

Accepted Manuscript

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PII: S0045-6535(18)31429-2

DOI: [10.1016/j.chemosphere.2018.07.164](https://doi.org/10.1016/j.chemosphere.2018.07.164)

Reference: CHEM 21879

To appear in: *ECSN*

Received Date: 22 March 2018

Revised Date: 26 July 2018

Accepted Date: 27 July 2018

Please cite this article as: Ansari, S., Waheed, S., Ali, U., Jones, K.C., Sweetman, A.J., Halsall, C., Malik, R.N., Assessing residual status and spatial variation of current-use pesticides under the influence of environmental factors in major cash crop growing areas of Pakistan, *Chemosphere* (2018), doi: 10.1016/j.chemosphere.2018.07.164.

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

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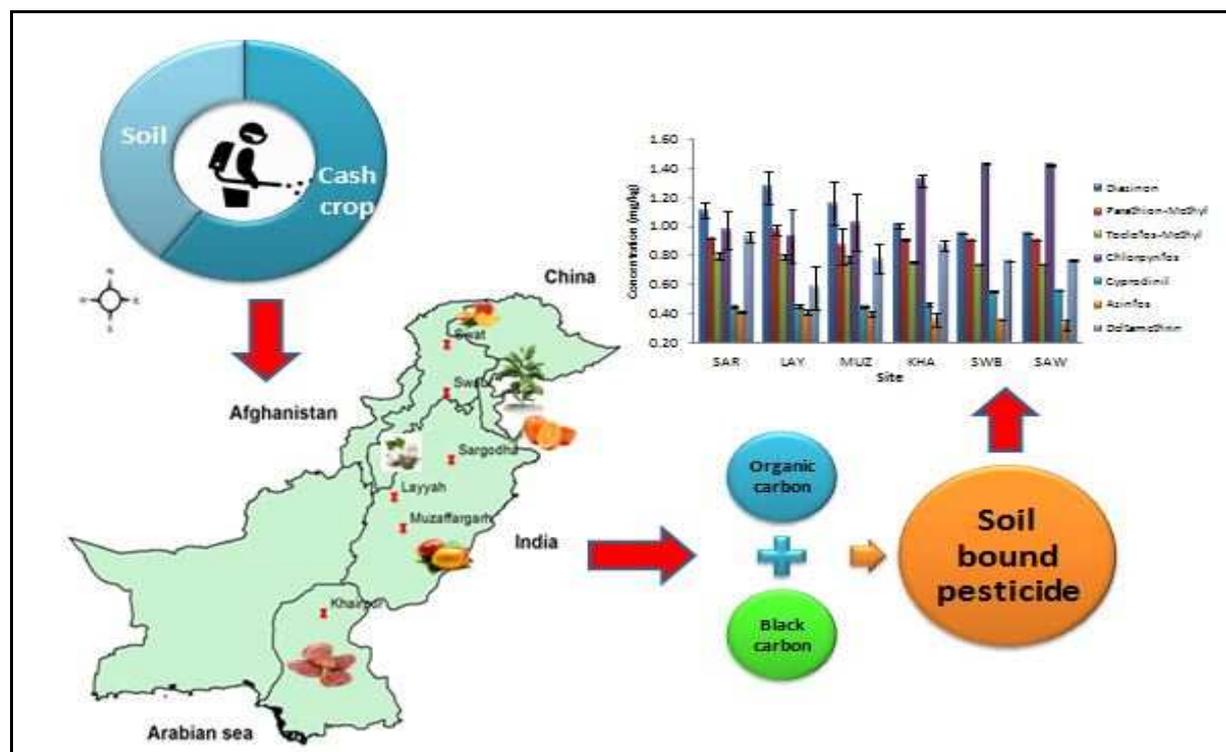
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Graphical Abstract

1 Abstract

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

13 **Keywords:** Current-use pesticides; Cash Crops; Total Organic carbon; Black carbon; Stable
14 Carbon isotope; Clay minerals

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21 1. Introduction

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

28 World pesticide expenditures accounted for more than \$35.8 billion in 2006 and \$39.4
29 billion in 2007. In late 1990s, Asia and Latin America use of pesticides drastically ascended by
30 5.4% annually, higher than reported global average of 4.4% (Oerke et al., 1994). China, India,
31 Korea, Pakistan, Malaysia and Thailand are some of the major contributors (Abhilash and Singh,
32 2009). Pakistan is one of the leading countries of South Asia responsible for massive pesticide
33 use. About 27% of the total pesticides consumption is used on fruits and vegetable crops
34 (Panhwar et al., 2014) while cotton cash crop accounts for 80-90% pesticide utilization. Recently
35 disclosed figures reveal an accelerated production in Pakistan (PBS, 2015) and about 33% of
36 farms in the country reportedly apply insecticides. Developing countries take limited steps for
37 exposure control of these pesticides and Pakistan being an agrarian society is involved in
38 consumption and import of pesticides without having any exposure control measures.

39 Current used pesticides are organic in nature. Indiscriminate factors such as soil/site
40 properties, pesticide properties (concentration, volatility etc.) and climate such as temperature,
41 precipitation can affect the mobility and behavior of such pesticides in soil. The most prominent
42 among them being organic carbon content (Baskaran et al., 1996; Wauchope et al., 2002;
43 Bronner and Goss, 2010), clay minerals and half-life. Soil minerals also play a composite effect

44 in terms of active sorption sites for both TOC and pesticides. TOC in top soils chemically filters
45 and absorbs pesticides and may also increase the activity of microorganisms thereby increase
46 biodegradation. Its properties like content and nature are dominant traits (Olvera-Velona et al.,
47 2008). Organic carbon is associated with the O alkyl, alkyl, carboxyl and aromatic fractions.
48 Black carbon is dominated by carboxyl and aromatic fractions (Motoki et al., 2014). Organic
49 pesticides bind to un-charred biomass (TOC) via absorption mechanisms. Contrastingly they
50 adsorb on surface of charred carbon content (BC), largely due to atomic surfaces and micro
51 pores. BC has lately been reported as a better sorbent for organic pesticides (Ahmad et al., 2006;
52 Motoki et al., 2014; Kumar et al., 2015). Composition of soil minerals is another trait that
53 influence carbon storage. The presence of multivalent cations such as Ca^{2+} , Al^{3+} or Fe^{3+} drives
54 TOC binding (Xiao, 2015). Long term TOC pool status in soil media can also be effectively
55 predicted through stable carbon fractions (C^{12} and C^{13}). Agricultural expansion and
56 intensification has resulted in continuous cropping leading to simultaneous declines in TOC as
57 well as enrichment of $\delta^{13}\text{C}$ (Awiti et al., 2008). Carbonate- ^{13}C values described as $\delta^{13}\text{C}$
58 (carbonate-SOC) values can depict changes in TOC content, its yield and soil respiration fluxes
59 (Stevenson et al., 2005).

60 Crop protection measures are an unavoidable practice to augment food yield. Accelerated
61 production is followed by bioaccumulation in food causing eminent threat (Liu et al., 2016a).
62 The World trade organization (WTO) agreements (TBT/SPS) measures have contributed to
63 ensure food safety in trading system focusing on third countries. Pesticide residue is marked as
64 one of top five reasons for rejections by top international markets (UNIDO, 2015). Pakistan is
65 among the top 15 countries under the category of import rejections of food in USA (UNIDO,
66 2013)(UNIDO, 2013)(UNIDO, 2013)(UNIDO, 2013). Import samples assessed in USA by FDA

67 2013 reveals a violation rate of 21.1 % by Pakistan. Pakistan being an economy relying heavily
68 on agro exports, concept of the threshold-based application of pest control measures is an
69 important approach.

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

79 **2. Material and Methods**

80 **2.1. Study area**

81 For the present study six major cash crop growing cities of Pakistan were selected as
82 shown in Figure 1. Target sites include Swat, Swabi, Sargodha, Layyah, Muzaffargarh and
83 Khairpur spatially distributed from North to South of Pakistan. Each site is famous for harvesting
84 distinctive cash crops such as peaches, tobacco, oranges, cotton, mangoes and dates respectively.
85 Spatial diversity of sites was kept in mind prior to selection to evaluate the influence of
86 environmental factors on pesticide retention. Details regarding sampling station and sample
87 acquirement are stated in supporting information. For sampling, three samples were collected
88 from each site, hence a total of 18 top soil (0-6 cm) bulk samples were collected from six cash
89 crop sites. Three representative samples (1 Sample=composite of 3) were taken from local farms

90 (n=3) at each sampling location. Samples were dug at a distance of 500 meters from one another
91 to form composites for homogeneity. Top soil samples were removed by hand trowel, securely
92 packed in polyethylene bags and taken to the Environmental Biology Lab, Quaid-i-Azam
93 University Islamabad Pakistan. The bulk soil samples were stored at -4°C in the lab before being
94 transferred to UK for analysis. The concentrations of pesticides (Diazinon, Chlorpyrifos,
95 Parathion-Methyl and Azinfos) in cash crops of each respective site were obtained from Plant
96 Protection Department, Pakistan for year 2015-2016.

97 **2.2. Gas Chromatography-Mass spectrometry Analysis**

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

102 The analytes were quantified with a Finnigan TRACE GC-MS system. Soil samples were
103 sieved and stored in freezer. Prior to analysis samples were allowed to thaw. 5 g of each sample
104 was placed in a centrifuge tube. The dried sample was spiked with known concentration of
105 pesticide to act as a recovery standard. A blank containing 3 g of Na₂SO₄ was included after
106 every 10 samples. Extraction was carried out with 30 ml of Hexane-Ethyl acetate solution (2:3).
107 Extraction procedure was performed three times. Extracts were concentrated to 1 ml by a slow
108 torrent of nitrogen gas. For extract cleanup 6 g of alumina and 1 cm thick sodium sulphate were
109 used. Column was rinsed prior to sample introduction with 20 ml of ethyl acetate. Extract elution
110 was carried out from column by ethyl acetate. The final solution was blow dried and dissolved
111 with 1ml Hexane. Finally, samples were analyzed by Finnigan Trace GC-MS. The temperature
112 setting for transfer line, injector interface and ion source was set at 280, 250 and 230 °C,

113 respectively. The temperature programming of the GC oven was done as: 80 °C for 0.5 min, 20 °C
114 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
115 residues were quantified by the external standard calibration curve method. To ensure quality of
116 quantification methods analytical grade reagents were used. Recovery for samples extracted was
117 80-90 %. Linearity curves ($r^2=0.995$) were obtained by spiked samples for instrument
118 calibration.

119 **2.3. Total organic carbon and black carbon (CTO-375 method)**

120 The soil samples were prepared by weighing up to 4 g, followed by sieving and finely
121 grounded to smooth powder. Chemo-thermal oxidation (CTO-375) method was used as standard
122 protocol for BC residue analysis. BC samples were pre-treated with 1N HCl and stirred at
123 intervals for 1 hour. Next (2-3 g) of acidified samples were dried and subjected to thermal
124 oxidation (375 °C, 18 hr) by providing suitable conditions in a muffle furnace under constraint air
125 flow for removal of non-pyrogenic carbon (Gustafsson et al., 2001; Agarwal and Bucheli,
126 2011). The residual organic carbon content was determined as BC by using a TOC analyzer.
127 Similarly, TOC residual quantification also required 4 g of sample. Each batch was dried,
128 homogenized and acidified with 10% HCl for eliminating inorganic carbon. Later it was rinsed
129 with de ionized water thrice and dried overnight at 60°C. The TOC content was determined with
130 TOC analyzer.

131 **2.4. Stable Carbon isotope ($\delta^{13}\text{C}$) analysis**

132 The stable isotope analyses were executed with a modified Varian Mat GD- 150 Mass
133 Spectrometer. Stable isotope ratio $\delta^{13}\text{C}$ is measured in Total dissolved inorganic carbon. For
134 isotope analysis on mass spectrometer, soil samples have been converted into gas phase. For the
135 extraction of CO₂ gas from Total dissolved inorganic carbon of soil a 1g of soil sample was

136 poured into the Pyrex reaction flask. A small burette containing H_3PO_4 acid was then attached to
137 the reaction flask. The reaction flask assembly was connected to the vacuum line. Dewar flask
138 containing liquid N_2 -acetonmixture (temperature: -800°C) was attached to the moisture traps in
139 the vacuum system. About 5 ml H_3PO_4 acid was added to the pre-evacuated reaction flask. The
140 CO_2 gas was evolved as a result of reaction between inorganic carbon component/fraction of
141 sample and the phosphoric acid according to the following equation:



143 The moisture produced during the reaction was removed by cryogenic trap of -800°C .
144 The CO_2 gas was passed through vacuum line and purified by freezing in U-trap dipped in liquid
145 nitrogen flask. Other gases were pumped out from line. The liquid N_2 flask from CO_2 trap was
146 removed to expand CO_2 in vacuum linear which was finally collected in an ampoule dipped in
147 liquid nitrogen flask at the other end of line. The ampoule was labeled and removed from the line
148 for isotope ratio measurements onto the Isotope Ratio Mass spectrometer (IRMS). The overall
149 analytical errors are $\pm 0.01\%$ for $\delta^{13}\text{C}$ measurements. To ensure precision, standard deviation of
150 the mass spectrometer was also computed and standard deviation of each sample was ensured to
151 be within permissible limit.

152 **2.5. Clay mineral fraction assessment by XRF**

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

159 3. Results and Discussion

160 3.1. Concentration profile of current-use pesticides

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

163 3.1.1. Soils

164 The concentration profiles of pesticides in cash crop soils are given in Table 1. Among all
165 target analytes, chlorpyrifos occurred in highest mean concentration (1.18 mg kg^{-1}). The average
166 concentrations presented in Figure 1 indicates that contaminants occurred were in order of
167 chlorpyrifos > diazinon > parathion-methyl > deltamethrin > tolclofos-methyl > cyprodinil >
168 azinfos. The least reported pesticide was azinfos with an average concentration of 0.37 mg kg^{-1} .
169 Concentration of Azinfos studied in comparison to Chlorpyrifos was also found to be less
170 persistent in orchards (Reinecke and Reinecke, 2007).

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

176 The soil pesticide concentration profile was compared to the worldwide reported studies
177 Supporting information. The residual concentration of Chlorpyrifos was much higher as
178 compared to studies in primary agricultural areas of China (Liu et al., 2016a), Dehli, India
179 (Bhupander et al., 2011), Western Cape and South Africa (Reinecke and Reinecke, 2007). They
180 were comparable to concentration recorded in Bhawalpur, Pakistan (Anwar et al., 2014). In

181 Swat, Pakistan ([Nafees et al., 2008a](#)) residues reported were lower in general than current study.
182 In contrast to previous studies Parathion-Methyl was detected in higher concentration than
183 reported in Bhawalpur, Pakistan ([Anwar et al., 2014](#)). It has also been banned by Pakistan Plant
184 Protection Department. Diazinon reported in our study was comparatively less than the residues
185 assessed in agricultural and urban soils of Peshawar, Charsadda and Swat ([Jan et al., 2003](#)),
186 ([Nafees et al., 2008a](#)). The estimated values of Azinfos were also lower in studies executed in
187 Western Cape, South Africa ([Reinecke and Reinecke, 2007](#)) and Eastern, Washington State USA
188 ([Simcox et al., 1995](#)) as compared to current study. Concerning Cyprodinil study was conducted
189 in Spain, Galacia ([Rial-Otero et al., 2004](#); [Arias et al., 2005](#)). It reports lower concentrations of
190 Cyprodinil a new generation fungicides and frequently used in vineyards. Deltamethrin was also
191 reported in lower residual values in a study of Hariyana, India ([Bhupander et al., 2011](#)) in
192 comparison to our results. This comparison suggests that contamination of cash crop soils in
193 Pakistan is significant in terms of pesticides and elevated status is pertaining to environmental
194 problems.

195 **3.1.2. Cash crops**

196 The concentration profiles of pesticides in six cash crops are presented in Table 1.
197 Pesticides were detected in order of Diazinon > Azinfos > Chlorpyrifos > Parathion-Methyl.
198 Diazinon concentration ranged from 0.01-5.21 mg kg⁻¹ with highest mean (2.61 mg kg⁻¹) in
199 mangoes (MUZ). Several studies report pesticide residues in food items supporting information.
200 Diazinon had been monitored in various food crops and variety of fruits. The residues mentioned
201 in this study were comparable to the ranges reported for peach and oranges ([Gebara et al., 2005](#);
202 [Knežević and Serdar, 2009](#)). Concentrations for Parathion-Methyl (0.02-0.18 mg kg⁻¹) were
203 equivalent to ranges reported by literature in grains, fruits and vegetables ([Hjorth et al., 2011](#);

204 Ogah and Coker, 2012; Liu et al., 2016b). Chlorpyrifos had been the most assessed pesticide in
205 numerous fruits and vegetables. Residues concentrated in peach samples in this study were
206 several folds higher than Xiamen, China (Chen et al., 2011). Mean value for Azinfos in target
207 commodities was 0.32 mg kg^{-1} . A study conducted on Croatian fruits and vegetables revealed
208 comparable Azinfos averages, where orange and peach samples sustained residues above
209 maximum residue limits (MRLs) (Knežević and Serdar, 2009).

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

224 **3.2. Soil properties and its association with pesticides**

225 Physic chemical characteristics of soil are listed in Table 2. The pH for all sampling
226 locations was moderately alkaline and varied from 7.33-8.40. Soil texture was one of the most

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

246 **3.3. Spatial trend identification of cash crop sites using PCA**

247 The results for PCA applied as an ordination method on soil samples are summarized in
248 Supporting information. PCA Euclidean biplots are represented in Figure 2 in order to show
249 spatial variability of pesticides in study area. PCA is an imperative and valuable tool for

250 classifying data in terms of eigenvectors and eigenvalue. Classification of sampling sites was
251 also determined on basis of physic chemical properties of soil at following sites. According to
252 the significant eigenvalue four principal components were identified by Enter number method
253 and the first component with the highest eigenvalue of 5.429 explained maximum variance in
254 data set. The eigenvalue of all extracted factors were greater than 1. These four principal
255 components extracted with PCA had a contribution of 75% to its total variance. The first two
256 axis explained most of the variance i.e. PC 1 36% and PC 2 20%. According to Figure 2 the
257 sampling points were represented as dependent variables while target contaminants and physic
258 chemical properties of soil were represented as independent variables. Arrows were drawn from
259 the joint centered ordination axis to the points representing each variable.

260 The first Principal Component (PC 1) correlated positively with loading Diazinon,
261 Parathion-Methyl, Tolclofos-Methyl, Azinfos, BC, Silt%. That signified the dominant role of BC
262 in analyte binding process. A negative relation was found for Chlorpyrifos, Cyprodinil, TOC%,
263 Sand% and Clay% at PC 1. Soil samples from Swabi and Swat substantially clustered along
264 TOC%. These sites were also known to support elevated values of Chlorpyrifos and Cyprodinil
265 according to previous results. TOC is well known for nonionic pesticide binding in soils but
266 recently its aromatic fraction (BC) has proven to be a more effective sorbent (Ahmad et al.,
267 2001). Deltamethrin being an exception exhibited negative correlation with pH and no relation
268 with TOC or BC. (Zhu, 2002) also found Deltamethrin to be least persistent in high pH soils
269 despite higher organic matter content. Particle size distribution influenced TOC and BC
270 retention. TOC strongly correlated to Sand% and Clay%. The sites supporting highest TOC were
271 sandy loam and loam in texture (Swat and Swabi) which explained a positive correlation of TOC
272 with sand content. The correlation coupled with study conducted by (Azlan et al., 2012) in

273 Malaysia where sandy clay loam soils supported high TOC. In contrast BC accumulation was
274 regulated by silt content. Micro aggregates (Silt and Clay fractions) are dominant BC retaining
275 fractions with more pronounced role of larger fractions (silt) (Zong et al., 2016). The long arrows
276 of Diazinon, TOC% and Deltamethrin confirmed a gradual change in their concentration while
277 rest of the variables had short arrows indicating rapid alteration. Previously represented results of
278 Pearson correlation were in total agreement with PCA findings. The results support the
279 hypothesis that BC and TOC were main drivers of pesticide distribution in soils of cash crop.

280 **3.4. TOC and BC allocation in cash crop soils**

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

290 **3.4.1. Black carbon source credentials**

291 The ratios calculated for BC source identification are graphically presented in Figure 3.
292 BC/TOC ratios ranged from 0.03 to 0.65. At Khairpur, Swabi and Swat biomass burning was the
293 main source of BC. Ratios at Sargodha and Layyah highlighted fossil fuel burning, traffic or
294 industrial BC origin as well as miscellaneous source. BC formed during burning supports
295 residues derived from partially combusted plants to inert graphite carbon (Rumpel et al., 2006).

296 According to (Novakov et al., 2000; Wang et al., 2014) BC/TOC < 0.11 indicates incomplete
297 combustion of biomass and values greater than 0.5 suggest industrial, fossil fuel burning and
298 traffic source. BC/TOC ratios acted as an ideal indicator for identifying source of BC. As our
299 study area comprised of agricultural sites existing along road sides thus potential BC sources
300 could be diverse. These ratios account for BC source characterization in several studies. Ratios in
301 Changbai China (0.10-0.44) (Schellekens et al., 2017) and Shanghai China (0.14-0.17) (Wang et
302 al., 2014) indicate dominant char inputs. While Industrial and roadside soils of Anshan, China
303 (0.45-0.95) (Zong et al., 2016) as well as German croplands revealed dominant soot fraction
304 (fossil fuel burning) (Brodowski et al., 2007). Similarly, miscellaneous sources also contributed
305 to BC formation. Averages in our study were comparable to BC/TOC ratios reported in rural and
306 urban settings of Beijing China (Liu et al., 2011).

307 **3.4.2. Climatic conditions as marker for TOC retention**

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

314 Regression analysis expressed positive correlation ($r^2 = 0.846$) of altitude with
315 accumulation of TOC pools in soil Figure 4(a). Rise in Altitude dominantly coincides with
316 elevated TOC pools in recent studies conducted in Karakoram Pakistan (Shedayi et al., 2016;
317 Bojko and Kabala, 2017). Since TOC magnitude elevates with rising mountain toposequences.
318 The altitudinal gradient vitally distributes TOC and is preferably included in models for its

319 estimation. TOC shared an inverse trend with mean monthly temperature. MAP and MAT
320 analysis revealed significant but comparatively less dominant role in TOC retention as shown in
321 Figure 4. Previously quantitative relationships between TOC, temperature and precipitation have
322 also been documented (Azlan et al., 2012). Dry ecosystems account for greater TOC losses. No
323 regression could be assessed for the mean monthly precipitation because of dry spell of rain in
324 December. Relative humidity had a comparatively weak positive correlation with TOC. In humid
325 climates, both production and degradation of TOC increases with more profound decomposition
326 (Jobbágy and Jackson, 2000). Our targeted cash crop sites supporting variable terrain and
327 weather conditions, supporting labile pools in top soils, which are sensitive to alterations in
328 temperature, precipitation and altitude (Shedayi et al., 2016). Altitude mediated TOC distribution
329 is influenced by high rainfall inputs, declining temperatures, resulting in gradual fall in
330 degradation patterns. Our results also reflect prominent role of climatic factors in tracing TOC
331 persistence.

332 **3.4.3. Stable carbon isotopic enrichment as an indicator of TOC stability**

333 The mean values for $\delta^{13}\text{C}$ of SIC in cash crop soils are summarized in Table 2. The $\delta^{13}\text{C}$
334 values measured at six sites ranged from -1.75 to -8.49 ‰. The concentrations indicated low
335 TOC inputs in cash crop soils as compared to carbonate fraction. $\delta^{13}\text{C}$ values predicted high
336 TOC content at SAW and SWB. The results were in agreement with $\delta^{13}\text{C}$ of carbonates in
337 agricultural soils of France (Bertrand et al., 2007). Regression analysis shown in Figure 4(f) also
338 represented a strong negative correlation ($R^2=0.936$) between mean TOC % and $\delta^{13}\text{C}$ enrichment
339 for six sites. These results provided a strong base for determining TOC pool retention in cash
340 crop soils. The $\delta^{13}\text{C}$ values were assessed in SIC because our study area supported alkaline
341 conditions. Semiarid soils are naturally alkaline limited precipitation and reduced leaching cause

342 carbonates to accumulate in the soil profile (Cochran et al., 2007). Secondly $\delta^{13}\text{C}$ values of SIC
343 are ideal indicators for TOC because its less prone to loss than TOC. Stable carbon isotope ratios
344 of SIC (CO_2 , HCO_3^- , CO_3^{2-}) depended on the $\delta^{13}\text{C}$ of soil- CO_2 and dissolved carbonate that
345 originated from limestone, relatively enriched in ^{13}C at 0%. $\delta^{13}\text{C}$ values in the range of -3-2‰
346 represented limestone dissolution and lower estimates denoted SIC rich in organic carbon
347 (Coleman, 2012). The precursors for the carbonates in the soil are mainly ancient marine
348 carbonate rocks with carbon isotopic composition between +2 and -2‰.

349 3.5. Clay mineral bound TOC and pesticide sorption in soils

350 Mean clay mineral contents for cash crop soil characterization are summarized in Table
351 2. Silica and Aluminum oxide (Al_2O_3) reportedly the most abundant mineral fractions occurred
352 in the range of 47.98-59.11% and 11.09-12.86% respectively. Occurrences of Silica, Aluminum
353 oxide and Calcium oxide (CaO) were above their quantified natural elemental fractions in soils.
354 Mean range for Ferric oxide (Fe_2O_3) was 4.3-4.9%. Magnesium oxide contributed in a moderate
355 manner.

356 The regression analysis depicted in Figure 4(g) revealed significant TOC and clay
357 mineral interactions. Al_2O_3 and Fe_2O_3 exhibited a strong positive correlation with TOC retention.
358 Clay minerals play a major part in long term organic carbon retention in soil. TOC is normally
359 retained in mineral top soils (0-40cm) (Jonard et al., 2017). These reactive minerals with specific
360 surface areas are binding sites for TOC. Specifically weathering products such as nanometer
361 sized Fe oxides and Al-silicates supporting diverse charge. TOC adsorption to Fe_2O_3 is mainly
362 defined by ligand exchange mechanism. It is the dominant phenomenon for TOC retention in
363 soils that are rich in oxides where Fe^{3+} and Al^{3+} form cation bridges with organic carbon (Keil

364 and Mayer, 2014). Clay minerals and TOC are reported to synergistically bind pesticides in soil,
365 but influence of TOC in mineral availability for pesticides is not fully understood.

366 **3.6. Occupational exposure to current-use pesticide**

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

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

386 **3.7. Plant uptake of current-use pesticides from soil**

387 The bio concentration ratios equated for target pesticides are summarized in Table 3. The
388 results indicated accumulation trend of contaminants in cash crops in following order; Azinfos >
389 Diazinon > Chlorpyrifos > Parathion-Methyl. Highest uptake of Azinfos (2.49) was equated for
390 cotton at LAY-1. Cotton and mango samples also exhibited accelerated influx of Diazinon from
391 soil media at stations LAY-1 and MUZ-2. The overall trend indicates that mainly Azinfos is the
392 most lipophilic contaminant in terms of plant uptake in this study for most cash crops.
393 Chlorpyrifos bio concentration ratios (0.04-0.22) were comparable to uptake values reported in
394 *Ricinus communis* L. by (Rissato et al., 2015). Parathion-Methyl revealed lowest biomass uptake
395 (0.03-0.11) with lowest ratios reported in Dates. Study conducted on removal of soil bound
396 Parathion-Methyl residues by oat plant revealed only 5.1 % of total residues were retained in
397 green part of plants (Fuhremann and Lichtenstein, 1978). Organic contaminants have the
398 tendency to concentrate in plant mass depending upon there lipophilicity. The averaged ratios
399 accounted in this study demonstrated variability in uptakes with generally lower bio mass
400 retention of Chlorpyrifos and Parathion-Methyl. (Liu et al., 2016a) also predicted low OC, OP
401 and PY (pyrethroids) uptake by persimmons and jujube fruits. Soil bound pesticide residues,
402 pesticide concentrations and physic-chemical properties of the pesticides are driving factors
403 controlling uptakes.

404 **4. Conclusions**

405 The quantified results draw attention towards Chlorpyrifos and Diazinon supporting
406 highest residues in study area. Pesticides specifically organophosphates retention is principally
407 influenced by TOC and BC content. BC derived from fossil fuel rather than biomass is found
408 effective in bounding affinitive pesticides. Topographic and climatic variations influence TOC
409 distribution in cash crop soils. Specifically, altitudinal gradient is a salient feature in TOC

410 retention. Raised TOC storage in high altitude toposequences can be attributed to minimal
411 temperatures and elevated precipitation. Among target pesticides, Chlorpyrifos and Cyprodinil
412 are functionally absorbed by labile TOC pools. Recalcitrant fraction (BC) is strongly correlated
413 with Diazinon and Tolclofos-Methyl. Specifically, in lower altitudinal sites containing more soot
414 incorporated BC. Swat and Swabi with stable carbon isotopic ratios of SIC below -3‰
415 confirmed high TOC pools as compared to rest of sites. Clay minerals Aluminum oxide and
416 Ferric oxide are major binding agents for TOC. Prominent residues of Diazinon and Azinfos are
417 reported in cash crops of targeted study area. Bio concentration ratios (BCR) also confirm
418 dominant soil to plant uptake of Diazinon and Azinfos chiefly in cotton, mango and orange crop.
419 The ingestion of pesticide bound soil residues does not inflict any significant harm to farmer's
420 health. However synergistic effect of multiple pesticide residues long term ingestion cannot be
421 ignored. The baseline information provided by this study on status of CUPs and their persistence
422 in cash crops soil and their uptake must be taken into consideration for identifying need for
423 monitoring of cash crop soils from an agro economical prospect. Continuous monitoring is
424 crucial act for these areas owing to their global importance in terms of exportable commodities
425 and status of environmental factors ideally retaining pesticides in these sites.

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33 **Table 1. Descriptive analysis of selected pesticide concentrations (mgkg⁻¹) in soil and plants of cash crop sites**

Sites	Commodity	Diazinon		Parathion-Methyl		Tolclofos-Methyl	Chlorpyrifos		Cyprodinil	Azinfos		Delta-methrin	
		Soil	Plant	Soil	Plant	Soil	Soil	Plant	Soil	Soil	Plant	Soil	
SAR	Orange	Min-Max	0.99-1.44	0.01-0.12	0.91-0.94	0.025-0.03	0.75-0.97	0.19-1.39	N.D-0.24	0.44-0.46	0.37-0.44	0.20-0.29	0.81-1.14
		Mean±SD	1.113±0.15	0.06±0.04	0.92±0.01	0.027±0.001	0.8±0.07	0.97±0.39	0.97±0.09	0.45±0.01	0.42±0.02	0.23±0.03	0.93±0.1
		Median	1.04	0.04	0.91	0.027	0.77	1.1	0.05	0.45	0.42	0.22	0.91
LAY	Cotton	Min-Max	1.02-2.09	0.13-5.21	0.90-1.15	0.02-0.16	0.75-0.9	N.D-1.41	0.12-0.31	0.44-0.54	0.37-0.52	0.20-1.26	N.D-1.03
		Mean±SD	1.27±0.35	1.65±0.76	0.98±0.1	0.08±0.05	0.79±0.05	0.93±0.55	0.23±0.05	0.46±0.03	0.42±0.05	0.83±0.37	0.58±0.44
		Median	1.1	0.69	0.93	0.1	0.78	1.11	0.26	0.45	0.41	0.8	0.76
MUZ	Mango	Min-Max	0.97-2.34	0.10-5.21	N.D-1.45	0.02-0.18	0.74-0.93	N.D-1.54	0.04-0.26	0.44-0.46	0.36-0.50	0.06-0.58	N.D-0.98
		Mean±SD	1.16±0.45	2.49±1.8	0.87±0.37	0.05±0.005	0.78±0.06	1.03±0.59	1.16±0.09	0.45±0.01	0.40±0.04	0.30±0.19	0.78±0.3
		Median	1.02	2.61	0.91	0.03	0.76	1.27	0.19	0.45	0.39	0.26	0.85
KHA	Date	Min-Max	0.95-1.07	0.02-0.13	0.90-0.93	0.02-0.03	0.74-0.78	1.14-1.54	0.04-0.22	0.44-0.54	N.D-0.44	0.04-0.31	0.74-1.06
		Mean±SD	1.01±0.04	0.083±0.04	0.91±0.01	0.0261±0.001	0.76±0.01	1.32±0.13	0.15±0.07	0.47±0.04	0.36±0.14	0.23±0.08	0.87±0.12
		Median	0.99	0.1	0.91	0.02	0.76	1.33	0.2	0.45	0.39	0.24	0.87
SWB	Tobacco	Min-Max	0.95-0.97	0.10-0.14	0.90-0.91	0.02-0.03	0.73-0.74	1.42-1.47	0.23-0.31	0.54-0.56	0.36-0.37	0.23-0.26	0.76-0.77
		Mean±SD	0.95±0.01	0.12±0.01	0.91±0.00	0.03±0.001	0.74±0.00	1.43±0.02	0.27±0.03	0.55±0.01	0.36±0.00	0.24±0.01	0.77±0.00
		Median	0.95	0.12	0.91	0.03	0.74	1.42	0.28	0.55	0.36	0.24	0.77
SAW	Peach	Min-Max	0.95-0.95	0.08-0.12	0.91-0.91	0.02-0.04	0.74-0.74	1.40-1.44	0.16-0.26	0.56-0.57	N.D-0.37	0.02-0.26	0.76-0.77
		Mean±SD	0.95±0.00	0.99±0.01	0.91±0.00	0.03±0.004	0.74±0.00	1.42±0.01	0.23±0.03	0.56±0.00	0.32±0.12	0.13±0.07	0.77±0.00
		Median	0.95	0.1	0.91	0.3	0.74	1.43	0.24	0.56	0.36	0.14	0.77
Total	Min-Max	0.95-2.34	0.01-5.21	N.D-1.45	0.02-0.18	0.73-0.97	N.D-1.54	N.D-0.31	0.45-0.57	N.D-0.52	0.02-1.26	N.D-1.14	
	Mean±SD	1.08±0.26	0.75	0.92±0.15	0.04	0.77±0.05	1.18±0.41	0.19	0.49±0.05	0.38±0.08	0.32	0.78±0.24	
p-value		0.043	0.0003	0.804	0.001	0.008	0.009	0.0001	0.0001	0.09	0.0009	0.052	

p value is significant at < 0.05

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37 **Table 2. Descriptive analysis of soil parameters in cash crop sites**

Sites		Soil moisture %	pH	EC(uS)	Sand%	Silt%	Clay%	TOC%	BC%	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	CaO %	MgO %	SO ₃ %	K ₂ O %	Na ₂ O %	δ ¹³ C ‰		
	Min-Max	11.0-15.0	7.33-7.35	170-308	37-38.50	47.9-49.50	12-15.10	0.71-0.83	0.31-0.45											
SAR	Mean	13.33	7.34	230	37.6	48.47	13.93	0.77	0.36	49.59	11.27	4.3	4.44	2.66	-0.03	2.59	0.9	1.86	-	
	Min-Max	15-17	7.48-8.40	2710-2850	14-15.70	72.3-77	9.0-12.0	0.49-0.67	0.29-0.32											
LAY	Mean	16	7.93	2786	14.6	74.47	10.97	0.56	0.3	49.2	11.12	4.42	4.52	2.64	-0.92	2.18	1.29	1.75	-	
	Min-Max	15-17	7.52-7.96	265-470	20-43	47-61	10.0-19.0	0.81-0.93	0.18-0.24											
MUZ	Mean	15.67	7.78	373	34	52.77	13.23	0.87	0.21	47.98	11.09	4.51	6.72	2.62	-0.02	2.58	0.87	1.98	-	
	Min-Max	14-21	7.41-7.77	320-455	15-19	59-62	22-23	0.89-0.97	0.10-0.14											
KHA	Mean	16.67	7.58	375	17	60.67	22.33	0.93	0.12	57.26	11.75	4.55	10.23	2.32	-0.34	2.5	1.09	2.27	-	
	Min-Max	12.0-17.0	7.79-7.86	2150-2890	19.7-36.0	47.0-74.0	6-	1.29-1.35	0.09-0.10											
SWB	Mean	15	7.83	2556	29.4	56.7	13.8	1.31	0.09	58.84	12.74	4.99	10.3	2.6	-0.93	2.22	1.31	3.37	-	
	Min-Max	19-20	7.63-7.92	2500-3500	74-81.20	3.0-7	13.2-20	1.90-2.30	0.07-0.13											
SAW	Mean	19.67	7.82	2966	77.4	5.2	17.4	2.1	0.09	59.11	12.86	4.98	9.68	2.6	-0.87	2.25	1.32	8.49	-	
	Min-Max	21-Dec	7.33-8.40	170-3500	14-81.20	3.0-77	23-Jun	0.49-2.30	0.07-0.45	47.98-59.11	11.09-12.86	4.3-4.99	4.44-10.3	2.32-2.66	-0.91	2.18-2.59	0.87-1.32			
Total	Mean	16.06	7.71	1548.06	34.99	49.71	15.28	1.09	0.2	53.66	11.81	4.63	7.65	2.57	-0.52	2.39	1.13	3.29	-	

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Table 3. Bio-concentration ratios of cash crops for selected pesticides

Site ID	Diazinon	Parathion-Methyl	Chlorpyrifos	Azinfos
SAR-1	0.073	0.030	0.222	0.510
SAR-2	0.043	0.029	0.074	0.582
SAR-3	0.055	0.028	0.091	0.541
Mean (Oranges)	0.057	0.029	0.129	0.544
LAY-1	2.476	0.089	0.036	2.455
LAY-2	0.346	0.106	0.189	2.492
LAY-3	0.661	0.058	0.227	1.004
Mean (Cotton)	1.161	0.084	0.151	1.984
MUZ-1	0.350	0.030	0.050	0.182
MUZ-2	4.299	0.079	0.085	1.337
MUZ-3	2.743	0.041	0.089	0.640
Mean (Mangoes)	2.464	0.056	0.075	0.720
KHA-1	0.077	0.028	0.118	0.439
KHA-2	0.053	0.028	0.081	0.515
KHA-3	0.121	0.029	0.154	0.653
Mean (Dates)	0.084	0.028	0.118	0.535
SWB-1	0.136	0.028	0.171	0.662
SWB-2	0.115	0.029	0.209	0.695
SWB-3	0.111	0.029	0.193	0.653
Mean (Tobacco)	0.121	0.029	0.191	0.670
SAW-1	0.105	0.028	0.163	0.405
SAW-2	0.105	0.037	0.175	0.254
SAW-3	0.102	0.035	0.147	0.321
Mean (Peaches)	0.104	0.033	0.162	0.327
Total mean	0.665	0.042	0.137	0.797
Min-Max	0.04-4.30	0.03-0.11	0.04-0.22	0.18-2.49

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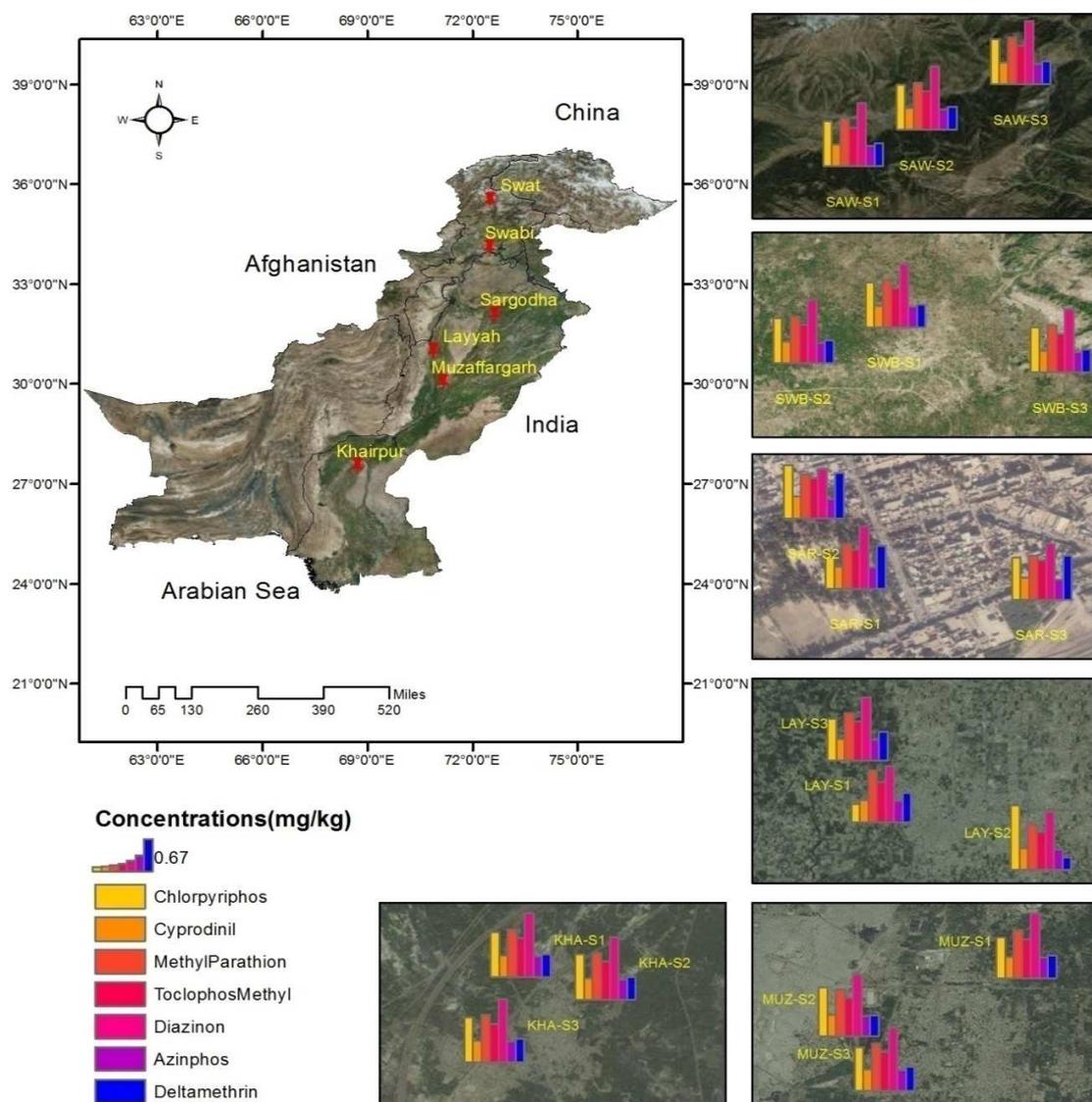
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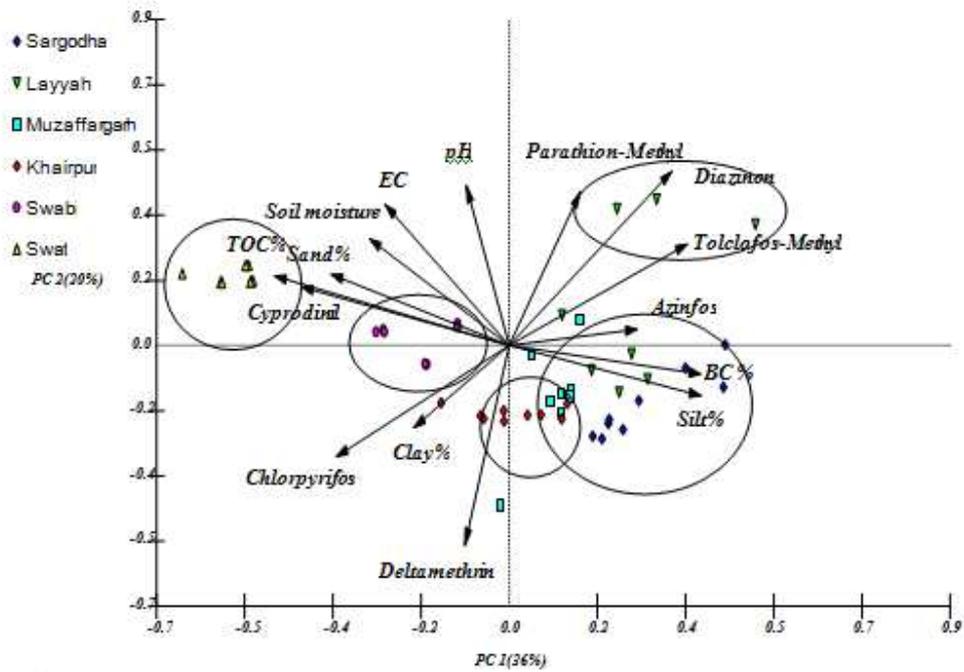
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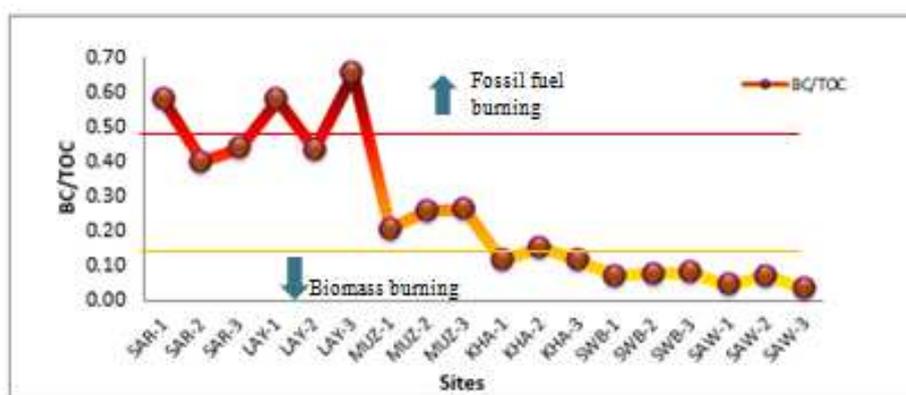
Figure 1. Targeted sampling sites and concentration profile of pesticides at selected sampling stations from cash crop growing areas of Pakistan.



Factor scaling: 1.20

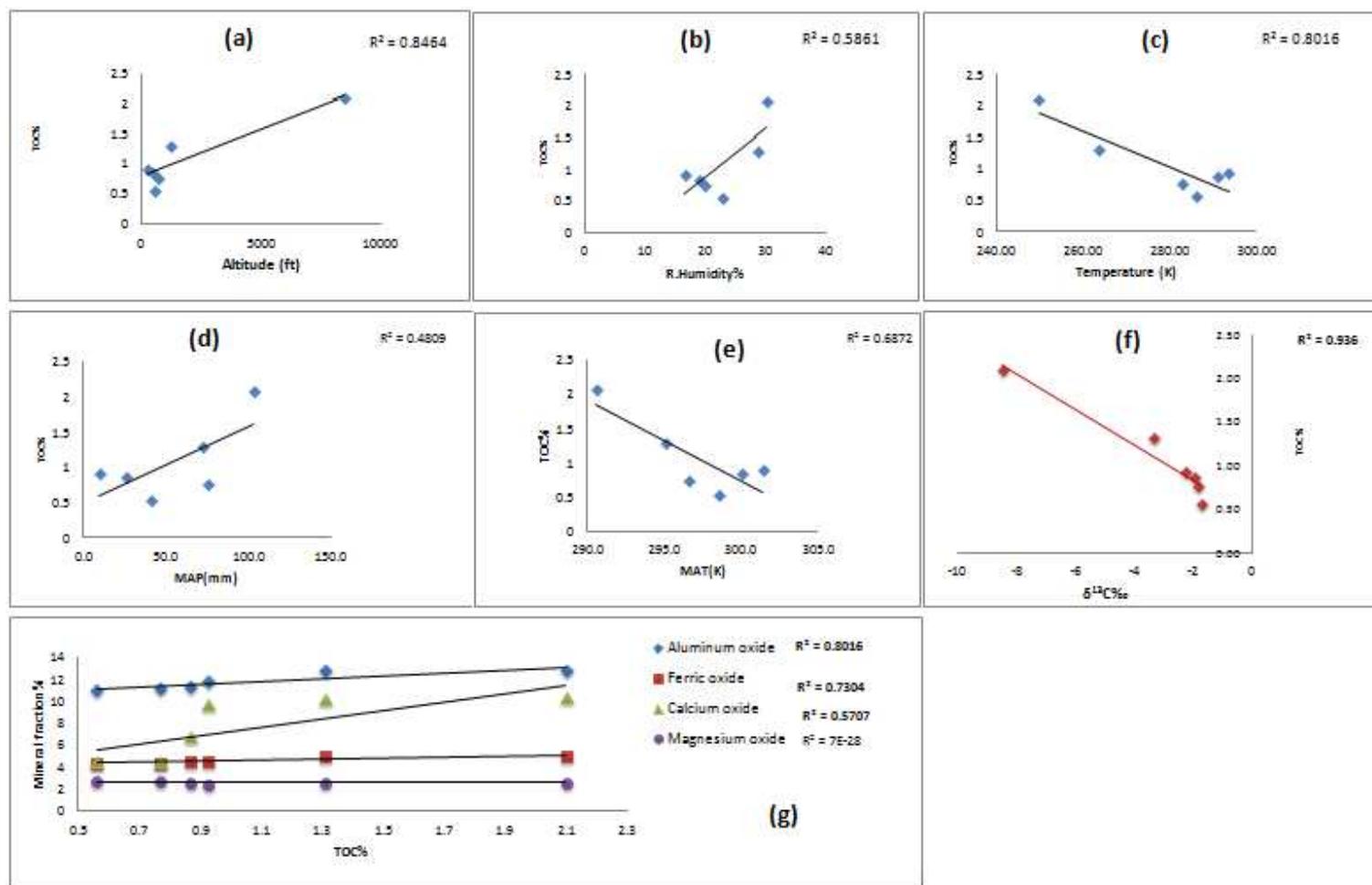
Figure 2. Spatial classification of cash crop sites represented by Principal Component Analysis Biplot

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



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41 Figure 4. Regression analysis between TOC and variables in cash crop sites (a) Altitude (b) Relative humidity (c) Mean monthly temperature (d)

42 Mean Annual Precipitation (e) Mean Annual Temperature (MAT) (f) $\delta^{13}C$ (g) Clay mineral fractions

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1 Highlights:

- 2 • Current-use pesticides status in soil media for six major cash crop growing areas of
3 Pakistan
- 4 • TOC and BC levels and distribution in cash crop growing areas and their influential role
5 in sorption of current-use pesticides
- 6 • Inspecting organic carbon distribution pattern using stable carbon isotope as a tracer
- 7 • Effect of clay minerals and climatic factors on organic carbon retention and pesticide
8 sorption

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