

Accepted Manuscript

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PII: S0045-6535(18)31154-8
DOI: [10.1016/j.chemosphere.2018.06.078](https://doi.org/10.1016/j.chemosphere.2018.06.078)
Reference: CHEM 21610

To appear in: *ECSN*

Received Date: 29 March 2018

Revised Date: 30 May 2018

Accepted Date: 11 June 2018

Please cite this article as: Dollinger, J., Schacht, V.J., Gaus, C., Grant, S., Effect of surfactant application practices on the vertical transport potential of hydrophobic pesticides in agrosystems, *Chemosphere* (2018), doi: [10.1016/j.chemosphere.2018.06.078](https://doi.org/10.1016/j.chemosphere.2018.06.078).

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Effect of surfactant application practices on the vertical transport potential of hydrophobic pesticides in agrosystems

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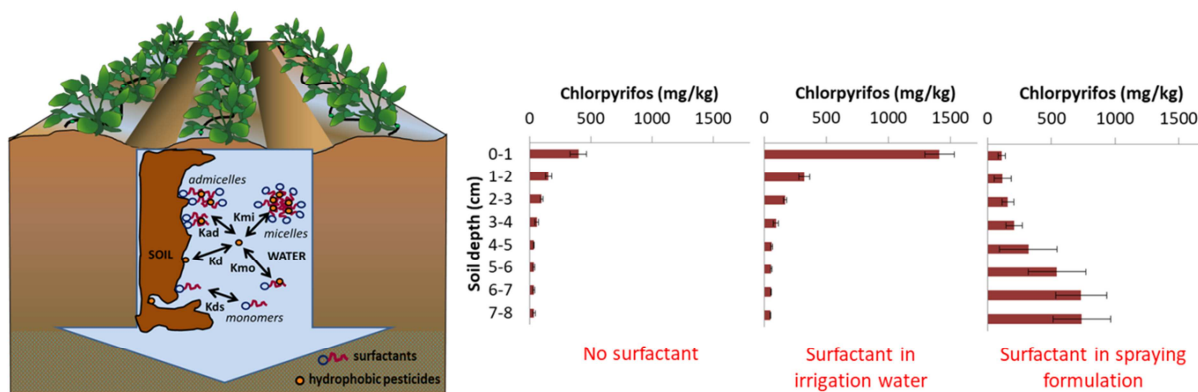
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Abstract: Surfactants have the potential to modify the environmental behavior of hydrophobic pesticides leading to an enhanced or reduced mobility risk. This risk is often overlooked in registration procedures due to a lack of suitable methodologies to quantify the transport potential of pesticides with surfactants. In this study we present a novel methodology designed to study the surfactant facilitated transport of pesticides under controlled equilibrium and dynamic hydrologic conditions. Using this methodology, we investigated the risk of chlorpyrifos enhanced mobility for two common surfactant application practices in agrosystems: pesticide spraying and irrigation with waste water. With the dynamic experiments we showed that a single irrigation event with artificial reclaimed water containing the nonionic surfactant Triton X100 at a concentration of 15 mg/L reduced the leaching of chlorpyrifos by 20% while the presence of the same surfactant in the chlorpyrifos spraying formulation reduced the leaching amount by 60%. However, in the first case 90% of the chlorpyrifos fraction remaining in soil was retained in the upper 3 cm while in the second case, 72% was transported to the bottom layers. The presence of Triton X100 in irrigation water or spraying formulation retards the leaching of chlorpyrifos but enhances its downward transport.



24

25

26 **Keywords:** Risk assessment; Hydrophobic pesticides; Surfactants; Mobility; Sorption, Soil-water
 27 partition coefficient.

28

29 **Highlights:**

- 30 • Surfactants modify hydrophobic pesticide mobility in soils.
- 31 • We designed a methodology to study surfactant facilitated transport of pesticides.
- 32 • Single irrigation event with waste water containing TritonX100 reduced chlorpyrifos leaching.
- 33 • TritonX100 in spraying formulation increase chlorpyrifos mobility in soil.

34

35

36 **1. Introduction**

37 Hydrophobic pesticides are widely considered immobile in soil due to their very low water solubility
 38 and high affinity for organic carbon (Arias-Estévez et al., 2008). However, a significant number of
 39 hydrophobic pesticides have been detected worldwide in groundwater and remote ecosystems (Arias-
 40 Estévez et al., 2008; Elliott et al., 2000; Gebremariam et al., 2012). These findings of enhanced
 41 unintentional mobility in soil may be explained by preferential water flow or transport with soil
 42 colloids (Arias-Estévez et al., 2008; Elliott et al., 2000; Persson et al., 2008). Furthermore, pesticide
 43 transport in association with surfactants, i.e. surfactant facilitated transport, has also been suggested to

44 contribute to the leaching and off-site transport behavior of hydrophobic pesticides (Lee et al., 2000;
45 Müller et al., 2007).

46 Surfactant monomers are composed of a hydrophobic tail and a hydrophilic head (Ying, 2006). Above
47 a specific concentration, the critical micelle concentration (CMC), the monomers aggregate into
48 micelles. These water soluble surfactant monomers and micelles contain hydrophobic micro-
49 environments providing an efficient partitioning site for hydrophobic organic compounds increasing
50 their apparent water solubility (Krogh et al., 2003; Ying, 2006; Zhang et al., 2009). Despite the
51 recognition of this solubility enhancement process as a potentially significant unintentional transport
52 pathway for hydrophobic pesticides, and the ubiquitous presence of surfactants in agrosystems, the
53 risk associated with surfactant use has been overlooked to date.

54 There are two major sources of surfactants in agrosystems. Firstly, surfactants (predominantly
55 alkylphenol ethoxylates (APEO)) are added to commercial pesticide formulations at up to 20% (w/v)
56 or are used as spray adjuvants to facilitate pesticide amendments (Krogh et al., 2003). Secondly, the
57 common agricultural practice of waste water irrigation may also contribute to a substantial amount of
58 surfactants in agrosystems. Surfactant concentrations in reclaimed water have been reported to reach
59 up to 54 mg/L (Fernández-Gálvez and Mingorance, 2010; Krogh et al., 2003) made up of different
60 types of surfactants differing by the composition of the hydrophobic tail and the ionization of the
61 hydrophilic head. For nonionic surfactants like APEO, the most commonly used surfactant type for
62 agricultural, industrial and household applications, the concentration in reclaimed water was reported
63 to vary between 0.75 and 11.3 ± 3.9 mg/L (Fernández-Gálvez and Mingorance, 2010; Hernández Leal
64 et al., 2011).

65 Although potentially significant, the off-site transport risk for pesticides with surfactants is not
66 assessed during pesticide registration procedures. This may be due to the difficulty of studying this
67 specific pathway in-situ or in the lab because of the simultaneous action of other preferential transfer
68 pathways such as colloidal transport and preferential flow. Few methodologies are available to assess
69 the role of surfactants on the mobility of hydrophobic compounds. Existing methods are mostly

70 focused on surfactants' use during soil washing for decontamination purposes, for which excessive
71 amounts of surfactants are intentionally applied. Moreover, these studies are mainly based on
72 equilibrium batch methods. Other studies investigate the effect of waste water irrigation on the
73 mobility of organic pollutants in the field or in the lab under both dynamic and equilibrium conditions
74 (Chefetz et al., 2008; Peña et al., 2011). However, the experimental designs implemented in those
75 studies don't enable the separate assessment of the different preferential pathways. Thus, methods
76 adapted to assess the risk of unintentional surfactant facilitated pesticide transport in both equilibrium
77 and dynamic conditions are lacking to date.

78 The aims of this study were thus i) to adapt batch and column technics to assess the risk of
79 unintentional surfactant facilitated transfer of hydrophobic pesticides in equilibrium and dynamic
80 conditions and ii) investigate the risk of surfactant facilitated pesticide transfer induced by two
81 common agricultural practices, pesticide spraying and irrigation with reclaimed water. We used
82 chlorpyrifos (CPF) and Triton X100 (TX100) as model compounds. CPF is one of the most widely
83 used organophosphorus pesticides being the main active ingredient of about 400 commercial mixtures.
84 An estimated 25 million kilograms of active ingredient are sprayed globally every year for pest control
85 on a large variety of crops (Gebremariam et al., 2012). Typically, this hydrophobic insecticide is
86 assumed immobile in soils based on its physico-chemical properties (EPHC, 2003; Gebremariam et
87 al., 2012). However, CPF has been detected worldwide in groundwater, drinking water wells and
88 remote ecosystems (Gebremariam et al., 2012). APEOs such as TX100 are very likely to be associated
89 with hydrophobic pesticides in soils as this surfactant type in particular is a major component of
90 commercial pesticide formulations. Furthermore, TX100 is recommended as a spray adjuvant for a
91 variety of insecticides, including CPF (Krogh et al., 2003; O'Connell, 2011). An artificial soil matrix
92 was designed to eliminate other pesticide transport processes and enable assessment of the surfactant
93 facilitated transfer risk. For this, constituents of soils playing a key role in hydrophobic pesticide and
94 surfactant mobility/retention i.e. clay minerals and humic acid, were immobilized onto silica sand and
95 further mixed in a proportion representative of soils in typical Australian agrosystems and other
96 Vertisols around the world.

97

98 **2. Material and methods**

99 **2.1. Model compounds & chemicals**

100 CPF, the selected model pesticide for this study was purchased from AccuStandard (New Haven,
101 USA). The model APEO, TX100, was purchased from Sigma Aldrich (Sydney, Australia). The
102 physico-chemical properties of both model compounds are listed in Table 1.

103 For the preparation of the artificial soil matrix, silica sand (50 to 70 mesh), humic acid, N-(3-
104 dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) and Polyvinyl alcohol (PVA) were
105 purchased from Sigma Aldrich. Two clays, montmorillonite and illite, were obtained from the Source
106 Clay Minerals Repository (University of Missouri). Pure deionized water was prepared using a
107 Millipore water purification system (Merck Millipore, Kilsynth, Australia). The solvents were of
108 analytical grade; toluene (99.99% purity), methanol (98% purity) and dichloromethane (99.8% purity)
109 and purchased from Merck.

110

111 **2.2. Soil matrix design and validation**

112 The OC and clay content in the artificial soil matrix were represented by humic acid, montmorillonite
113 and illite. The importance of these materials in sorption processes of hydrophobic pesticides and
114 surfactants, in particular CPF and TX100, onto soil has been demonstrated extensively (Amirianshoja
115 et al., 2013; Gebremariam et al., 2012; Laha et al., 2009; Rodríguez-Cruz et al., 2005; Valverde García
116 et al., 1992; Zhu et al., 2003). Humic acids are often used to represent soil organic matter in sorption
117 studies of hydrophobic compounds (Joo et al., 2012; Tanaka et al., 2005; Wan et al., 2011; Zhang et
118 al., 2009). Together with fulvic acids, humic acids make up the predominant fractions of soil organic
119 matter. Their distinction is operational rather than structural. Although sharing many characteristics,
120 humic acids are less polar than fulvic acids and thus assumed to drive the sorption processes of
121 hydrophobic compounds (Wang and Keller, 2009). Humic acid also seems to represent fairly well soil

122 organic matter for TX100 sorption assessment as the partition coefficients of TX100 to soil organic
123 matter and humic acid are reported to be similar (Zhang et al., 2009). Montmorillonite and illite were
124 selected as they are the most representative of the clay minerals constituting Queensland's Vertisols
125 (Chinn and Pillai, 2008).

126 The coating of silica sand with humic acid was performed with the EDC incubation method followed
127 by end-capping of the free amine groups as described by Koopal and collaborators (1998). Silica sand
128 was also coated with montmorillonite or illite. PVA was used to bind the clay minerals to silica sand
129 following the optimized method described by Jerez and collaborators (2006). The efficiency and
130 homogeneity of the coatings were checked with scanning electron microscope (see supplementary
131 material, Figure S1).

132 The humic acid- and clay-coated sands were mixed with proportions typical of organic carbon (OC)
133 and clay contents of Vertisols (Chinn and Pillai, 2008; Saffigna et al., 1989). The artificial soil matrix
134 was thus composed of 1% (w/w) humic acid-coated sand, 20% (w/w) montmorillonite-coated sand,
135 10% (w/w) illite coated sand and 69% (w/w) silica sand. The absolute contents of humic acid and clay
136 minerals were less than 1% and 30%, respectively. To assess if, CPF sorption coefficient of the
137 artificial soil matrix was still comparable with sorption on Vertisols, a multiple regression analysis
138 between literature-reported CPF sorption coefficients measured in Australian Vertisols (Gebremariam
139 et al., 2012) and their clay and OC content was performed. Indeed, if OC and clay explain most of the
140 CPF sorption coefficient variability than these constituents can be considered as the main drivers of
141 CPF sorption on Vertisols. This would validate the choice of the artificial matrix constituents. For the
142 artificial matrix to be representative of Vertisols, the sorption coefficients measured on the artificial
143 matrix and that estimated by the multiple regression equation, using the mass of the various coated
144 sands and not the mass of the actual constituents, should also be equivalent.

145

146 **2.3. Determination of CPF and TX100 sorption equilibria under static conditions**

147 The equilibrium partitioning of CPF and TX100 between the artificial soil matrix and water was
148 determined using batch tests adapted from OECD guidelines (OECD, 2000). Artificial soil (0.23 g)
149 was weighed out into 25 ml glass vials. Subsequently, 23 mL of the CPF or TX100 solutions,
150 containing 200 mg/L NaN₃ to prevent microbial degradation (Zhu et al., 2003), were added to reach a
151 soil to solution ratio of 1:100 (g/mL). The concentrations used to determine the sorption isotherms
152 were 20, 50, 100, 200 and 400 µg/L for CPF and 5, 15, 100 and 300 mg/L for TX100. The vials were
153 shaken at 100 rpm for 10 days at 24 ± 2 °C. The shaking duration was chosen based on preliminary
154 kinetic experiments to ensure equilibrium was reached. The vials were left for a few minutes for the
155 suspended soil matrix to settle; subsequently a 1 mL aliquot of the aqueous phase was sampled for
156 analysis of CPF (see section 2.5).

157 The amount of CPF and TX100 sorbed to the soil matrix was calculated by deducting the mass
158 remaining in the aqueous phase at equilibrium from the initial mass spiked into the aqueous phase.
159 The loss to glassware was evaluated for both molecules and found to be negligible. The data were
160 fitted to Freundlich and linear isotherms:

$$161 \quad C_s = K_f C_w^n \quad (1)$$

162 where C_s is the concentration in soil (mg/kg), C_w the aqueous concentration (mg/L) at equilibrium
163 and K_f ($\mu\text{g}^{(1-n)}/\text{l}^n/\text{kg}$) and n (-) the Freundlich affinity and non-linearity coefficients respectively. When
164 n was close to 1, a linear isotherm was assumed with $K_f = K_d$.

165 In addition to the above batch tests, the apparent K_d (K_d^*) of CPF at different TX100 concentrations
166 was determined. For this, batch tests with the simultaneous presence of TX100 and CPF were
167 performed. While the CPF concentration was kept constant at 100 µg/L for this series, the
168 concentration of TX100 varied from 5, 15, 50, 100 or 300 mg/L. These TX100 concentrations ranged
169 from below, to 2 times the average CMC reported in the literature. Aside from the solution
170 composition, the batch experiments were performed as described above.

171

172 **2.4. Determination of surfactant facilitated transfer under dynamic conditions**

173 *2.4.1 Column design*

174 PTFE columns with 80 mm length and 19 mm internal diameter were packed with the artificial soil
175 matrix and connected to an irrigation system as detailed in Figure 1. The micro-drippers were
176 calibrated to deliver a constant flow rate of 2 mL/min. Each column was composed of a pre-cleaned
177 semi-rigid PTFE tubing rigidified by an outer PVC tubing. The PVC tubing only provided the rigidity
178 and was not in contact with the soil matrix and the irrigation solution. 37 ± 2 g of artificial soil matrix
179 was packed in each column to the same height (8 cm) and with a similar density in all columns. The
180 soil matrix was held in place by a circular stainless steel grid (80 mesh pore size) fixed at the bottom
181 of the PVC cylinder.

182

183 *2.4.2 Agricultural scenarios*

184 The column experiments to quantify surfactant facilitated transfer represent two common agricultural
185 practices i.e. pesticide spraying and effluent irrigation. Three scenarios investigated the effect of i)
186 surfactant application during pesticides spraying (“formulation effect”), ii) surfactant application as a
187 result of irrigation with reclaimed water (“irrigation effect”) and iii) the combination of i) and ii)
188 (“irrigation & formulation effects”). The reference mobility of CPF (“control”) was determined under
189 the same conditions but without the addition of TX100 during pesticide application or irrigation.

190 The columns to investigate the irrigation effect and for the control were spiked with 45 μ g of CPF,
191 dissolved in 2.25 mL milliQ water containing 2 ‰ methanol to overcome dissolution issues due to
192 CPF’s low water solubility. This CPF amount corresponds to the recommended average dose of 1.50
193 kg/ha active ingredient for spraying on various types of crops (Nufarm, 2010). To investigate the
194 formulation effect and the combined irrigation & formulations effects, each column was spiked with
195 an artificial formulation composed of 45 μ g CPF and 10 mg TX100 (4.5 g/L) dissolved in 2.25 mL
196 milliQ water containing 2.7 ‰ methanol.

197 After spiking, all columns were aged for 7 days and subsequently irrigated with milliQ water (control
198 and irrigation effect) or a 15 mg/L TX100 solution (formulation effect and combined irrigation &
199 formulation effects representative of the high end of its concentration range measured in reclaimed
200 waters (Hernández Leal et al., 2011). The soil amendment and solution applications are detailed for
201 each investigated effect in Figure 2. Each experiment was conducted in triplicate. Adsorption of
202 TX100 on the PVC tubing and drippers was checked and found to be negligible.

203

204 *2.4.3 Sampling scheme and extraction procedure*

205 During the irrigation events, the leachates were collected at the outflow every 10 minutes and weighed
206 to determine their volume and subsequently to calculate the flow rates. For the formulation + irrigation
207 treatment, the flow rate had to be lowered to 1.5 mL/min to prevent leachate losses due to excessive
208 foaming at the column's outflow. As a result, the cumulated outflow volume was lower than for the
209 other treatments. CPF and TX100 concentration in all the leachate samples were measured. After the
210 irrigation events the columns were drained for 24 h then cut into 1 cm layers. The column layers in
211 their whole were weighed and transferred to 20 mL glass vials with Teflon lined caps. Before the
212 extraction of CPF and TX100, each layer was spiked with 200 ng of the internal standard; deuterated
213 Chlorpyrifos (CPF-d10). The extraction was performed with 5 mL dichloromethane (DCM) by
214 shaking for 2 h followed by 10 min sonication. The DCM extracts were collected and the procedure
215 was repeated once. The combined DCM extracts were blown down under nitrogen flux at room
216 temperature and re-dissolved in 1 mL methanol. This extraction procedure gave the best recovery rates
217 (95.3% for CPF and 67.7% for TX100) among several solvent combinations and shaking duration
218 tested.

219

220 **2.5. Chemical analyses**

221 TX100 and CPF in the aqueous phase samples were quantified using reverse-phase HPLC (Shimadzu,
222 LC-20AD) equipped with a UV-detector (Shimadzu, SPD-M20A). The separation was performed on a
223 4.6 mm ID and 150 mm length C18 column (Altima) under isocratic mode with a mobile phase
224 composition of 85% methanol and 15% milliQ water with a flow rate of 0.8 mL/min. The detection
225 wavelengths were 230 nm and 223 nm for CPF and TX100 respectively.

226 The quantification of TX100 and CPF in the soil extracts was performed using an AB/Sciex, API 5500
227 QTrap mass spectrometer (AB/Sciex, Concord, Ontario, Canada) with an electrospray ionization
228 interface operated in positive mode (ESI+) coupled to a Shimadzu Nexara HPLC system (Shimadzu
229 Corp., Kyoto, Japan). The separation was performed at 40°C on a 4.6 ID and 150 mm length C18
230 column (Altima) under isocratic mode with a mobile phase composed of 85% methanol, 15% milliQ
231 water and 5 mM ammonium acetate with a flow rate of 0.8 mL/min. The data acquisition was
232 performed with the multiple reaction monitoring (MRM) mode by monitoring the dissociation of the
233 given precursor ions to the product ions of specific masses. For CPF the monitored transition was m/z
234 350→198 for a cone voltage and a collision energy of 20 and 27 volts respectively. For CPF-d10 the
235 monitored transition was m/z 360→199 for a cone voltage and a collision energy of 23 and 28 volts
236 respectively. TX100 is a mixture of $C_{14}H_{22}O(C_2H_4O)_n$ with n varying from 7 to 10. The isomer
237 $C_{14}H_{22}O(C_2H_4O)_8$ was used for the quantification. For TX100 the monitored transition was m/z
238 576.4→447.4 (TX100-n8) for cone voltage and a collision energy of 16 and 30 volts respectively. The
239 transition of the other TX100 isomers; TX100-n7, TX100-n9 and TX100-n10 were also monitored.
240 The behavior of all isomers was equivalent but the sensitivity of the TX100-n8 isomer was greater
241 which is why it was selected for the analyses.

242

243

244 **3. Results and discussion**

245 **3.1. Artificial soil matrix validation**

246 Using an artificial soil matrix as the one designed in this study presents many advantages over the use
247 of real soil including the possibility to study the mechanisms of surfactant modified mobility of
248 hydrophobic pesticides without overlying the colloidal and preferential flow effects. To provide a
249 realistic estimation of the modified behavior of hydrophobic pesticides in a soil-water-surfactant
250 system, the artificial soil matrix should meet several criteria.

251 First of all, the artificial soil matrix should contain all real soil components that may impact surfactant
252 and pesticide mobility and retention, such as OC and clay, in an equivalent composition. The multiple
253 regression analysis investigating the relation between literature values for K_d of CPF and the
254 composition of the Australian soils on which the K_d were measured (Equation 2) showed a good
255 correlation between the K_d value and the clay and OC content of a given soil ($R^2 = 0.98$, p -value =
256 $1.26 \cdot 10^{-6}$):

$$257 \quad \mathbf{Kd (CPF) = 2.565 \cdot clay (\%) + 94.766 \cdot OC (\%) - 127.560 (R^2 = 0.98, n = 10)} \quad (2)$$

258 This means that the K_d for CPF on a given soil can be well predicted by the soil's clay and OC
259 contents (Figure 3) and indicates that these soil constituents are the main drivers of CPF sorption
260 processes onto soil as previously reported for other hydrophobic compounds (e.g., Chefetz et al., 2008;
261 Gebremariam et al., 2012; Weber et al., 2004). Thus, the artificial soil matrix contained all soil
262 constituents driving the sorption processes of hydrophobic compounds. Silica sand is considered inert
263 regarding CPF sorption.

264 The sorption coefficient of CPF to the artificial soil matrix was also well predicted by Equation 2
265 (Figure 3). The sorption of CPF in real soil is thus expected to be reasonably represented using the
266 artificial matrix.

267 Moreover, the stability of the coating to the silica substrate is essential to allow an unbiased transport
268 potential assessment under dynamic conditions. Indeed, if the coating isn't stable enough, colloidal
269 transfer may occur. Stability tests of the sand coating performed by Jerez and collaborators (2006)
270 highlighted a strong stability with 97 to 98% of the clay remaining bound to the sand after the through

271 flow of 10,000 pore volumes. The colloidal facilitated transfer within the artificial matrix used for this
272 study (10 to 12 pore volumes) is thus considered negligible.

273 Furthermore, the columns when packed homogeneously, are not submitted to any biotic or abiotic
274 sources of macroporosity. Therefore, no structural porosity is exhibited in the artificial soil matrix and
275 all preferential pathways potentially enhancing hydrophobic pesticides mobility in real soil, except for
276 surfactant facilitated transport, can be assumed negligible.

277 Capturing the main drivers of hydrophobic pesticide sorption to soil and ensuring the coating stability,
278 the artificial soil matrix was considered suitable for the quantification of the underlying surfactant
279 facilitated transfer processes (sorption on soil, surfactant admicelles, micelles or monomers and
280 leaching) of hydrophobic pesticides under both, equilibrium and dynamic conditions. Furthermore, in
281 future studies, the artificial soil matrix could also enable the quantification of the relative importance
282 of soil constituents separately. In addition, various grain-size of silica sand could be applied to
283 investigate the effect of different porosities and hydraulic conductivities.

284

285 **3.2. Chlorpyrifos partitioning in a soil-water-surfactant system at equilibrium**

286 CPF sorption onto the artificial soil matrix was well fitted by a linear isotherm ($n=1$, $R^2=0.99$) with a
287 corresponding K_d of 61.5 L/kg (Figure 4a). These results are consistent with previous studies on CPF
288 sorption onto soils with similar clay and OC contents (K_d of 40 – 546 L/kg) (Gebremariam et al.,
289 2012).

290 TX100 sorption onto the artificial soil matrix was also well fitted by a linear isotherm for the
291 investigated concentration range, even at concentrations exceeding the reported average CMC of 150
292 mg/L (Zhang et al., 2009; Zhou and Zhu, 2005) (Figure 4b). The TX100 sorption in our experiment
293 was still concentration-dependent at 300 mg/L (Figure 4b), suggesting that CMC was not reached at
294 this concentration. Previous studies showed TX100 sorption to soil reaching a plateau for aqueous
295 concentrations higher than 1 to 1.5 times the CMC at equilibrium (Lee et al., 2004, 2000; Zhou and

296 Zhu, 2005). This plateauing was explained by null sorption of surfactant micelles onto soil and the
297 constant concentration of surfactant monomers for concentrations at and above CMC. Thus, the CMC
298 of the TX100 used in the present study is likely above the reported average, which is consistent with
299 the CMC range (124.8 – 561.6 mg/L) provided by the manufacturer (Table 1).

300 At equilibrium aqueous concentrations of TX100 below 5 mg/L, the apparent sorption coefficient
301 (K_d^*) of CPF exceeds K_d and reaches a maximum of 150% (Figure 5). However, with an increased
302 TX100 concentration of 10 mg/L, K_d^* rapidly drops to below half the value of K_d and continues to
303 fall gradually with increasing TX100 concentration.

304 K_d^* of CPF in a soil-surfactant-water system results from two opposite effects. On one hand, in
305 addition to the clay- and OC-sorbed hydrophobic pesticides, the soil-sorbed surfactant monomers
306 potentially increase pesticide sorption to soil by providing an effective partitioning medium (Lee et al.,
307 2004; Wang and Keller, 2009; Zhou and Zhu, 2005). On the other hand, dissolved surfactant
308 monomers and particularly surfactant micelles enhance the apparent solubility of hydrophobic
309 pesticides thus decreasing their sorption onto soil (Lee et al., 2004; Zhou and Zhu, 2005). Thus, K_d^*
310 results from the partitioning of hydrophobic pesticides between water and soil (K_d), sorbed surfactants
311 (admicelles, K_{ad}), surfactant monomers (K_{mo}) and surfactant micelles (K_{mi}). The observed initial
312 increase in K_d^* (Figure 5) can thus be attributed to CPF partitioning into TX100 admicelles. At
313 TX100 concentrations above 5 mg/L, the increase in CPF apparent water solubility induces a relative
314 decrease in sorption to soil and admicelles. CPF partitioning into TX100 monomers probably follows a
315 L-type isotherm with CPF affinity for the TX100 monomer fraction increasing along with the
316 monomer concentration rise. At low TX100 concentration CPF has probably more affinity for the
317 admicelles fractions which changes in favor of monomers above 5 mg/L. These results indicate that
318 TX100 even at low concentrations may enhance the downward transfer of CPF in agricultural soils.
319 Similar observations for low-water soluble pesticides showed a lower K_d^* compared to K_d already at
320 surfactant concentrations below the CMC with a further decrease with increasing TX100
321 concentrations (Lee et al., 2004). In contrast, for hydrophobic compounds with relatively high water
322 solubility (e.g. PAHs, atrazine, diuron), surfactant monomers have been reported to be inefficient in

323 enhancing their apparent water solubility, and K_d^* was greater than K_d for these compounds at all
324 investigated concentrations below the CMC (Lee et al., 2004; Wang and Keller, 2008; Zhou and Zhu,
325 2005).

326 K_d^* characterizes the distribution of hydrophobic pesticides between the solid and aqueous phases in
327 complex soil-surfactant-water systems. Moreover, it provides a first but incomplete assessment of the
328 surfactant facilitated transport risk of hydrophobic pesticides. In addition, instead of K_d , K_d^* may also
329 be applied in modelling approaches to investigate the surfactant facilitated transport under various
330 pedoclimatic conditions for characterization of potential risks of unintentional pesticide mobility.
331 However, being the result of several partitioning and adsorption processes each with potentially
332 contrasting kinetics, K_d^* might provide inaccurate trends for non-steady state conditions. Dynamic
333 experiments thereby represent a better method to evaluate unintentional hydrophobic pesticide
334 mobility under field conditions. K_d^* can also be measured on real soil without overlying other
335 processes but not the dynamic experiments.

336

337 **3.3. Dynamic surfactant facilitated transfer of Chlorpyrifos under various agricultural** 338 **application scenarios**

339 Using columns packed with the artificial soil matrix to avoid overlaying preferential flow and colloidal
340 facilitated transfer processes, the surfactant modified mobility of CPF was assessed for 2 of the most
341 common surfactant application practices in agrosystems.

342 The soil distribution (Figure 6) and breakthrough curves (Figure S2) of both CPF and TX100 highlight
343 the contradictory effects of reduced mobility induced by CPF partitioning into TX100 admicelles and
344 sorption to soil, and enhanced mobility caused by the increase in CPF apparent water solubility by
345 TX100 monomers and micelles. Indeed, at low concentrations of TX100, almost all TX100 remained
346 sorbed at the upper layers of the columns (Figure 6e and S2e) leading to an increased retention of CPF
347 compared to the control (Figure 6a) due to CPF partitioning into admicelles. At higher concentrations

348 of TX100, the partitioning of CPF into TX100 admicelles induced a late breakthrough compared to the
349 control (Figure S2a). However, an increased CPF mobility was caused by the TX100 application,
350 resulting in the CPF accumulation in deeper soil layers (Figure 6c,d and S2c,d, Table S2). This co-
351 transport of CPF and TX100 was evident by their similar soil distribution (Figure 6c,d,f,g) and the
352 corresponding CPF and TX100 leachate's concentration patterns (Figures S2c,d,f,g).

353 Overall, the results from the dynamic column experiments, as well as from the equilibrium system,
354 illustrate enhanced apparent water solubility of CPF in the presence of TX100. Consistent with this,
355 based on K_d^* only, an enhanced downwards transfer of CPF would be expected for a TX100 solution
356 of 15 mg/L present in irrigation with waste water. In contrast, the dynamic experiments showed the
357 opposite effect with a high TX100 sorption at the upper soil layers increasing CPF sorption (Figure
358 6b). This may result from increased, i.e. faster, kinetics for the partitioning of CPF onto soil and
359 admicelles compared to the CPF partitioning into monomers. Nonetheless, as shown by our study for
360 the investigated agricultural scenarios, the formulation of CPF with APEO may initially retard CPF
361 leaching but progressively wash the soil surface layers eventually causing an accumulation in the
362 deeper soil layers. However, speculations about the influence of drip irrigation with effluent water
363 containing APEO on the observed pattern remains difficult as further agro-climatic properties may
364 influence the TX100 enhanced CPF mobility. These observations not only illustrate that the risk of
365 unintentional hydrophobic pesticide mobility generated by the addition of surfactants to agrosystems is
366 still poorly understood and difficult to predict, but also emphasize the importance of conducting
367 dynamic experiments complementary to batch tests.

368 As reviewed by Müller et al. (2007), the few column experiments studying the influence of effluent
369 irrigation on pesticide mobility showed conflicting results. An increased, decreased or non-modified
370 mobility depending on the pesticide and dissolved organic matter characteristics were observed (Peña
371 et al., 2011; Rodríguez-Liébana et al., 2018, 2014). In a review on column experiments
372 investigating the effect of surfactants in pesticide formulations on the leaching behavior of various
373 pesticides, Katagi (2008) concludes that the pesticide leaching behavior varied with surfactant type
374 and concentrations, pesticide physico-chemical characteristics and soil type.

375 The coexistence of various types of surfactants and other organic molecules in both pesticide
376 formulations (Katagi, 2008; Krogh et al., 2003) and reclaimed water (ElSayed and Prasher, 2013;
377 Gonzalez et al., 2010) may lead to complex and conflicting effects on pesticides leaching. For
378 pesticide formulations, the co-presence of nonionic and anionic surfactants with respectively
379 increasing and decreasing K_d^* (Pose-Juan et al., 2011, 2010) could mask or enhance the effects of
380 individual nonionic and anionic surfactants (Katagi, 2008; Peña et al., 2011).

381 Despite these influencing factors, the literature reports a general trend of increased pesticide mobility
382 and accumulation in deeper layers of the soil profile characterizes most experiments with relatively
383 high non-ionic surfactant concentrations (Katagi, 2008). However, trends of pesticide transport at
384 lower surfactant concentrations, realistic for agricultural applications, are more contrasted. Duration of
385 the irrigation period seem to play a significant role. Indeed, several studies reporting pesticide mobility
386 in soils irrigated with waste water or low-concentration non-ionic surfactant solutions for a short time
387 period reported lower pesticide leached amounts but progressive accumulation in the deeper layers of
388 the soil profile (Peña et al., 2011; Rodríguez-Liébana et al., 2018, 2014). In contrast, long term field
389 monitoring study in citrus groves (Israel) irrigated for 20 years with reclaimed water which revealed
390 that pesticides were present in all layers of the soil profile to a depth of 20 m, with increased
391 concentration with depth (Müller et al., 2007). Interestingly, in the citrus groves irrigated with
392 groundwater, the same pesticides were detected mainly at the soil surface (Müller et al., 2007)..

393 Consequently, validation of the results of the presented dynamic experiments (Figures 6 and S2) with
394 field observations of pesticide mobility under irrigation with reclaimed water needs to be carefully
395 assessed. Reclaimed water usually contains a mixture of anionic, nonionic and cationic surfactants as
396 well as humic acid-like substances or other types of dissolved organic matter (Gonzalez et al., 2010;
397 Hernández Leal et al., 2011; Hernández-Soriano et al., 2012). This mixture of potential facilitators
398 may lead to more complex interactions for pesticide mobility and its quantification needs to be
399 investigated further.

400 In the present study, the columns packed with the artificial soil matrix provide a simple and unbiased
401 mean to study the mechanisms underlying the unintentional surfactant facilitated transport of

402 hydrophobic pesticides in dynamic non-equilibrium conditions. The empirical data quantified with the
403 column experiments provide a simple way to evaluate the co-transport of various hydrophobic
404 pesticides for given agricultural and pedoclimatic contexts. Moreover, the breakthrough curves and
405 soil profiles can also be applied to calibrate models to investigate the effect of the above mentioned
406 variation factors and thereby precisely assess the risk of enhanced downward transfer associated with
407 surfactants.

408

409 **4. Conclusion**

410 Surfactants modify the behavior of hydrophobic pesticides in soils either by increasing or decreasing
411 their vertical transport depending on the surfactant type and concentration. Evaluating the surfactant
412 transport pathways of pesticides in real soil is biased by the co-action of other preferential transport
413 pathways. We thus designed an artificial soil matrix that is representative of Vertisols in terms of
414 'model' pesticide and surfactant sorption and can be used in both equilibrium and dynamic
415 experiments without overlying other preferential transport pathways. We combined batch and column
416 techniques to assess the mechanisms of surfactant modified transport of chlorpyrifos for 2 common
417 agricultural practices resulting in more or less concentrated surfactant amendments. We found that
418 single irrigation event with waste water containing TX100 could decrease the offsite transport of
419 chlorpyrifos by 20% while spraying formulations with TX100 increased its accumulation in the deeper
420 layers of the soil profiles. Surfactants modify the behavior of hydrophobic pesticides in soils but their
421 action is dependent on the surfactant type and concentration. The methodology presented in this study
422 allows the further necessary characterization of various surfactant/pesticides combinations as well as
423 contrasted pedo-climatic context for further evaluation of this preferential offsite transport pathway.

424

425 **Acknowledgements**

426 This study was supported by the Australian Research Council (Discovery grant DP120103923). We
427 would like to thank Ron Rash from The University of Queensland for his kind assistance with the
428 SEM analyses of the coated sand mixtures. We would also like to thank Markus Flury, Jorgus Jerez

429 and Luuk Koopal for providing additional information on the operational procedures for the various
430 sand coatings.

431

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555

Figure captions

Figure 1: Experimental column design

Figure 2: Investigated agricultural scenarios for surfactant facilitated transport of CPF

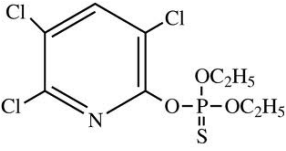
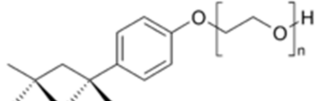
Figure 3: A comparison of measured and predicted K_d of CPF. The dotted line represents the $x=y$ equation. The black circles illustrate the K_d (CPF) of real soils (literature values see table S1) and the blue diamond the K_d (CPF) of the artificial soil matrix used in this study.

Figure 4: Sorption isotherm of CPF (a) and TX100 (b) to the artificial soil matrix. The error bars represent standard deviation ($n=3$).

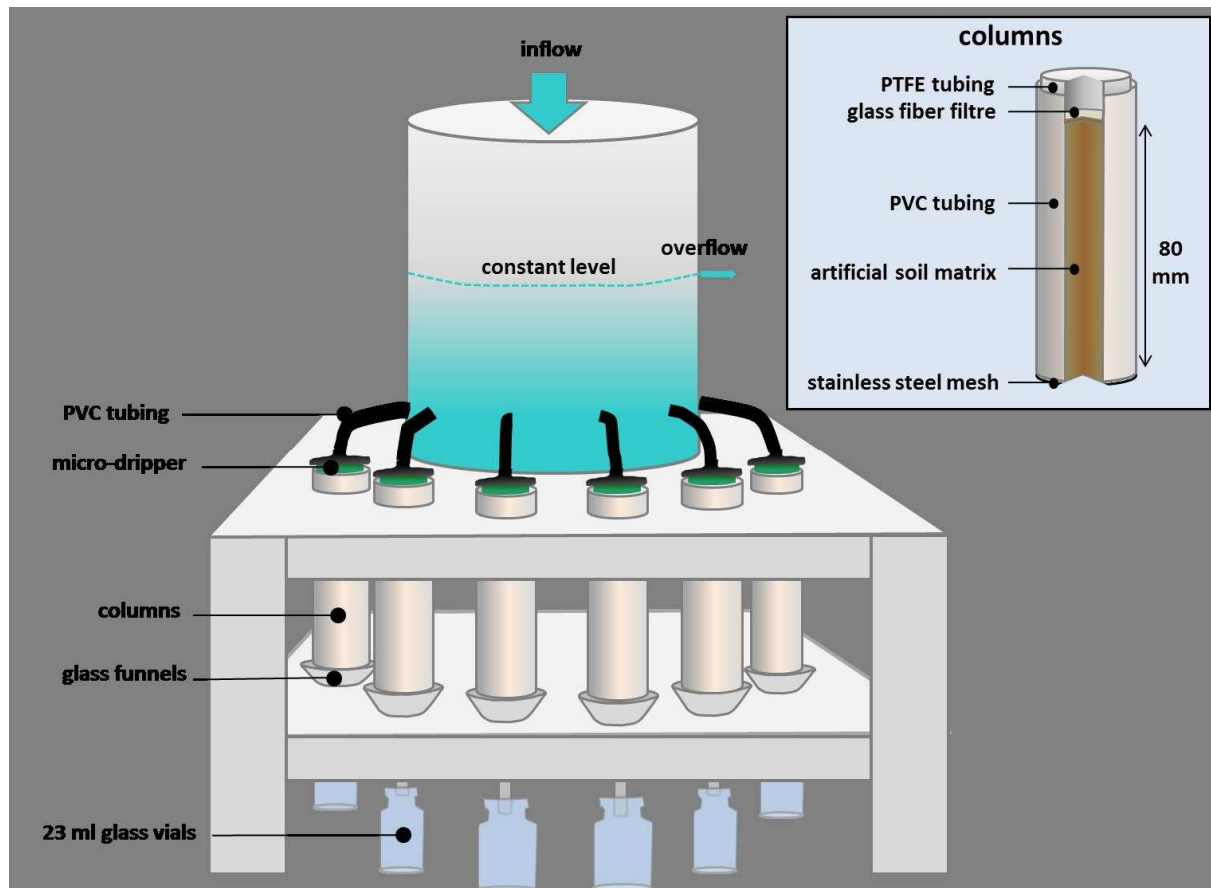
Figure 5: Apparent K_d (K_d^) of CPF in complex artificial soil-TX100-water systems relative to the reference K_d . Horizontal dotted line is where $K_d^* = K_d$.*

*Figure 6: Chlorpyrifos and Tritonx-100 distribution along the soil profiles after the following agricultural scenarios **a**: control, **b**: irrigation effect (CPF), **c**: formulation effect (CPF), **d**: formulation & irrigation effects (CPF), **e**: irrigation effect (TX100), **f**: formulation effect (TX100), **g**: formulation & irrigation effects (TX100). The error bars represent the standard deviation ($n=3$).*

Table 1: Physico-chemical properties of Chlorpyrifos and Triton X100

compound/ formula	molecular weight	water solubility	log Kow	field DT50	average Koc	CMC
	g/mol	mg/L			L/kg	mg/L
Chlorpyrifos  $C_9H_{11}Cl_3NO_3PS$	350.589 ¹⁵	1.05 ¹ to 2 ²	4.96 ^{3,4}	2 days to 4 years ^{1,4}	8163 ⁴	NR
Triton X100  $C_{14}H_{22}O(C_2H_4O)_n$ (n = 9.5)	624 ^a	Soluble ^a	NR	NR	NR	124.8 – 561.6 ^a

^a Properties provided by the manufacturer for TX100. NR: not relevant for this molecule. References are 1: Gebremariam et al. 2012; 2: Valverde Garcia et al. (1992); 3: NIH (2018) and 4: ANSES (2018)



**Amendment
procedure:**

Chlorpyrifos
1.50 kg/ha a.i.

Chlorpyrifos
1.50 kg/ha a.i.
TX100
4.5 g/L

**Irrigation
procedure:**

milliQ water
365 ± 25 mm

TX100 15 mg/L
355 ± 12 mm

milliQ water
350 ± 35 mm

TX100 15 mg/L
285 ± 14 mm

**Investigated
effect:**

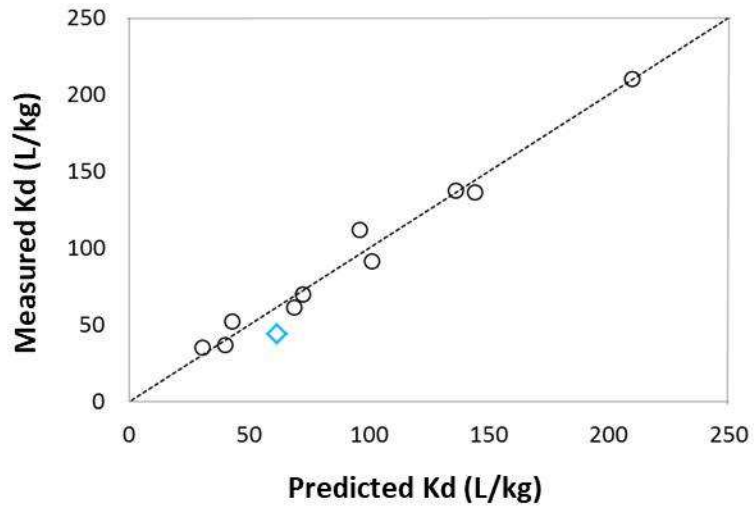
Control

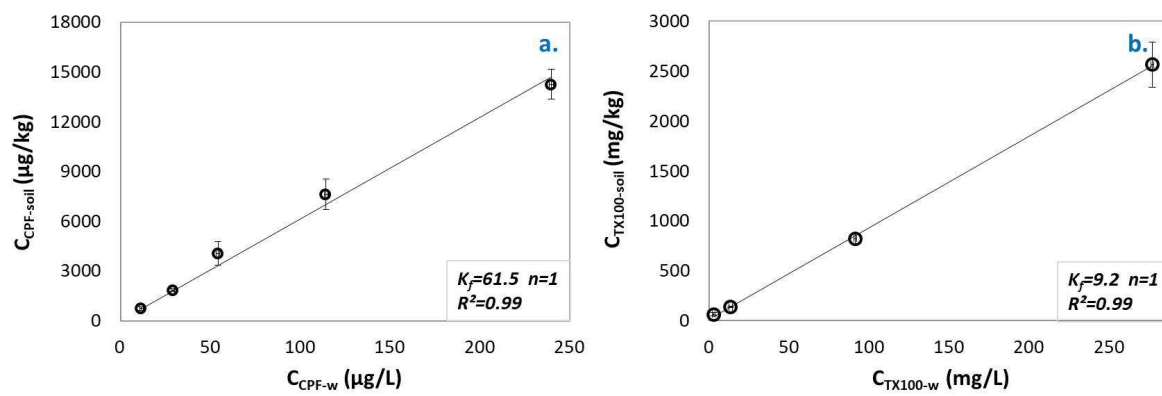
Irrigation effect

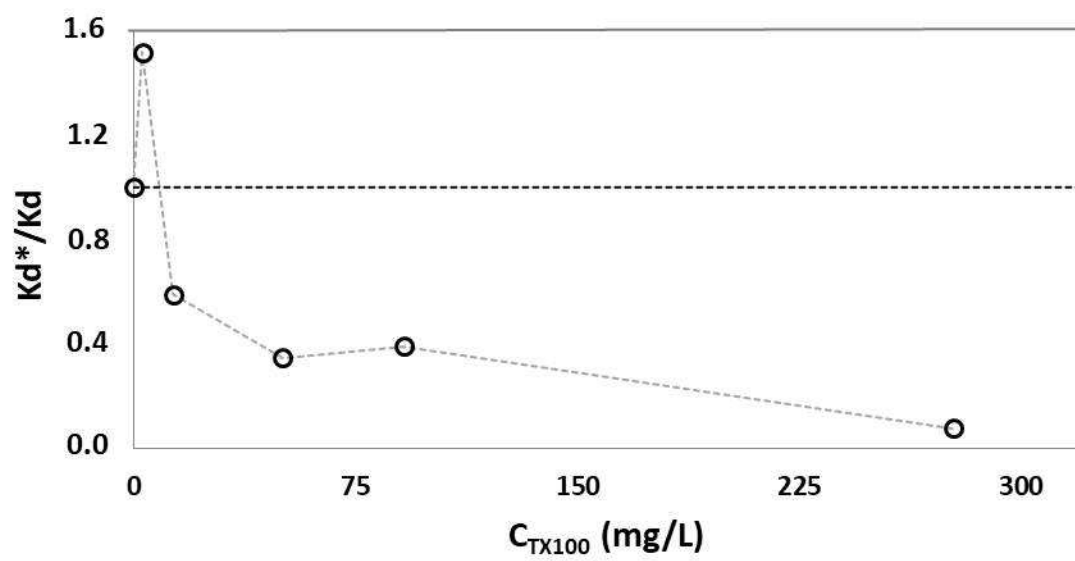
Formulation effect

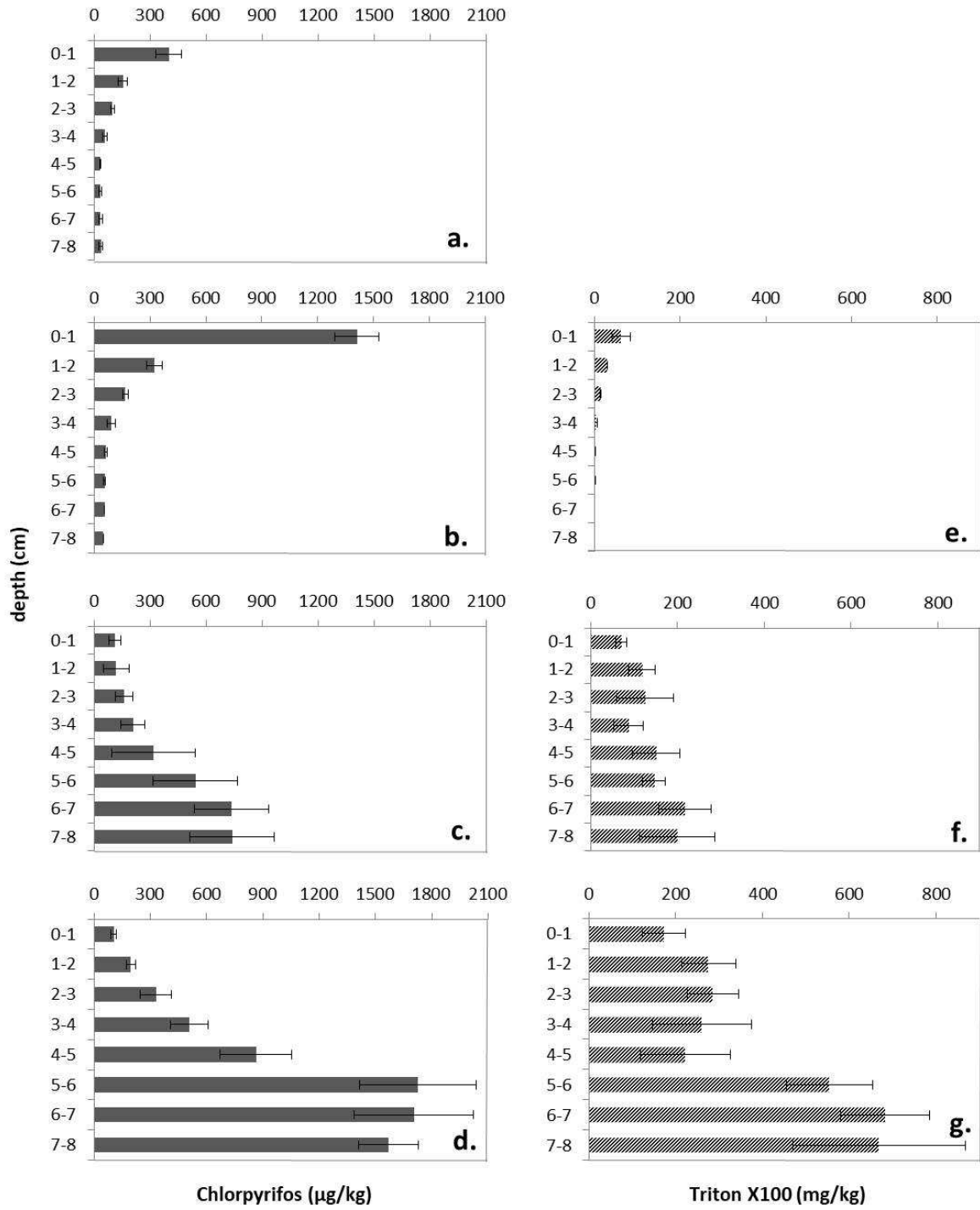
Irrigation &
Formulation effect

ACCEPTED MANUSCRIPT









A