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Assessing residual status and spatial variation of current-use pesticides under the influence of environmental factors in major cash crop growing areas of Pakistan

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Graphical Abstract
Abstract

The status of seven currently used pesticides were assessed under the influence of soil parameters in surface soils of cash crop growing areas of Pakistan. Chlorpyrifos occurred in highest mean concentration (1.18 mg kg\(^{-1}\)). Selected pesticides exhibited higher affinity towards both organic carbon and black carbon fractions. The \(\delta^{13}C\) stable carbon isotopic fraction of inorganic carbon was also used as a tracer and disclosed high retention of total organic carbon in Swat and Swabi sites. Statistical analysis revealed that carbon storage was primarily influenced by altitude and temperature. Soil clay mineral oxides of aluminum and iron positively correlated with organic carbon and selected pesticides (chlorpyrifos and cyprodinil). Soil to plant bio-concentration ratios predicted heightened uptake of azinfos and diazinon in major cash crop bio mass. Occupational risk via soil ingestion expressed no significant threat to the farmer community.

Keywords: Current-use pesticides; Cash Crops; Total Organic carbon; Black carbon; Stable Carbon isotope; Clay minerals
1. Introduction

The conventional cropping patterns adopted for cash crops incorporate a wide application of pesticides. No doubt huge losses in crop output caused via pest attack are controlled by such practices (Oerke et al., 1994). Soils are a prominent storage reservoir and simultaneously act as a fundamental exposure route for individuals including agricultural workers and non-target organisms (Davie-Martín et al., 2015). Such contaminants find their way via soil and food into human beings causing a major health risk (Liu et al., 2016a).

World pesticide expenditures accounted for more than $35.8 billion in 2006 and $39.4 billion in 2007. In late 1990s, Asia and Latin America use of pesticides drastically ascended by 5.4% annually, higher than reported global average of 4.4% (Oerke et al., 1994). China, India, Korea, Pakistan, Malaysia and Thailand are some of the major contributors (Abhilash and Singh, 2009). Pakistan is one of the leading countries of South Asia responsible for massive pesticide use. About 27% of the total pesticides consumption is used on fruits and vegetable crops (Panhwar et al., 2014) while cotton cash crop accounts for 80-90% pesticide utilization. Recently disclosed figures reveal an accelerated production in Pakistan (PBS, 2015) and about 33% of farms in the country reportedly apply insecticides. Developing countries take limited steps for exposure control of these pesticides and Pakistan being an agrarian society is involved in consumption and import of pesticides without having any exposure control measures.

Current used pesticides are organic in nature. Indiscriminate factors such as soil/site properties, pesticide properties (concentration, volatility etc.) and climate such as temperature, precipitation can affect the mobility and behavior of such pesticides in soil. The most prominent among them being organic carbon content (Baskaran et al., 1996; Wauchope et al., 2002; Bronner and Goss, 2010), clay minerals and half-life. Soil minerals also play a composite effect
in terms of active sorption sites for both TOC and pesticides. TOC in top soils chemically filters
and absorbs pesticides and may also increase the activity of microorganisms thereby increase
biodegradation. Its properties like content and nature are dominant traits (Olvera-Velona et al.,
2008). Organic carbon is associated with the O alkyl, alkyl, carboxyl and aromatic fractions.
Black carbon is dominated by carboxyl and aromatic fractions (Motoki et al., 2014). Organic
pesticides bind to un-charred biomass (TOC) via absorption mechanisms. Contrastingly they
adsorb on surface of charred carbon content (BC), largely due to atomic surfaces and micro
pores. BC has lately been reported as a better sorbent for organic pesticides (Ahmad et al., 2006;
Motoki et al., 2014; Kumar et al., 2015). Composition of soil minerals is another trait that
influence carbon storage. The presence of multivalent cations such as Ca$^{2+}$, Al$^{3+}$ or Fe$^{3+}$ drives
TOC binding (Xiao, 2015). Long term TOC pool status in soil media can also be effectively
predicted through stable carbon fractions (C$^{12}$ and C$^{13}$). Agricultural expansion and
intensification has resulted in continuous cropping leading to simultaneous declines in TOC as
well as enrichment of $\delta^{13}$C (Awiti et al., 2008). Carbonate-$^{13}$C values described as $\delta^{13}$C
(carbonate-SOC) values can depict changes in TOC content, its yield and soil respiration fluxes
(Stevenson et al., 2005).

Crop protection measures are an unavoidable practice to augment food yield. Accelerated
production is followed by bioaccumulation in food causing eminent threat (Liu et al., 2016a).
The World trade organization (WTO) agreements (TBT/SPS) measures have contributed to
ensure food safety in trading system focusing on third countries. Pesticide residue is marked as
one of top five reasons for rejections by top international markets (UNIDO, 2015). Pakistan is
among the top 15 countries under the category of import rejections of food in USA (UNIDO,
2013 reveals a violation rate of 21.1% by Pakistan. Pakistan being an economy relying heavily on agro exports, concept of the threshold-based application of pest control measures is an important approach.

Limited studies are available on status of current-use pesticides in soil and factors regulating their long term prevalence and mobility in soil media of cash crops. Extraneous measures taken for inspection of cash crop exports lead to rejections. Soil being an important sorption media and source for uptake by associated crop is analyzed in present study. The core objectives of this study were (i) to probe the retention dynamics of selected pesticides in surface soils of cash crop growing areas of Pakistan; (ii) to determine the contribution of organic carbon fractions in pesticide retention; (iii) to validate TOC status using stable carbon isotope ratios as markers and whether its retention is influenced by variability in climate and soil properties and (iv) to predict the uptake of pesticides by cash crops from soils.

2. Material and Methods

2.1. Study area

For the present study six major cash crop growing cities of Pakistan were selected as shown in Figure 1. Target sites include Swat, Swabi, Sargodha, Layyah, Muzaffargarh and Khairpur spatially distributed from North to South of Pakistan. Each site is famous for harvesting distinctive cash crops such as peaches, tobacco, oranges, cotton, mangoes and dates respectively. Spatial diversity of sites was kept in mind prior to selection to evaluate the influence of environmental factors on pesticide retention. Details regarding sampling station and sample acquirement are stated in supporting information. For sampling, three samples were collected from each site, hence a total of 18 top soil (0-6 cm) bulk samples were collected from six cash crop sites. Three representative samples (1 Sample=composite of 3) were taken from local farms.
(n=3) at each sampling location. Samples were dug at a distance of 500 meters from one another to form composites for homogeneity. Top soil samples were removed by hand trowel, securely packed in polyethylene bags and taken to the Environmental Biology Lab, Quaid-i-Azam University Islamabad Pakistan. The bulk soil samples were stored at -4°C in the lab before being transferred to UK for analysis. The concentrations of pesticides (Diazinon, Chlorpyrifos, Parathion-Methyl and Azinfos) in cash crops of each respective site were obtained from Plant Protection Department, Pakistan for year 2015-2016.

2.2. Gas Chromatography-Mass spectrometry Analysis

Residual analysis for seven selected pesticides including diazinon, chlorpyrifos, parathion-methyl, tolclofos-methyl, deltamethrin, cyprodinil and azinfos were performed on soil samples by Gas Chromatographic-Mass spectrometric analysis. Details regarding experimental design and analytical procedures are mentioned in the Supporting Information.

The analytes were quantified with a Finnigan TRACE GC-MS system. Soil samples were sieved and stored in freezer. Prior to analysis samples were allowed to thaw. 5 g of each sample was placed in a centrifuge tube. The dried sample was spiked with known concentration of pesticide to act as a recovery standard. A blank containing 3 g of Na$_2$SO$_4$ was included after every 10 samples. Extraction was carried out with 30 ml of Hexane-Ethyl acetate solution (2:3). Extraction procedure was performed three times. Extracts were concentrated to 1 ml by a slow torrent of nitrogen gas. For extract cleanup 6 g of alumina and 1 cm thick sodium sulphate were used. Column was rinsed prior to sample introduction with 20 ml of ethyl acetate. Extract elution was carried out from column by ethyl acetate. The final solution was blow dried and dissolved with 1ml Hexane. Finally, samples were analyzed by Finnigan Trace GC-MS. The temperature setting for transfer line, injector interface and ion source was set at 280, 250 and 230 °C,
respectively. The temperature programing of the GC oven was done as: 80 °C for 0.5 min, 20 °C min\(^{-1}\) to 160 °C, 4 °C min\(^{-1}\) to 240 °C and 10 °C min\(^{-1}\) to 295 °C and then hold for 10 min. The residues were quantified by the external standard calibration curve method. To ensure quality of quantification methods analytical grade reagents were used. Recovery for samples extracted was 80-90 %. Linearity curves (\(r^2=0.995\)) were obtained by spiked samples for instrument calibration.

2.3. Total organic carbon and black carbon (CTO-375 method)

The soil samples were prepared by weighing up to 4 g, followed by sieving and finely grounded to smooth powder. Chemo-thermal oxidation (CTO-375) method was used as standard protocol for BC residue analysis. BC samples were pre-treated with 1N HCl and stirred at intervals for 1 hour. Next (2-3 g) of acidified samples were dried and subjected to thermal oxidation (375 °C, 18 hr) by providing suitable conditions in a muffle furnace under constraint air flow for removal of non-pyrogenic carbon (Gustafsson et al., 2001; Agarwal and Bucheli, 2011). The residual organic carbon content was determined as BC by using a TOC analyzer. Similarly, TOC residual quantification also required 4 g of sample. Each batch was dried, homogenized and acidified with 10% HCl for eliminating inorganic carbon. Later it was rinsed with deionized water thrice and dried overnight at 60°C. The TOC content was determined with TOC analyzer.

2.4. Stable Carbon isotope (\(\delta^{13}C\)) analysis

The stable isotope analyses were executed with a modified Varian Mat GD-150 Mass Spectrometer. Stable isotope ratio \(\delta^{13}C\) is measured in Total dissolved inorganic carbon. For isotope analysis on mass spectrometer, soil samples have been converted into gas phase. For the extraction of CO\(_2\) gas from Total dissolved inorganic carbon of soil a 1g of soil sample was
poured into the Pyrex reaction flask. A small burette containing H$_3$PO$_4$ acid was then attached to the reaction flask. The reaction flask assembly was connected to the vacuum line. Dewar flask containing liquid N$_2$-acetone mixture (temperature: -800°C) was attached to the moisture traps in the vacuum system. About 5 ml H$_3$PO$_4$ acid was added to the pre-evacuated reaction flask. The CO$_2$ gas was evolved as a result of reaction between inorganic carbon component/fraction of sample and the phosphoric acid according to the following equation:

\[ \text{H}_3\text{PO}_4 + \text{Carbonate mineral} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

The moisture produced during the reaction was removed by cryogenic trap of -800°C. The CO$_2$ gas was passed through vacuum line and purified by freezing in U-trap dipped in liquid nitrogen flask. Other gases were pumped out from line. The liquid N$_2$ flask from CO$_2$ trap was removed to expand CO$_2$ in vacuum linear which was finally collected in an ampoule dipped in liquid nitrogen flask at the other end of line. The ampoule was labeled and removed from the line for isotope ratio measurements onto the Isotope Ratio Mass spectrometer (IRMS). The overall analytical errors are ± 0.01 ‰ for $\delta^{13}$C measurements. To ensure precision, standard deviation of the mass spectrometer was also computed and standard deviation of each sample was ensured to be within permissible limit.

2.5. Clay mineral fraction assessment by XRF

For the analysis of clay mineral content in soils of cash crop sites soil samples from each site were weighed 10 g. Initially samples were air-dried in a purified area, and then crushed down to break aggregates. Sample is further ground to achieve fine powder. This ensures contribution of adequate number of particles of each fraction of the heterogeneous mass. The sample is sieved through a sieve of 60 um size and particles above this limit are ground again until no grains larger than 60 µm are left.
3. Results and Discussion

3.1. Concentration profile of current-use pesticides

Concentration of selected pesticides in soil and cash crops are presented below and discussed in detail.

3.1.1. Soils

The concentration profiles of pesticides in cash crop soils are given in Table 1. Among all target analytes, chlorpyrifos occurred in highest mean concentration (1.18 mg kg\(^{-1}\)). The average concentrations presented in Figure 1 indicates that contaminants occurred were in order of chlorpyrifos > diazinon > parathion-methyl > deltamethrin > tolclofos-methyl > cyprodinil > azinfos. The least reported pesticide was azinfos with an average concentration of 0.37 mg kg\(^{-1}\).

Concentration of Azinfos studied in comparison to Chlorpyrifos was also found to be less persistent in orchards (Reinecke and Reinecke, 2007).

In general, spatial abundance of pesticides among six sites was as follows; Swabi > Khairpur > Swat > Sargodha > Muzaffargarh > Layyah. Target pesticides Tolclofos-Methyl, Chlorpyrifos and Cyprodinil showed a significant difference in their distribution and occurrence among six sites which predicted variability in factors responsible for persistence. Parathion-Methyl did not exhibit any significant spatial variability among six sampling sites.

The soil pesticide concentration profile was compared to the worldwide reported studies Supporting information. The residual concentration of Chlorpyrifos was much higher as compared to studies in primary agricultural areas of China (Liu et al., 2016a), Dehli, India (Bhupander et al., 2011), Western Cape and South Africa (Reinecke and Reinecke, 2007). They were comparable to concentration recorded in Bhawalpur, Pakistan (Anwar et al., 2014).
In contrast to previous studies Parathion-Methyl was detected in higher concentration than reported in Bhawalpur, Pakistan (Anwar et al., 2014). It has also been banned by Pakistan Plant Protection Department. Diazinon reported in our study was comparatively less than the residues assessed in agricultural and urban soils of Peshawar, Charsadda and Swat (Jan et al., 2003), (Nafees et al., 2008a). The estimated values of Azinphos were also lower in studies executed in Western Cape, South Africa (Reinecke and Reinecke, 2007) and Eastern, Washington State USA (Simcox et al., 1995) as compared to current study. Concerning Cyprodinil study was conducted in Spain, Galacia (Rial-Otero et al., 2004; Arias et al., 2005). It reports lower concentrations of Cyprodinil a new generation fungicides and frequently used in vineyards. Deltamethrin was also reported in lower residual values in a study of Haryana, India (Bhupander et al., 2011) in comparison to our results. This comparison suggests that contamination of cash crop soils in Pakistan is significant in terms of pesticides and elevated status is pertaining to environmental problems.

3.1.2. Cash crops

The concentration profiles of pesticides in six cash crops are presented in Table 1. Pesticides were detected in order of Diazinon > Azinphos > Chlorpyrifos > Parathion-Methyl. Diazinon concentration ranged from 0.01-5.21 mg kg$^{-1}$ with highest mean (2.61 mg kg$^{-1}$) in mangoes (MUZ). Several studies report pesticide residues in food items supporting information. Diazinon had been monitored in various food crops and variety of fruits. The residues mentioned in this study were comparable to the ranges reported for peach and oranges (Gebara et al., 2005; Knežević and Serdar, 2009). Concentrations for Parathion-Methyl (0.02-0.18 mg kg$^{-1}$) were equivalent to ranges reported by literature in grains, fruits and vegetables (Hjorth et al., 2011;
Ogah and Coker, 2012; Liu et al., 2016b). Chlorpyrifos had been the most assessed pesticide in numerous fruits and vegetables. Residues concentrated in peach samples in this study were several folds higher than Xiamen, China (Chen et al., 2011). Mean value for Azinfos in target commodities was 0.32 mg kg\(^{-1}\). A study conducted on Croatian fruits and vegetables revealed comparable Azinfos averages, where orange and peach samples sustained residues above maximum residue limits (MRLs) (Knežević and Serdar, 2009).

Pesticide residues consumed as part of food can prove a menace. Thus MRLs are established to regulate safe pesticide limits in consumer products for both domestic and international markets. The MRLs set by EU, Japan, China, US and FAO/WHO are summarized in Supporting Information. The comparison of mean concentrations and global MRLs revealed violation in cash crops. Pesticide residues in fruits (orange, peach, mangoes and dates) were above approved EU MRLs. Although pesticides were also reported significantly lower than FAO/WHO MRLs with the exception of Diazinon (Peach and mangoes) and Azinfos (mangoes). Nonfood crops are majorly ignored when it comes to assigning residue limits. No acceptable limits were available for tobacco and cotton fiber. However, guidelines are available for industries and organizations dealing with tobacco products. Russian MRLs area regulated for Diazinon residues in tobacco (0.05 mg kg\(^{-1}\)). Guidance residue limits (GRLs) are also provided for tobacco growers by CORESTA (Cooperation Centre for Scientific Research Relative to Tobacco). The tobacco residues reported in this study were below instructed GRLs except for Diazinon.

3.2. Soil properties and its association with pesticides

Physic chemical characteristics of soil are listed in Table 2. The pH for all sampling locations was moderately alkaline and varied from 7.33-8.40. Soil texture was one of the most
chief factors regulating maximum spatial variability in our respective study area. Soil moisture content was in range of 11-21% in cash crop soils. It was found most abundant in soils of Khairpur (14-21%) and Swat (19-20%). The textural analysis exhibit that study area soils were dominated by silty loam soils. Swat bore sandy loam soils in contrast to rest of sites. Sand was reported dominant feature of all soil in Swat Valley (Nafees et al., 2008b). The results of EC indicated a high degree of salinity in LAY, SAW and SWB as compared to rest of the sites. Both organic carbon fractions occurred in moderately low concentration which was majorly due to poor ability of agricultural top soils to support organic carbon pools (Cochran et al., 2007). TOC and BC ranged from 0.49-2.30 % and 0.07-0.45% in cash crop top soils respectively. The correlation output represented in Supporting information showed that Diazinon, Tolclofos-Methyl and Azinfos represented a strong positive correlation with BC% and Chlorpyrifos and Cyprodinil exhibited a significant correlation for TOC% which was in agreement with study of (Dec et al., 1997; Loewy et al., 2011; Motoki et al., 2014). TOC and BC shared a prominent negative correlation. According to (Rumpel et al., 2006) the negative correlation found between BC reflected higher amounts of TOC existing as BC in surface soils. Deltamethrin supported a negative correlation with pH. Deltamethrin was found to be more persistent in acidic as compared to non-acidic soils by (Zhu, 2002). The rest of specified soil parameters did not significantly impact target pesticides according to Pearson correlation analysis significant at 0.01 and 0.05.

3.3. Spatial trend identification of cash crop sites using PCA

The results for PCA applied as an ordination method on soil samples are summarized in Supporting information. PCA Euclidean biplots are represented in Figure 2 in order to show spatial variability of pesticides in study area. PCA is an imperative and valuable tool for
classifying data in terms of eigenvectors and eigenvalue. Classification of sampling sites was also determined on basis of physic chemical properties of soil at following sites. According to the significant eigenvalue four principal components were identified by Enter number method and the first component with the highest eigenvalue of 5.429 explained maximum variance in data set. The eigenvalue of all extracted factors were greater than 1. These four principal components extracted with PCA had a contribution of 75% to its total variance. The first two axis explained most of the variance i.e. PC 1 36% and PC 2 20%. According to Figure 2 the sampling points were represented as dependent variables while target contaminants and physic chemical properties of soil were represented as independent variables. Arrows were drawn from the joint centered ordination axis to the points representing each variable.

The first Principal Component (PC 1) correlated positively with loading Diazinon, Parathion-Methyl, Tolclofos-Methyl, Azinfos, BC, Silt%. That signified the dominant role of BC in analyte binding process. A negative relation was found for Chlorpyrifos, Cyprodinil, TOC%, Sand% and Clay% at PC 1. Soil samples from Swabi and Swat substantially clustered along TOC%. These sites were also known to support elevated values of Chlorpyrifos and Cyprodinil according to previous results. TOC is well known for nonionic pesticide binding in soils but recently its aromatic fraction (BC) has proven to be a more effective sorbent (Ahmad et al., 2001). Deltamethrin being an exception exhibited negative correlation with pH and no relation with TOC or BC. (Zhu, 2002) also found Deltamethrin to be least persistent in high pH soils despite higher organic matter content. Particle size distribution influenced TOC and BC retention. TOC strongly correlated to Sand% and Clay%. The sites supporting highest TOC were sandy loam and loam in texture (Swat and Swabi) which explained a positive correlation of TOC with sand content. The correlation coupled with study conducted by (Azlan et al., 2012) in
Malaysia where sandy clay loam soils supported high TOC. In contrast BC accumulation was regulated by silt content. Micro aggregates (Silt and Clay fractions) are dominant BC retaining fractions with more pronounced role of larger fractions (silt) (Zong et al., 2016). The long arrows of Diazinon, TOC% and Deltamethrin confirmed a gradual change in their concentration while rest of the variables had short arrows indicating rapid alteration. Previously represented results of Pearson correlation were in total agreement with PCA findings. The results support the hypothesis that BC and TOC were main drivers of pesticide distribution in soils of cash crop.

3.4. TOC and BC allocation in cash crop soils

The BC and TOC concentration profile is presented in Table 2. Mean values of BC and TOC in cash crop soils were 0.20 % and 1.09 % respectively. Cash crop sites at Sargodha and Layyah showed dominant BC accumulation. BC as percentage of TOC was low in Swabi and Swat as compared to rest of the sites. TOC pools show more reliance on land use changes in top soils (Wang et al., 2017), while BC is dependent on input and storage conditions (mineralogy, texture) (Lehndorff et al., 2016). TOC quantified in our study was generally low in content. Nonetheless the averages were in agreement with anthropogenic soils of Brazil (1.1-2.2 %) (Schellekens et al., 2017), Shanghai, China (Wang et al., 2014) and orchard (1.66 %) and farmlands (1.56 %) of Northern Iran (Ajami et al., 2016).

3.4.1. Black carbon source credentials

The ratios calculated for BC source identification are graphically presented in Figure 3. BC/TOC ratios ranged from 0.03 to 0.65. At Khairpur, Swabi and Swat biomass burning was the main source of BC. Ratios at Sargodha and Layyah highlighted fossil fuel burning, traffic or industrial BC origin as well as miscellaneous source. BC formed during burning supports residues derived from partially combusted plants to inert graphite carbon (Rumpel et al., 2006).
According to (Novakov et al., 2000; Wang et al., 2014) BC/TOC < 0.11 indicates incomplete combustion of biomass and values greater than 0.5 suggest industrial, fossil fuel burning and traffic source. BC/TOC ratios acted as an ideal indicator for identifying source of BC. As our study area comprised of agricultural sites existing along road sides thus potential BC sources could be diverse. These ratios account for BC source characterization in several studies. Ratios in Changbai China (0.10-0.44) (Schellekens et al., 2017) and Shanghai China (0.14-0.17) (Wang et al., 2014) indicate dominant char inputs. While Industrial and roadside soils of Anshan, China (0.45-0.95) (Zong et al., 2016) as well as German croplands revealed dominant soot fraction (fossil fuel burning) (Brodowski et al., 2007). Similarly, miscellaneous sources also contributed to BC formation. Averages in our study were comparable to BC/TOC ratios reported in rural and urban settings of Beijing China (Liu et al., 2011).

3.4.2. Climatic conditions as marker for TOC retention

Average values of climatic factors (temperature, altitude, relative humidity and precipitation) for the respective sites are mentioned in supporting information (Table S6). The mean monthly data was acquired by running HYSPLIT trajectory model. Mean annual precipitation (MAP) and Mean annual temperature (MAT) values for target sites were roughly estimated from ranges available for the nearest weather station by Pakistan Meteorological Department.

Regression analysis expressed positive correlation ($r^2 = 0.846$) of altitude with accumulation of TOC pools in soil Figure 4(a). Rise in Altitude dominantly coincides with elevated TOC pools in recent studies conducted in Karakoram Pakistan (Shedayi et al., 2016; Bojko and Kabala, 2017). Since TOC magnitude elevates with rising mountain toposequences. The altitudinal gradient vitally distributes TOC and is preferably included in models for its
estimation. TOC shared an inverse trend with mean monthly temperature. MAP and MAT analysis revealed significant but comparatively less dominant role in TOC retention as shown in Figure 4. Previously quantitative relationships between TOC, temperature and precipitation have also been documented (Azlan et al., 2012). Dry ecosystems account for greater TOC losses. No regression could be assessed for the mean monthly precipitation because of dry spell of rain in December. Relative humidity had a comparatively weak positive correlation with TOC. In humid climates, both production and degradation of TOC increases with more profound decomposition (Jobbágy and Jackson, 2000). Our targeted cash crop sites supporting variable terrain and weather conditions, supporting labile pools in top soils, which are sensitive to alterations in temperature, precipitation and altitude (Shedavi et al., 2016). Altitude mediated TOC distribution is influenced by high rainfall inputs, declining temperatures, resulting in gradual fall in degradation patterns. Our results also reflect prominent role of climatic factors in tracing TOC persistence.

3.4.3. Stable carbon isotopic enrichment as an indicator of TOC stability

The mean values for $\delta^{13}$C of SIC in cash crop soils are summarized in Table 2. The $\delta^{13}$C values measured at six sites ranged from -1.75 to -8.49 ‰. The concentrations indicated low TOC inputs in cash crop soils as compared to carbonate fraction. $\delta^{13}$C values predicted high TOC content at SAW and SWB. The results were in agreement with $\delta^{13}$C of carbonates in agricultural soils of France (Bertrand et al., 2007). Regression analysis shown in Figure 4(f) also represented a strong negative correlation ($R^2=0.936$) between mean TOC % and $\delta^{13}$C enrichment for six sites. These results provided a strong base for determining TOC pool retention in cash crop soils. The $\delta^{13}$C values were assessed in SIC because our study area supported alkaline conditions. Semiarid soils are naturally alkaline limited precipitation and reduced leaching cause
carbonates to accumulate in the soil profile (Cochran et al., 2007). Secondly $\delta^{13}C$ values of SIC are ideal indicators for TOC because its less prone to loss than TOC. Stable carbon isotope ratios of SIC (CO$_2$, HCO$_3^-$, CO$_3^{2-}$) depended on the $\delta^{13}C$ of soil-CO$_2$ and dissolved carbonate that originated from limestone, relatively enriched in $^{13}C$ at 0‰. $\delta^{13}C$ values in the range of -3-2‰ represented limestone dissolution and lower estimates denoted SIC rich in organic carbon (Coleman, 2012). The precursors for the carbonates in the soil are mainly ancient marine carbonate rocks with carbon isotopic composition between +2 and -2‰.

3.5. Clay mineral bound TOC and pesticide sorption in soils

Mean clay mineral contents for cash crop soil characterization are summarized in Table 2. Silica and Aluminum oxide (Al$_2$O$_3$) reportedly the most abundant mineral fractions occurred in the range of 47.98-59.11% and 11.09-12.86% respectively. Occurrences of Silica, Aluminum oxide and Calcium oxide (CaO) were above their quantified natural elemental fractions in soils. Mean range for Ferric oxide (Fe$_2$O$_3$) was 4.3-4.9%. Magnesium oxide contributed in a moderate manner.

The regression analysis depicted in Figure 4(g) revealed significant TOC and clay mineral interactions. Al$_2$O$_3$ and Fe$_2$O$_3$ exhibited a strong positive correlation with TOC retention. Clay minerals play a major part in long term organic carbon retention in soil. TOC is normally retained in mineral top soils (0-40cm) (Jonard et al., 2017). These reactive minerals with specific surface areas are binding sites for TOC. Specifically weathering products such as nanometer sized Fe oxides and Al-silicates supporting diverse charge. TOC adsorption to Fe$_2$O$_3$ is mainly defined by ligand exchange mechanism. It is the dominant phenomenon for TOC retention in soils that are rich in oxides where Fe$^{3+}$ and Al$^{3+}$ form cation bridges with organic carbon (Keil...
Clay minerals and TOC are reported to synergistically bind pesticides in soil, but influence of TOC in mineral availability for pesticides is not fully understood.

### 3.6. Occupational exposure to current-use pesticide

The cumulative occupational risk of pesticide ingestion via soil residues is presented in supporting information (Table S8 and S9). Evaluated results revealed remarkably low risk of exposure by soil media. Hazard quotient (HQ) did not exceed 1 (Threshold value) at any sampling station. The magnitude of risk from each target contaminant ranked in order of Parathion-Methyl > Diazinon > Chlorpyrifos > Azinfos > Deltamethrin > Cyprodinil. Average daily intake levels summarized in supporting information (Table S7) were multifold order of magnitude lower than reference doses (RfD) of pesticides. The highest daily intake was cumulated for Chlorpyrifos (1.01452E-06) in comparison to rest of pesticides. Hazard Quotient (HQ) for each contaminant was quantified. Since non-carcinogenic Chronic Oral Exposure doses have not been evaluated for some pesticides their risk could not be calculated. The RfD values in terms of chronic exposure and US EPA recommended exposure factors are listed in Supporting information.

The results reported in this study contradict with studies highlighting ingestion as a core route of exposure in terms of pesticides. Primarily owing to the focus of literature on pesticide ingestion via food instead of soil. Study performed by (Simcox et al., 1995) reported greater sorption of Azinfos to dust particles in relation to soil media, making dust the prominent exposure medium. Estimated HQ did not predict risk to workers potentially exposed to multiple organophosphate and pyrethroid pesticides. However current-use pesticides are typically formulated with synergists (Saillenfait et al., 2015). Thus, cumulative risk should not be ignored.

### 3.7. Plant uptake of current-use pesticides from soil
The bio concentration ratios equated for target pesticides are summarized in Table 3. The results indicated accumulation trend of contaminants in cash crops in following order; Azinfos > Diazinon > Chlorpyrifos > Parathion-Methyl. Highest uptake of Azinfos (2.49) was equated for cotton at LAY-1. Cotton and mango samples also exhibited accelerated influx of Diazinon from soil media at stations LAY-1 and MUZ-2. The overall trend indicates that mainly Azinfos is the most lipophilic contaminant in terms of plant uptake in this study for most cash crops. Chlorpyrifos bio concentration ratios (0.04-0.22) were comparable to uptake values reported in Ricinus communis L. by (Rissato et al., 2015). Parathion-Methyl revealed lowest biomass uptake (0.03-0.11) with lowest ratios reported in Dates. Study conducted on removal of soil bound Parathion-Methyl residues by oat plant revealed only 5.1 % of total residues were retained in green part of plants (Fuhrmann and Lichtenstein, 1978). Organic contaminants have the tendency to concentrate in plant mass depending upon their lipophilicity. The averaged ratios accounted in this study demonstrated variability in uptakes with generally lower biomass retention of Chlorpyrifos and Parathion-Methyl. (Liu et al., 2016a) also predicted low OC, OP and PY (pyrethroids) uptake by persimmons and jujube fruits. Soil bound pesticide residues, pesticide concentrations and physic-chemical properties of the pesticides are driving factors controlling uptakes.

4. Conclusions

The quantified results draw attention towards Chlorpyrifos and Diazinon supporting highest residues in study area. Pesticides specifically organophosphates retention is principally influenced by TOC and BC content. BC derived from fossil fuel rather than biomass is found effective in bounding affinitive pesticides. Topographic and climatic variations influence TOC distribution in cash crop soils. Specifically, altitudinal gradient is a salient feature in TOC
retention. Raised TOC storage in high altitude toposequences can be attributed to minimal
temperatures and elevated precipitation. Among target pesticides, Chlorpyrifos and Cyprodinil
are functionally absorbed by labile TOC pools. Recalcitrant fraction (BC) is strongly correlated
with Diazinon and Toclofos-Methyl. Specifically, in lower altitudinal sites containing more soot
incorporated BC. Swat and Swabi with stable carbon isotopic ratios of SIC below -3‰
confirmed high TOC pools as compared to rest of sites. Clay minerals Aluminum oxide and
Ferric oxide are major binding agents for TOC. Prominent residues of Diazinon and Azinfos are
reported in cash crops of targeted study area. Bio concentration ratios (BCR) also confirm
dominant soil to plant uptake of Diazinon and Azinfos chiefly in cotton, mango and orange crop.
The ingestion of pesticide bound soil residues does not inflict any significant harm to farmer’s
health. However synergistic effect of multiple pesticide residues long term ingestion cannot be
ignored. The baseline information provided by this study on status of CUPs and their persistence
in cash crops soil and their uptake must be taken into consideration for identifying need for
monitoring of cash crop soils from an agro economical prospect. Continuous monitoring is
crucial act for these areas owing to their global importance in terms of exportable commodities
and status of environmental factors ideally retaining pesticides in these sites.

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method to quantify black carbon in soils. Environmental pollution 159, 532-538.
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List of Figures:

Figure 1: Targeted sampling sites and concentration profile of pesticides at selected sampling stations from cash crop growing areas of Pakistan.

Figure 2: Spatial classification of cash crop sites represented by Principal Component Analysis Bi plot

Figure 3: BC/TOC ratios for Black Carbon source identification at cash crop sites

Figure 4: Regression analysis between TOC and variables in cash crop sites (a) Altitude (b) Relative humidity (c) Mean monthly temperature (d) Mean Annual Precipitation (e) Mean Annual Temperature (MAT) (f) $\delta^{13}$C (g) Clay mineral fractions
List of Tables:

1. Table 1: Descriptive analysis of selected pesticide concentrations in soil and plants of cash crop sites
2. Table 2: Descriptive analysis of soil parameters in cash crop sites
3. Table 3: Bio-concentration ratios of cash crops for selected pesticides
### Table 1. Descriptive analysis of selected pesticide concentrations (mg kg\(^{-1}\)) in soil and plants of cash crop sites

<table>
<thead>
<tr>
<th>Sites</th>
<th>Commodity</th>
<th>Diazinon</th>
<th>Parathion-Methyl</th>
<th>Telofos-Methyl</th>
<th>Chlorpyrifos</th>
<th>Cyprodinil</th>
<th>Azinfos</th>
<th>Deltamethrin</th>
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<tbody>
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<td>Plant</td>
<td>Soil</td>
<td>Soil</td>
<td>Soil</td>
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<td>0.04</td>
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*p value* is significant at < 0.05
Table 2. Descriptive analysis of soil parameters in cash crop sites

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<th>Clay%</th>
<th>TOC%</th>
<th>BC%</th>
<th>SiO2 %</th>
<th>Al2O3 %</th>
<th>Fe2O3 %</th>
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Table 3. Bio-concentration ratios of cash crops for selected pesticides

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<th>Chlorpyrifos</th>
<th>Azinfos</th>
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<td>0.653</td>
</tr>
<tr>
<td>Mean (Dates)</td>
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<td>0.028</td>
<td>0.118</td>
<td>0.535</td>
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<tr>
<td>SWB-1</td>
<td>0.136</td>
<td>0.028</td>
<td>0.171</td>
<td>0.662</td>
</tr>
<tr>
<td>SWB-2</td>
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<td>SWB-3</td>
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<td>Mean (Tobacco)</td>
<td>0.121</td>
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<td>0.191</td>
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<tr>
<td>SAW-1</td>
<td>0.105</td>
<td>0.028</td>
<td>0.163</td>
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<tr>
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<td>0.105</td>
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<td>0.254</td>
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<tr>
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<td>0.035</td>
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<td>0.321</td>
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<tr>
<td>Mean (Peaches)</td>
<td>0.104</td>
<td>0.033</td>
<td>0.162</td>
<td>0.327</td>
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<tr>
<td>Total mean</td>
<td>0.665</td>
<td>0.042</td>
<td>0.137</td>
<td>0.797</td>
</tr>
<tr>
<td>Min-Max</td>
<td>0.04-4.30</td>
<td>0.03-0.11</td>
<td>0.04-0.22</td>
<td>0.18-2.49</td>
</tr>
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</table>
Figure 1. Targeted sampling sites and concentration profile of pesticides at selected sampling stations from cash crop growing areas of Pakistan.
Figure 2. Spatial classification of cash crop sites represented by Principal Component Analysis Biplot.
Figure 3. BC/TOC ratios for Black Carbon source identification at cash crop sites
Figure 4. Regression analysis between TOC and variables in cash crop sites (a) Altitude (b) Relative humidity (c) Mean monthly temperature (d) Mean Annual Precipitation (e) Mean Annual Temperature (MAT) (f) $\delta^{13}$C (g) Clay mineral fractions
Highlights:

• Current-use pesticides status in soil media for six major cash crop growing areas of Pakistan

• TOC and BC levels and distribution in cash crop growing areas and their influential role in sorption of current-use pesticides

• Inspecting organic carbon distribution pattern using stable carbon isotope as a tracer

• Effect of clay minerals and climatic factors on organic carbon retention and pesticide sorption