Accepted Manuscript

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

Sundas Ansari, Sidra Waheed, Usman Ali, Kevin C. Jones, Andrew James Sweetman, Crispin Halsall, Riffat Naseem Malik

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.

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**

3 Sundas Ansari[a], Sidra Waheed[a], Usman Ali[a], Kevin C. Jones[b], Andrew James Sweetman[b],
4 Crispin Halsall[b], Riffat Naseem Malik[a]

5 [a]Department of Environmental Sciences, Faculty of Biological Sciences, Quaid-i-Azam
6 University, Islamabad 45320, Pakistan

7 [b]Centre for Chemicals Management, Lancaster Environment Centre, Lancaster University,
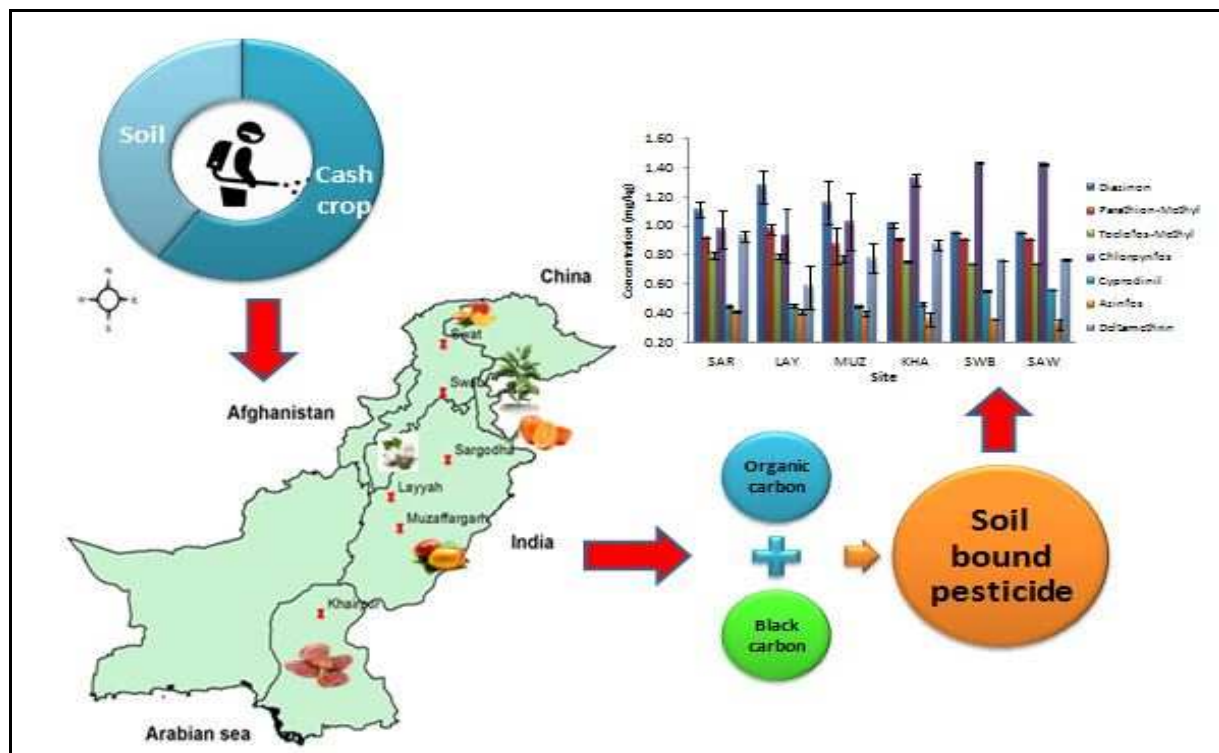8 12 Bailrigg, Lancaster LA1 4YQ, UK

9
10
11 ***Corresponding Author:** Usman Ali
12 **Address:** Department of Environmental Sciences, Faculty of Biological Sciences, Quaid-i-Azam
13 University, Islamabad 45320, Pakistan
14 Telephone: 00925190643017
15 **Email:** usman9217@gmail.com
16

1

2   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 $\delta^{13}C$ 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 azinfos 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

15

16

17

18

19

20

3

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 $\delta^{13}C$ (Awiti et al., 2008). Carbonate-^{13}C values described as $\delta^{13}C$

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

5

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 Na_2SO_4 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 ^{o}C,

7

113 respectively. The temperature programing of the GC oven was done as: 80 oC for 0.5 min, 20 oC

114 min-1 to 160 ^{o}C, 4 ^{o}C min^{-1} to 240 ^{o}C and 10 ^{o}C min^{-1} to 295 ^{o}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 ^{o}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 (δ^{13}C) analysis**

132   The stable isotope analyses were executed with a modified Varian Mat GD- 150 Mass

133 Spectrometer. Stable isotope ratio δ^{13}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 CO_2 gas from Total dissolved inorganic carbon of soil a 1g of soil sample was

8

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^oC) 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:

142 $$H_3PO_4 + \text{Carbonate mineral} \rightarrow CO_2 + H_2O$$

143 The moisture produced during the reaction was removed by cryogenic trap of -800^oC.

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 ± 0.01 ‰ for $\delta^{13}C$ 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.

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 um size and particles above this limit are ground again

158 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

10

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 area 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

12

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

13

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

14

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).

15

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

16

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 $\delta^{13}C$ of SIC in cash crop soils are summarized in Table 2. The $\delta^{13}C$

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. $\delta^{13}C$ values predicted high

336   TOC content at SAW and SWB .The results were in agreement with $\delta^{13}C$ 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 $\delta^{13}C$ enrichment

339   for six sites. These results provided a strong base for determining TOC pool retention in cash

340   crop soils. The $\delta^{13}C$ 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 $\delta^{13}C$ 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 $\delta^{13}C$ of soil-CO_2 and dissolved carbonate that

345   originated from limestone, relatively enriched in ^{13}C at 0‰. $\delta^{13}C$ 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%.

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.

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.

3.7.   Plant uptake of current-use pesticides from soil

19

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.

References

427 Abhilash, P., Singh, N., 2009. Pesticide use and application: An Indian scenario. Journal of hazardous
428 materials 165, 1-12.
429 Agarwal, T., Bucheli, T.D., 2011. Adaptation, validation and application of the chemo-thermal oxidation
430 method to quantify black carbon in soils. Environmental pollution 159, 532-538.
431 Ahmad, R., Kookana, R.S., Alston, A.M., Skjemstad, J.O., 2001. The nature of soil organic matter affects
432 sorption of pesticides. 1. Relationships with carbon chemistry as determined by 13C CPMAS NMR
433 spectroscopy. Environmental science & technology 35, 878-884.
434 Ahmad, R., Nelson, P., Kookana, R.S., 2006. The molecular composition of soil organic matter as
435 determined by 13C NMR and elemental analyses and correlation with pesticide sorption. European
436 Journal of Soil Science 57, 883-893.
437 Ajami, M., Heidari, A., Khormali, F., Gorji, M., Ayoubi, S., 2016. Environmental factors controlling soil
438 organic carbon storage in loess soils of a subhumid region, northern Iran. Geoderma 281, 1-10.

439 Anwar, T., Ahmad, I., Tahir, S., 2014. Gas Chromatographic Analysis of Pesticide Residues in Soil of
440 Bahawalpur District, Punjab, Pakistan. Pakistan Journal of Zoology 46, 231-236.
441 Arias, M., Torrente, A., López, E., Soto, B., Simal-Gándara, J., 2005. Adsorption-desorption dynamics of
442 cyprodinil and fludioxonil in vineyard soils. Journal of Agricultural and Food Chemistry 53, 5675-5681.
443 Awiti, A.O., Walsh, M.G., Kinyamario, J., 2008. Dynamics of topsoil carbon and nitrogen along a tropical
444 forest–cropland chronosequence: Evidence from stable isotope analysis and spectroscopy. Agriculture,
445 Ecosystems & Environment 127, 265-272.
446 Azlan, A., Aweng, E., Ibrahim, C., Noorhaidah, A., 2012. Correlation between soil organic matter, total
447 organic matter and water content with climate and depths of soil at different land use in Kelantan,
448 Malaysia. Journal of Applied Sciences and Environmental Management 16.
449 Baskaran, S., Bolan, N., Rahman, A., Tillman, R., 1996. Pesticide sorption by allophanic and
450 non-allophanic soils of New Zealand. New Zealand Journal of Agricultural Research 39, 297-310.
451 Bertrand, I., Delfosse, O., Mary, B., 2007. Carbon and nitrogen mineralization in acidic, limed and
452 calcareous agricultural soils: apparent and actual effects. Soil Biology and Biochemistry 39, 276-288.
453 Bhupander, K., Richa, G., Gargi, G., Meenu, M., Kumar, S.S., Dev, P., Sanjay, K., Sekhar, S.C., 2011.
454 Residues of pesticides and herbicides in soils from agriculture areas of Delhi region, India. Journal of
455 Environmental and Earth Science 1, 1-8.
456 Bojko, O., Kabala, C., 2017. Organic carbon pools in mountain soils—Sources of variability and predicted
457 changes in relation to climate and land use changes. CATENA 149, 209-220.
458 Brodowski, S., Amelung, W., Haumaier, L., Zech, W., 2007. Black carbon contribution to stable humus in
459 German arable soils. Geoderma 139, 220-228.
460 Bronner, G., Goss, K.-U., 2010. Predicting sorption of pesticides and other multifunctional organic
461 chemicals to soil organic carbon. Environmental Science & Technology 45, 1313-1319.
462 Chan, Y., 2008. Increasing soil organic carbon of agricultural land. Primefact 735, 1-5.
463 Chen, C., Qian, Y., Chen, Q., Tao, C., Li, C., Li, Y., 2011. Evaluation of pesticide residues in fruits and
464 vegetables from Xiamen, China. Food Control 22, 1114-1120.
465 Cochran, R., Collins, H., Kennedy, A., Bezdicek, D., 2007. Soil carbon pools and fluxes after land
466 conversion in a semiarid shrub-steppe ecosystem. Biology and Fertility of Soils 43, 479-489.
467 Coleman, D.C., 2012. Carbon isotope techniques. Academic Press.
468 Davie-Martin, C.L., Hageman, K.J., Chin, Y.-P., Rougé, V., Fujita, Y., 2015. Influence of temperature,
469 relative humidity, and soil properties on the soil–air partitioning of semivolatile pesticides: Laboratory
470 measurements and predictive models. Environmental Science & Technology 49, 10431-10439.
471 Dec, J., Haider, K., Rangaswamy, V., Schäffer, A., Fernandes, E., Bollag, J.-M., 1997. Formation of soil-
472 bound residues of cyprodinil and their plant uptake. Journal of Agricultural and Food Chemistry 45, 514-
473 520.
474 Fuhremann, T.W., Lichtenstein, E.P., 1978. Release of soil-bound methyl [14C] parathion residues and
475 their uptake by earthworms and oat plants. Journal of Agricultural and Food Chemistry 26, 605-610.
476 Gebara, A., Ciscato, C., S. Ferreira, M., Monteiro, S., 2005. Pesticide residues in vegetables and fruits
477 monitored in Sao Paulo city, Brazil, 1994–2001. Bulletin of environmental contamination and toxicology
478 75, 163-169.
479 Gustafsson, Ö., Bucheli, T.D., Kukulska, Z., Andersson, M., Largeau, C., Rouzaud, J.N., Reddy, C.M.,
480 Eglinton, T.I., 2001. Evaluation of a protocol for the quantification of black carbon in sediments. Global
481 Biogeochemical Cycles 15, 881-890.
482 Hjorth, K., Johansen, K., Holen, B., Andersson, A., Christensen, H.B., Siivinen, K., Toome, M., 2011.
483 Pesticide residues in fruits and vegetables from South America–A Nordic project. Food Control 22, 1701-
484 1706.
485 Jan, M.R., Nafees, M., Shah, J., Begum, S., Rehman, S., 2003. Determination of pesticide content in
486 selected soils and water samples. American Laboratory 35, 21-22.

487 Jobbágy, E.G., Jackson, R.B., 2000. The vertical distribution of soil organic carbon and its relation to
488 climate and vegetation. Ecological applications 10, 423-436.
489 Jonard, M., Nicolas, M., Coomes, D.A., Caignet, I., Saenger, A., Ponette, Q., 2017. Forest soils in France
490 are sequestering substantial amounts of carbon. Science of the Total Environment 574, 616-628.
491 Keil, R., Mayer, L., 2014. 12.12-Mineral matrices and organic matter.
492 Knežević, Z., Serdar, M., 2009. Screening of fresh fruit and vegetables for pesticide residues on Croatian
493 market. Food Control 20, 419-422.
494 Kumar, R., Barth, M., Nair, V., Pfister, G., Suresh Babu, S., Satheesh, S., Krishna Moorthy, K., Carmichael,
495 G., Lu, Z., Streets, D., 2015. Sources of black carbon aerosols in South Asia and surrounding regions
496 during the Integrated Campaign for Aerosols, Gases and Radiation Budget (ICARB). Atmospheric
497 Chemistry and Physics 15, 5415-5428.
498 Lehndorff, E., Houtermans, M., Winkler, P., Kaiser, K., Kölbl, A., Romani, M., Said-Pullicino, D., Utami, S.,
499 Zhang, G., Cao, Z., 2016. Black carbon and black nitrogen storage under long-term paddy and non-paddy
500 management in major reference soil groups. Geoderma 284, 214-225.
501 Liu, S., Xia, X., Zhai, Y., Wang, R., Liu, T., Zhang, S., 2011. Black carbon (BC) in urban and surrounding
502 rural soils of Beijing, China: spatial distribution and relationship with polycyclic aromatic hydrocarbons
503 (PAHs). Chemosphere 82, 223-228.
504 Liu, Y., Li, S., Ni, Z., Qu, M., Zhong, D., Ye, C., Tang, F., 2016a. Pesticides in persimmons, jujubes and soil
505 from China: Residue levels, risk assessment and relationship between fruits and soils. Science of the
506 total environment 542, 620-628.
507 Liu, Y., Shen, D., Li, S., Ni, Z., Ding, M., Ye, C., Tang, F., 2016b. Residue levels and risk assessment of
508 pesticides in nuts of China. Chemosphere 144, 645-651.
509 Loewy, R.M., Monza, L.B., Kirs, V.E., Savini, M.C., 2011. Pesticide distribution in an agricultural
510 environment in Argentina. Journal of Environmental Science and Health, Part B 46, 662-670.
511 Motoki, Y., Iwafune, T., Seike, N., Otani, T., Asano, M., 2014. Effects of organic carbon quality on the
512 sorption behavior of pesticides in Japanese soils. J. Pestic. Sci 39, 105-114.
513 Nafees, M., Jan, M.R., Khan, H., 2008a. Pesticide use in Swat Valley, Pakistan: exploring remedial
514 measures to mitigate environmental and socioeconomic impacts. Mountain Research and Development
515 28, 201-204.
516 Nafees, M., Jan, M.R., Khan, H., Ali, A., 2008b. Status of soil texture and required associated soil
517 conservation measure of River Swat catchments area, NWFP, Pakistan. Sarhad Journal of Agriculture 24,
518 251-259.
519 Novakov, T., Andreae, M., Gabriel, R., Kirchstetter, T., Mayol-Bracero, O., Ramanathan, V., 2000. Origin
520 of carbonaceous aerosols over the tropical Indian Ocean: Biomass burning or fossil fuels. Geophys. Res.
521 Lett 27, 4061-4064.
522 Oerke, E.-C., Schonbeck, H., F Weber, A., Rainey, W., Jorgensen, S., SN Jorgensen, L., Runge, C.,
523 Lotterman, R., E Creason, J., Urbina, N., 1994. Crop production and crop protection: estimated losses in
524 major food and cash crops. IICA, Bogotá (Colombia).
525 Ogah, C., Coker, H., 2012. Quantification of organophosphate and carbamate pesticide residues in
526 maize. Journal of Applied Pharmaceutical Science 2, 93.
527 Olvera-Velona, A., Benoit, P., Barriuso, E., Ortiz-Hernandez, L., 2008. Sorption and desorption of
528 organophosphate pesticides, parathion and cadusafos, on tropical agricultural soils. Agronomy for
529 sustainable development 28, 231-238.
530 Panhwar, A.A., Sheikh, S.A., Soomro, A.H., Abro, G.H., 2014. Removal of Pesticide Residues from Tomato
531 and its Products. Journal of Basic & Applied Sciences 10, 559.
532 PBS, 2015. Compendium on environmental statistics of Pakistan. in: Statistics, P.B.o. (Ed.), Pakistan.
533 Reinecke, S., Reinecke, A., 2007. The impact of organophosphate pesticides in orchards on earthworms
534 in the Western Cape, South Africa. Ecotoxicology and environmental safety 66, 244-251.

535 Rial-Otero, R., González-Rodríguez, R.M., Cancho-Grande, B., Simal-Gándara, J., 2004. Parameters
536 affecting extraction of selected fungicides from vineyard soils. Journal of Agricultural and Food
537 Chemistry 52, 7227-7234.
538 Rissato, S.R., Galhiane, M.S., Fernandes, J.R., Gerenutti, M., Gomes, H.M., Ribeiro, R., de Almeida, M.V.,
539 2015. Evaluation of Ricinus communis L. for the phytoremediation of polluted soil with organochlorine
540 pesticides. BioMed research international 2015.
541 Rumpel, C., Alexis, M., Chabbi, A., Chaplot, V., Rasse, D.P., Valentin, C., Mariotti, A., 2006. Black carbon
542 contribution to soil organic matter composition in tropical sloping land under slash and burn agriculture.
543 Geoderma 130, 35-46.
544 Saillenfait, A.-M., Ndiaye, D., Sabaté, J.-P., 2015. Pyrethroids: exposure and health effects–an update.
545 International journal of hygiene and environmental health 218, 281-292.
546 Schellekens, J., Almeida-Santos, T., Macedo, R.S., Buurman, P., Kuyper, T.W., Vidal-Torrado, P., 2017.
547 Molecular composition of several soil organic matter fractions from anthropogenic black soils (Terra
548 Preta de Índio) in Amazonia—A pyrolysis-GC/MS study. Geoderma 288, 154-165.
549 Shedayi, A.A., Xu, M., Naseer, I., Khan, B., 2016. Altitudinal gradients of soil and vegetation carbon and
550 nitrogen in a high altitude nature reserve of Karakoram ranges. SpringerPlus 5, 1.
551 Simcox, N.J., Fenske, R.A., Wolz, S.A., Lee, I.-C., Kalman, D.A., 1995. Pesticides in household dust and soil:
552 exposure pathways for children of agricultural families. Environmental health perspectives 103, 1126.
553 Stevenson, B., Kelly, E., McDonald, E., Busacca, A., 2005. The stable carbon isotope composition of soil
554 organic carbon and pedogenic carbonates along a bioclimatic gradient in the Palouse region,
555 Washington State, USA. Geoderma 124, 37-47.
556 UNIDO, 2013. Meeting Standards, Winning Markets Meeting Standards, Winning Markets: Regional
557 Trade Standards Compliance Report, East Asia.
558 UNIDO, 2015. Meeting Standards, Winning Markets: Trade Standards Compliance. pp. 1-137.
559 Wang, Q., Liu, M., Yu, Y., Du, F., Wang, X., 2014. Black carbon in soils from different land use areas of
560 Shanghai, China: level, sources and relationship with polycyclic aromatic hydrocarbons. Applied
561 Geochemistry 47, 36-43.
562 Wang, Z., Liu, S., Huang, C., Liu, Y., Bu, Z., 2017. Impact of land use change on profile distributions of
563 organic carbon fractions in peat and mineral soils in Northeast China. CATENA 152, 1-8.
564 Wauchope, R.D., Yeh, S., Linders, J.B.H.J., Kloskowski, R., Tanaka, K., Rubin, B., Katayama, A., Kördel, W.,
565 Gerstl, Z., Lane, M., 2002. Pesticide soil sorption parameters: theory, measurement, uses, limitations
566 and reliability. Pest management science 58, 419-445.
567 Weber, J.B., Wilkerson, G.G., Reinhardt, C.F., 2004. Calculating pesticide sorption coefficients (K d) using
568 selected soil properties. Chemosphere 55, 157-166.
569 Wenrui, Y., Rusong, W., Chuanbin, Z., Feng, L., 2009. Distribution and health risk assessment of
570 organochlorine pesticides (OCPs) in industrial site soils: A case study of urban renewal in Beijing, China.
571 Journal of Environmental Sciences 21, 366-372.
572 Xiao, C., 2015. Soil Organic Carbon Storage (Sequestration) Principles and Management. Olympia
573 Washington, pp. 1-71.
574 Zhu, H., 2002. Retention and movement of reactive chemicals in soils. Chinese Academy of Sciences.
575 Zong, Y., Xiao, Q., Lu, S., 2016. Black carbon (BC) of urban topsoil of steel industrial city (Anshan),
576 Northeastern China: Concentration, source identification and environmental implication. Science of the
577 Total Environment 569, 990-996.

578

1 **List of Figures:**

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

1 **List of Tables:**

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

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		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
	Orange	Median	1.04	0.04	0.91	0.027	0.77	1.1	0.05	0.45	0.42	0.22	0.91
LAY		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
	Cotton	Median	1.1	0.69	0.93	0.1	0.78	1.11	0.26	0.45	0.41	0.8	0.76
MUZ		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
	Mango	Median	1.02	2.61	0.91	0.03	0.76	1.27	0.19	0.45	0.39	0.26	0.85
KHA		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
	Date	Median	0.99	0.1	0.91	0.02	0.76	1.33	0.2	0.45	0.39	0.24	0.87
SWB		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
	Tobacco	Median	0.95	0.12	0.91	0.03	0.74	1.42	0.28	0.55	0.36	0.24	0.77
SAW		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
	Peach	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

34   *p value* **is significant at < 0.05**

35

36

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_2O_3 %	Fe_2O_3 %	CaO %	MgO %	SO_3 %	K_2O %	Na_2O %	$\delta^{13}C$ ‰
	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

38

39

40

41

42

43

44

45 **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

46
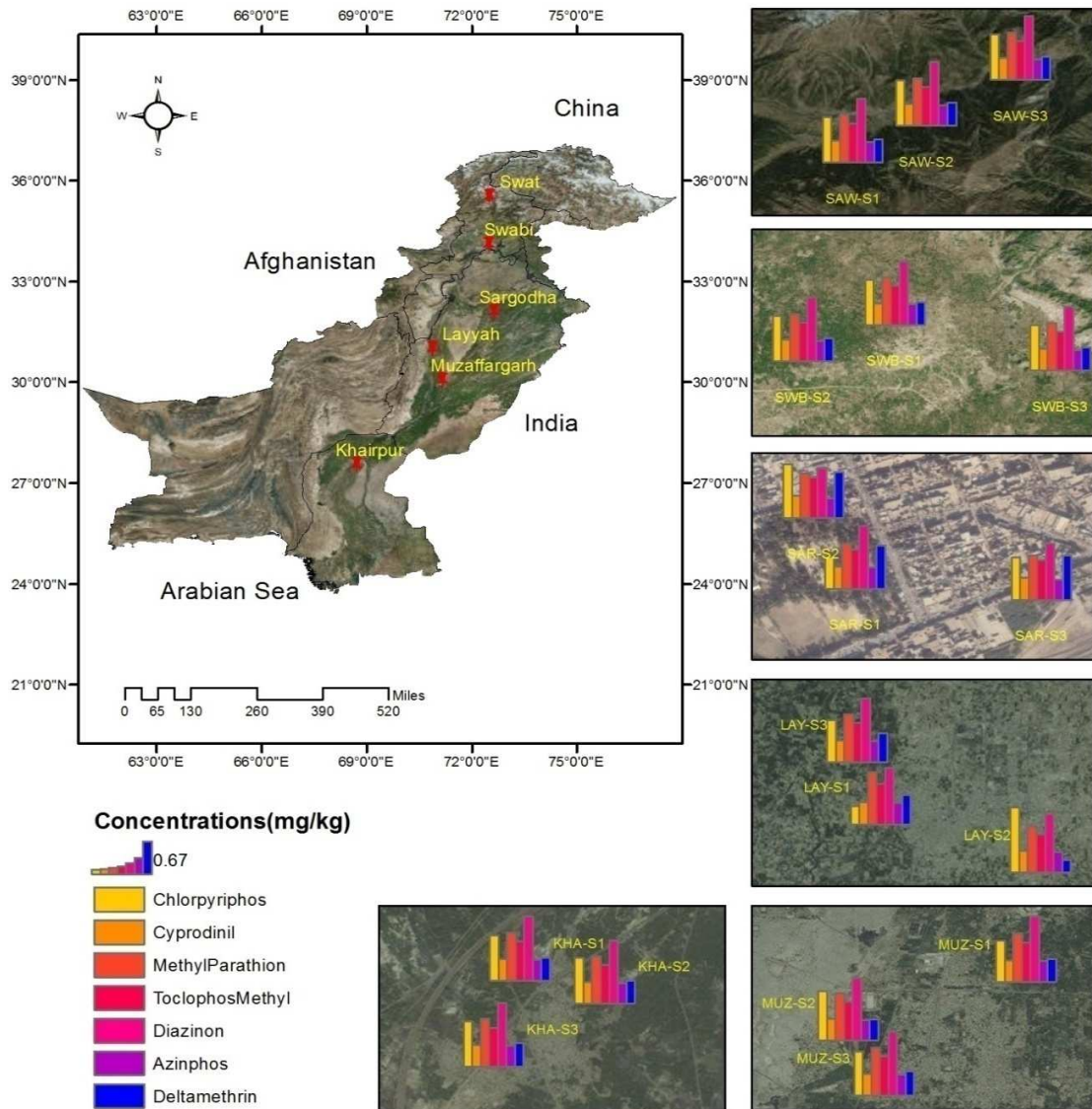
47

48

49

50

51

52

53

1
2   Figure 1. Targeted sampling sites and concentration profile of pesticides at selected sampling
3   stations from cash crop growing areas of Pakistan.
4
5
6
7
8
9
10
11
12

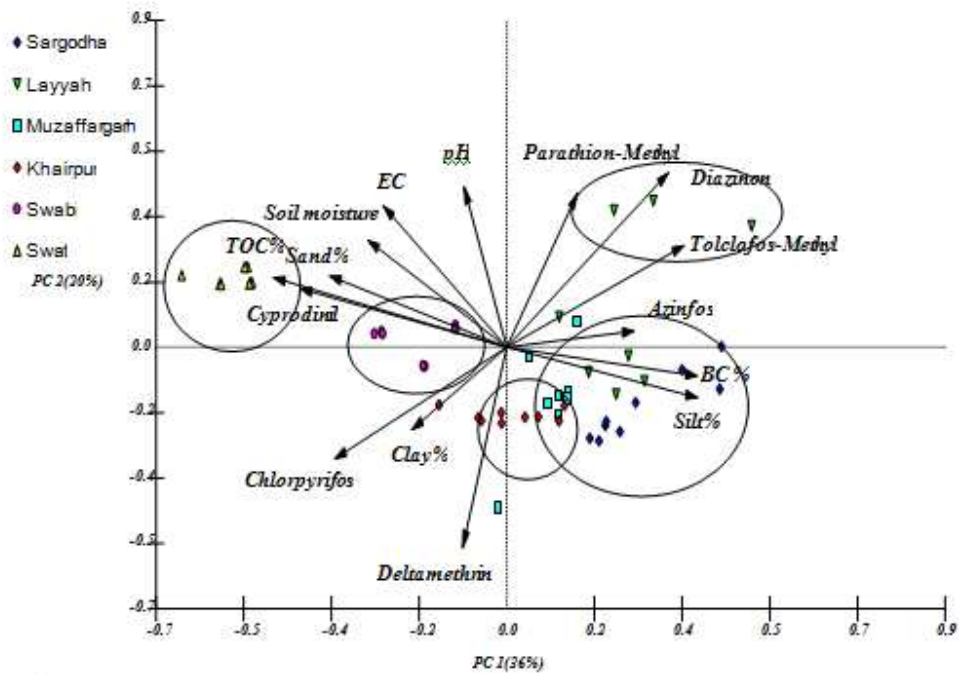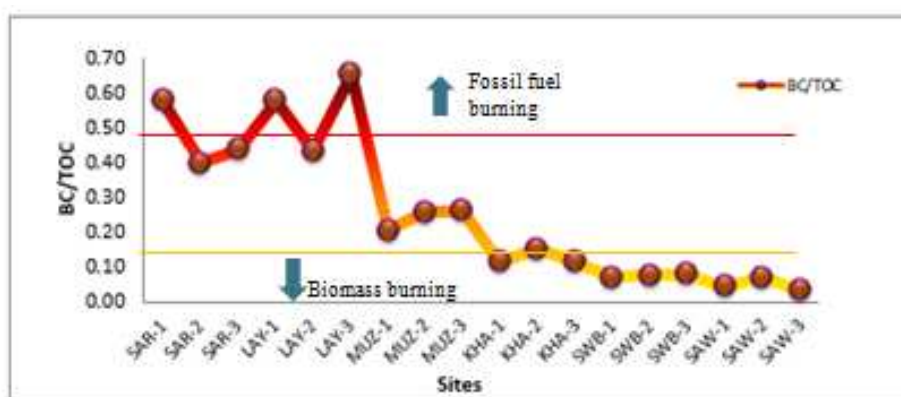Figure 2. Spatial classification of cash crop sites represented by Principal Component Analysis Bi plot

32

33   Figure 3. BC/TOC ratios for Black Carbon source identification at cash crop sites
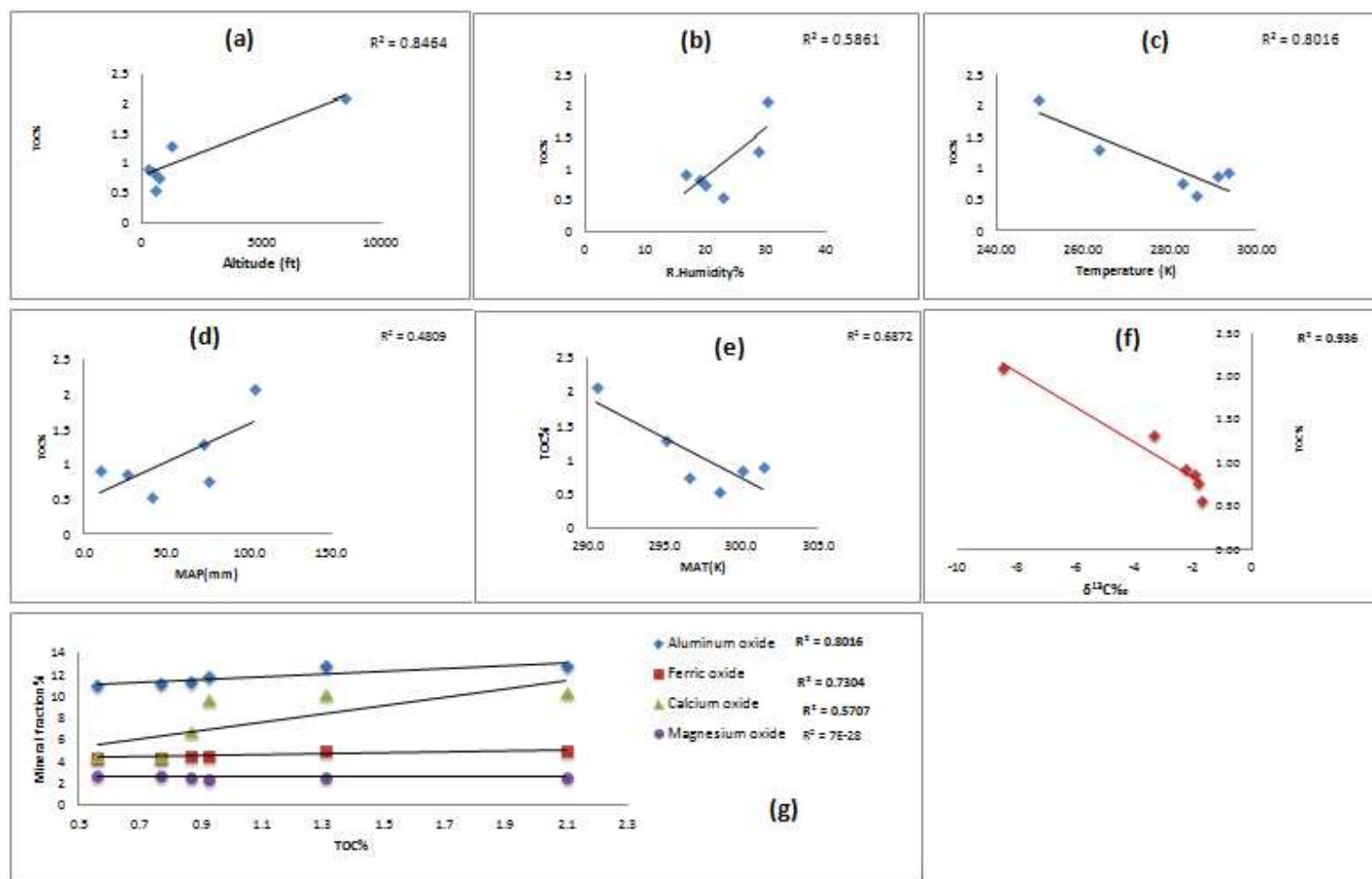
34

35

36

37

38

39

40

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

43

44

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

9
10