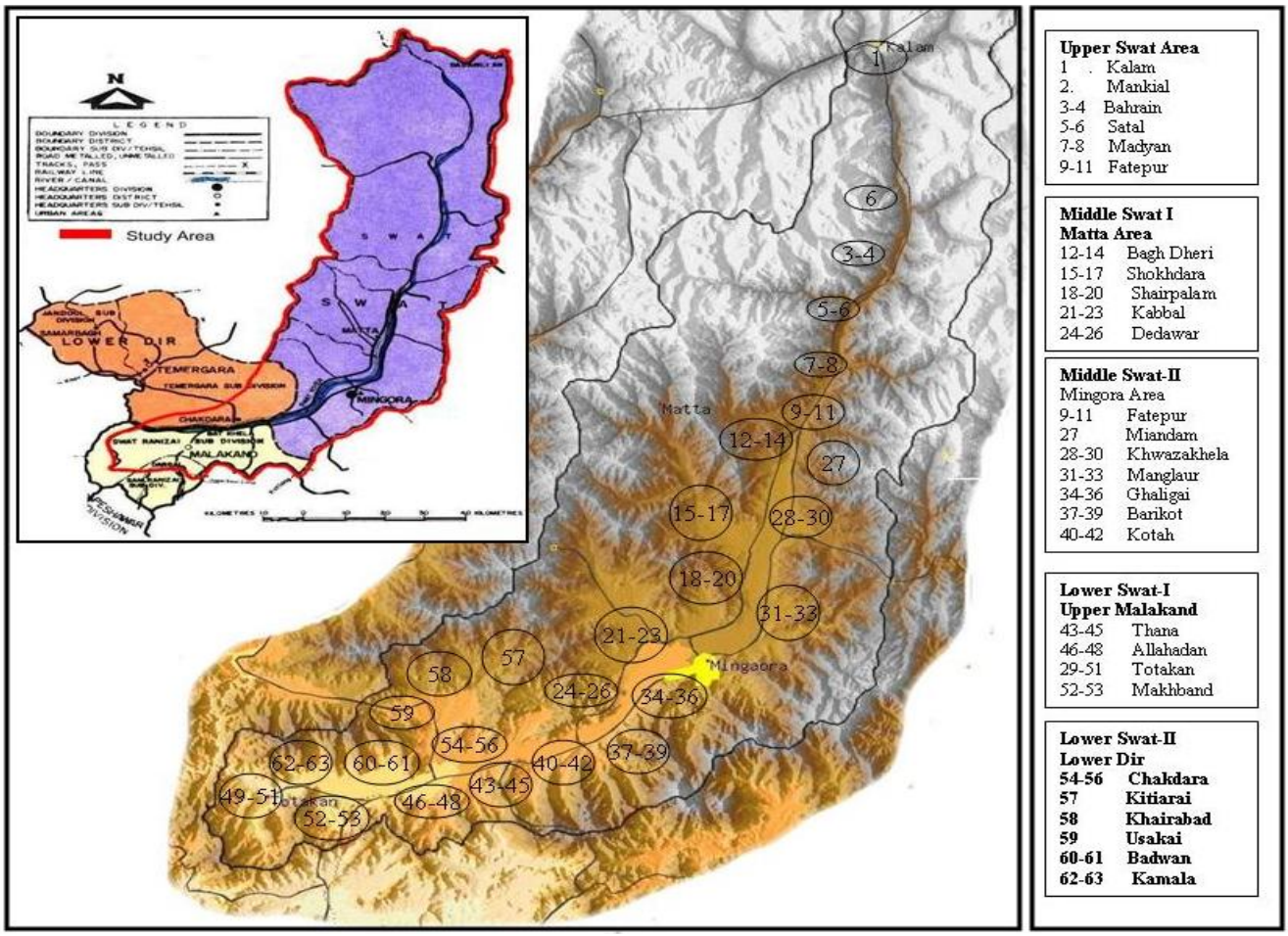

Figure 1. Map of Study Area Showing sample sites

Table 1. Concentration of Residual Pesticides in Selected Soil Samples collected from 27 villages of Swat Valley (result are in mgKg^{-1})

Region	Area	No. of Sample	Endosulfan				Cypermethrin			
			Min.	Max.	Avg.	STDV	Min.	Max.	Avg.	TDV
Upper Swat	Rainfed	4	0.24	1.12	0.62	0.40	4.67	9.14	7.19	2.04
	Irrigated	7	0.00	6.83	2.24	2.31	9.07	27.91	21.42	6.23
Middle Swat Northern (Matta) side of River Swat	Rainfed	5	0.00	0.29	0.08	0.12	0.82	27.62	9.51	11.80
	Irrigated	10	0.15	12.62	4.59	5.42	2.63	71.74	47.55	11.47
Middle Swat Southern (Mingora) side of River Swat	Rainfed	6	0.00	1.51	0.28	0.61	4.25	23.53	13.70	7.63
	Irrigated	10	1.03	12.67	4.43	9.59	14.36	73.75	51.32	8.13
Lower Swat Sothern (Malakand) Side of River Swat	Rainfed	4	0.00	0.00	0.00	0.00	0.14	9.52	3.02	4.37
	Irrigated	7	0.00	11.27	3.54	4.13	0.05	45.24	29.59	19.55
Lower Swat Northern (Chakdara) Side of River Swat	Rainfed	6	0.00	0.00	0.00	0.00	0.00	14.72	4.19	5.36
	Irrigated	4	0.13	7.54	2.74	3.28	11.21	47.82	31.95	16.94

Province, namely, Swat, Malakand (Swat Ranizai Tehsil) and Lower Dir (Adenzai Tehsil). District Swat is divided into two main regions, upper Swat (Kalam areas) and middle Swat (Mingora and Matta areas), while Malakand and Lower Dir district fall in lower Swat Region. The area is mountainous (Figure 1) and only 23% area is available for agriculture (Nafees, 2008). More than 50% area is under irrigation, irrigated from River Swat. The irrigated area is mainly used for horticultural agricultural activities (Nafees *et al*., 2008a).

Results and discussion

The trend in pesticides use in Swat Valley was observed as towards increase. Increase in residual pesticides concentration was observed when moving from North to South and a decrease was observed on either side of River Swat (East and West). Irrigated area of upper Swat, Kalam and lower Swat (Malakand) were the only areas where the concentration of residual pesticides appeared nil for endosulfan which is attributed to low use of pesticides. Kalam is a cold wet region and suitable for growing off-season vegetables for the southern part of Pakistan. At present, the residual pesticide level is low but an increasing trend in the use of pesticide was observed. Endosulfan was observed higher in irrigated plain areas such is middle Swat with the average value of 4.59 and 4.43 ppm with a Standard Deviation (STDV) of 5.12 and 9.59 for Matta and Mingora area, respectively. Cypermethrine was in the range of 47.55 and 51.32 ppm with STDV of 21.47 and 18.13 for Matta and Mingora side, respectively (Table 1). This high residue level can be attributed to high use of pesticides. Other factors contributing to this high residual level include low slope and loamy soil texture when compared with Kalam (Figure 2 and 3). This relation can be confirmed from the study conducted in Fresno County, California by Spurlock *et al*. (2006) and Gaza Strip by Shomar *et al*. (2006). In irrigated areas of lower Swat regions (Malakand and Chakdara) horticulture is not a dominant activity and were comparatively low with pesticides residues of 29.59 and 31.95 ppm, respectively.

The ultimate sink is River Swat receiving large quantity of pesticides (Jan *et al*., 2003). Downstream of Madayan, plain area starts (Figure 1) and residual pesticides concentration increase in the middle Swat because of horticulture. In the lower Swat region texture becomes a little rich and got the ability to retain pesticides (Figure 3). Besides, use of pesticides for vegetable and horticulture, River Swat water is also used for irrigation, and therefore, the concentration of residual pesticides shoots further. In rainfed area, as mostly herbicides are used and pesticides residual concentration of cypermethrin was observed as low when compared with irrigated one. The interviews show that pesticides, cypermethrin and endosulfan are also being used for fishing in River Swat and its tributaries (Figure 4).

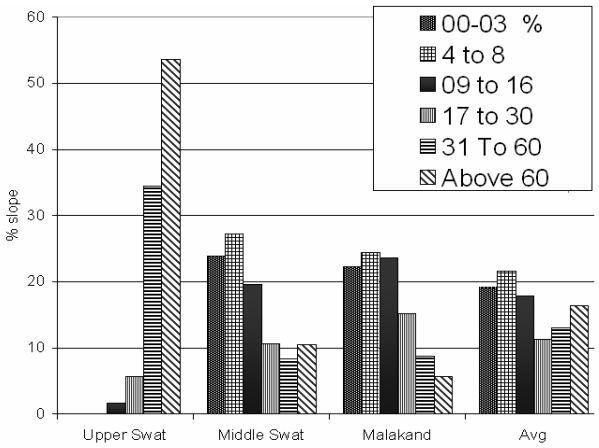

Figure 2. Comparison of average slope for different regions of Swat Valley (Source: Nafees *et al*., 2008b)

The River Swat is used for irrigation through out its entire stretch and can contribute to soil residual level. As downstream this water is used for irrigation this is why it appeared as a potential hazard as revealed from the study conducted by Karam *et al*. (2000) in district Mardan, situated downstream of River Swat NWFP, Pakistan.

The interview survey also revealed that the increase in pesticide residue level in soil can possibly be attributed to misuse in agriculture application. In the study area we met 32 people who were affected by pesticides during spray, specifically from cypermethrin and endosulfan. The survey revealed that pesticide poisoning is not taken as serious and is considered as routine. Only 180 people related it to health impact while another bulk of 150 people observed no adverse health relation and 70 people showed complete ignorance in this regard (Fig. 2). This is not the only causing increasing residual level of the mentioned pesticides but also has got negative impacts on the apicultural activates.

Conclusion

Most of the soil samples collected from Swat Valley had residual concentration of pesticides, cypermethrin and endosulfan. It was observed that the middle Swat region had high concentration of the mentioned pesticides. The residual contents can possibly be attributed to misuse related to agriculture and fishing. The combined use (agriculture and fishing) may have negative affect on human beings and aquatic flora and fauna of River Swat but further detail study is suggested.

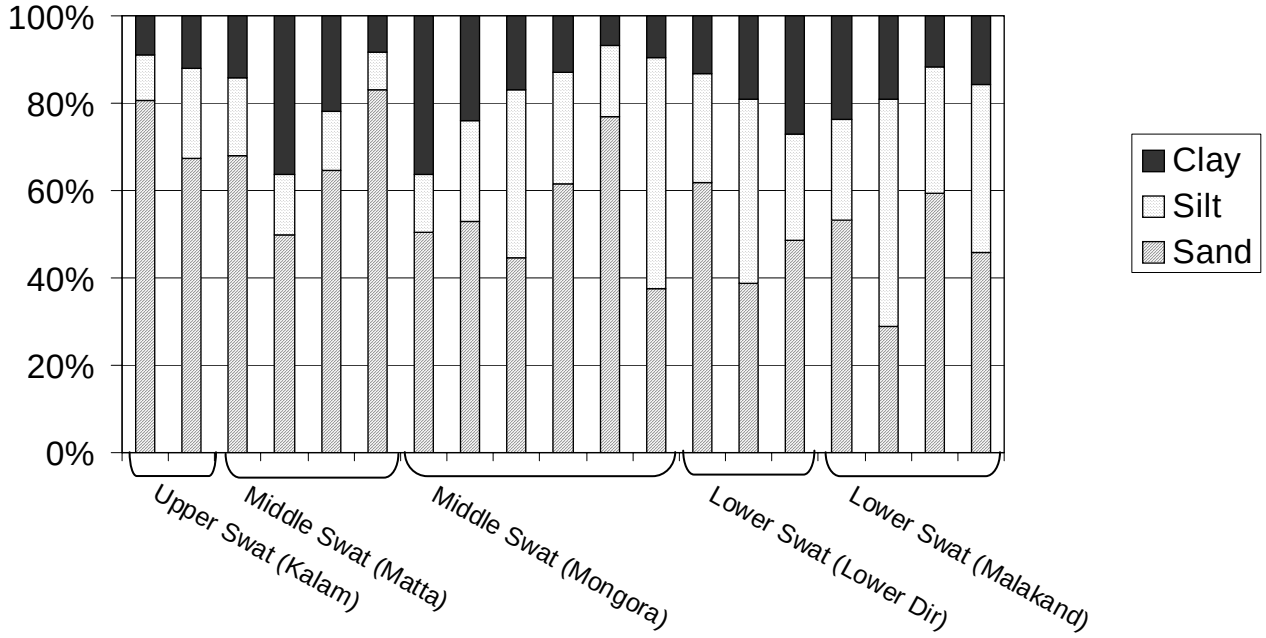

Figure 3. Soil texture of Swat Valley (Source Nafees *et al*., 2008 b)

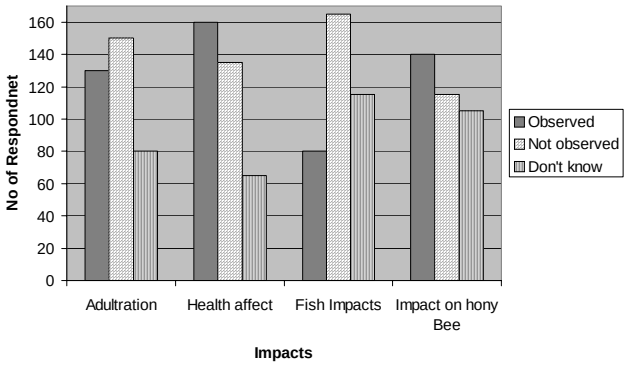

Figure 4. Respondent's observation to pesticides uses and its impacts

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