

Movement of Dichlorvos in Farm Soils: Batch and Column Studies.

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1 **Movement of dichlorvos in farm soils: batch and column studies.**

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10
11 **Abstract**

12 Soils are the principal environmental fate of pesticides in agricultural areas. Thus, the
13 kinetics, extension, and strength of the adsorption process become critical. Dichlorvos
14 (DDVP) is an organophosphorous pesticide that is used both in agriculture and livestock
15 production. Sorption/desorption assays of DDVP in two agricultural soils (with different
16 textural characteristics) from Pampa Plain (Argentina) were performed in both batch and
17 column systems. From batch studies, kinetics and sorption/desorption equilibrium
18 parameters were estimated. Our results showed that the maxima adsorption is reached
19 after 30 h of time of contact and followed a pseudo-first-order rate. Adsorption/desorption
20 data were well fitted to the Freundlich model obtaining high adsorption constants of 90
21 $\mu\text{g}^{(1-1/n)} \text{ mL}^{(1/n)} \text{ g}^{-1}$ and 21 $\mu\text{g}^{(1-1/n)} \text{ mL}^{(1/n)} \text{ g}^{-1}$ for the clay loam and sandy loam soil,
22 respectively. The isotherms were non-linear in both cases and the desorption process was
23 unfavourable. Also, positive hysteresis was present for the sandy loam soil. From column
24 studies, breakthrough curves were used to evaluate the mobility of DDVP in the soils at
25 1, 10, and 50 mg L⁻¹ of DDVP. Eluted profiles were asymmetrical as well they presented

26 retardation effects that were in connection with the results in batch conditions. Non-
27 equilibrium sorption was stated for the DDVP movement through columns. Thus, high
28 mobility was observed for DDVP in both soils despite their textural differences.

29

30 **Keywords:** *agricultural soils; insecticide mobility; adsorption; desorption, non-*
31 *equilibrium sorption*

32

33 **1. Introduction**

34 In the last decades, agricultural countries have undergone an important expansion in their
35 activities due to the development of new technologies and an increase in the specialization
36 to attain worldwide food demands. Therefore, there was an increase in the use of
37 phytosanitary products (mainly herbicides, insecticides, and fungicides) to improve crop
38 production yield. However, the excessive application of pesticides has become an
39 important environmental issue due to the high environmental concentrations found and
40 the deleterious effects on non-target individuals [1, 2, 3,4]. Organophosphate pesticides
41 are used in both agriculture and animal production being dichlorvos (2,2-dichlorovinyl
42 dimethyl phosphate, DDVP) one of the most employed of this family. DDVP is an
43 acetylcholinesterase inhibitor that is effective against mushroom flies, aphids, spider
44 mites, caterpillars, and whiteflies in the greenhouse, outdoor fruit, and vegetable crops.
45 Moreover, it is used to treat a variety of parasitic worm infections in livestock, dogs, and
46 humans [1]. Exposure to DDVP in living organisms can lead to several affections related
47 to neurological, reproductive, immunological, hepatic, renal, respiratory, and metabolic
48 systems [3, 5]. In cultivated regions, soils and streams play an important role in the
49 transport and fate of pesticides used in crops and farms. There, pesticides can undergo
50 several processes such as adsorption, leaching, run-off, volatilization, and degradation

51 (biotic or abiotic) affecting the environmental concentrations [6, 7, 8]. DDVP has a short
52 half-lifetime in freshwater (2.8 days at pH=7 and 20°C) [9] and soils (4 days at pH= 6.2-
53 7.4 and 25°C) [10]. However, dissolved organic matter in freshwater could affect the
54 DDVP behaviour reducing both, its photodegradation rate [8] and its biodisponibility
55 [11]. Moreover, groundwater contamination is not expected, according to its low
56 Gustafson index of 0.69 [12]. According to European regulations, the maximum limit for
57 priority substances in the inland waters is 0.0006 $\mu\text{g L}^{-1}$ according to water policy [13].
58 However, DDVP was detected ranging from 0.05 to 7.50 μgL^{-1} in freshwater [14, 15]. In
59 Argentina, DDVP was the most detected insecticide in fish species collected from farm
60 areas located at the Pampa Plain [16].

61 Adsorption studies are crucial to predict environmental fate constituting a valuable tool
62 to perform risk assessment evaluations [17]. Sorption studies of pesticides in soils were
63 extensively reported in the literature, however, among the insecticides, DDVP adsorption
64 studies are scarce [18]. Furthermore, there are no studies on the interaction of dichlorvos
65 with Argentinean soils. This study describes the adsorption behaviour of DDVP from
66 batch and column experiments carried out on two soils with different textural properties
67 and destined for agricultural and livestock activities.

68

69 **2. Materials and Methods**

70 *2.1 Chemicals*

71 All reagents were analytical grade, and they were used without further purification.
72 Dichlorvos was purchased from Sigma-Aldrich Pestanal (Germany); phosphoric acid,
73 Anedra (Argentina); sodium azide, Biopack (Argentina), and calcium chloride, Merck
74 (Germany). Methanol, Sintorgan (Argentina), and acetonitrile, J.T.Baker (USA) were

75 HPLC - grade. Solutions were prepared using deionized water obtained from a milli-Q
76 purification system and kept at 4°C.

77

78 *2.2 Soils*

79 Three soil samples were taken from two farms within Buenos Aires province (Argentina),
80 referred to as:

81

82 **9S** – 9 de Julio: 35° 21'19'' S and 60° 41'48'' W

83 **MS** – Mercedes: 34° 40'29'' S and 59° 25'14'' W

84

85 Soil samples were collected from a depth of 5 – 20 cm of soil. They were air-dried, passed
86 through a 2 mm sieve, and stored in plastic bags at room temperature until use. Soils were
87 characterized according to standard procedures [19]: potentiometric method (pH and
88 Electrical Conductivity), Walkley-Black method (organic matter content), ammonium
89 acetate distillation (cation exchange capacity, C.E.C.), and hydrometric (texture).

90

91 *2.3 Batch experiments*

92 Batch adsorption/desorption experiments were performed at room temperature by
93 triplicate according to the OECD Technical Guideline 106 [20]. To determine the
94 adsorption and desorption parameters a ratio of 6 g of soil per 100 mL of solution was set
95 from preliminary experiments (data not shown). Thus, soils were pre-equilibrated with
96 CaCl₂ 0.01M and NaN₃ 0.1M solutions during 12 h. After that, dispersions were added
97 with the necessary volume of a DDVP solution until a final concentration of 5 µg mL⁻¹.
98 A volume of 500 mL was kept under agitation for 30 h on shade conditions to avoid
99 dichlorvos photodegradation. During this time, dispersion samples of 5 mL were

100 periodically collected to investigate the variation of DDVP concentration in the
101 supernatant. Collected samples were centrifuged and soil particles were removed using a
102 nylon filter (0.45 μm) coupled to a syringe where any adsorption was detected. DDVP
103 was quantified by HPLC as was described below (see Section 2.5). From these results,
104 the equilibrium time was stated as the time at which DDVP concentration remains
105 constant in the solution. Adsorption/desorption isotherms were constructed varying the
106 starting DDVP concentration ranging from 5 to 500 $\mu\text{g mL}^{-1}$. A mass of 0.6 g of each soil
107 (previously equilibrated with CaCl_2 and NaN_3 solutions) was in contact with 10 mL of
108 DDVP solution and the dispersions were stirred for 30 hs. The concentration of DDVP
109 adsorbed is calculated as:

110

$$111 \quad q_e^{\text{ads}} = \frac{(C_0 - C_e)V}{m} \quad (1)$$

112

113 where C_0 and C_e are both the DDVP concentrations in the solution at initial and at
114 equilibrium time, respectively, expressed as $\mu\text{g mL}^{-1}$, V is the solution volume (mL) and
115 m is the soil mass (g).

116 Desorption assays were conducted with the remaining solid of the adsorption studies
117 described before. Soils were re-suspended in 10 mL of CaCl_2 and the new dispersions
118 were shaken for 30 hours. Finally, the amount of DDVP desorbed was calculated as:

119

$$120 \quad q_e^{\text{des}} = q_e^{\text{ads}} - \frac{C_e V}{m} \quad (2)$$

121

122 where q_e^{ads} was previously calculated by Eq. 1, C_e is the DDVP concentration obtained
123 in the desorption experiment (expressed as $\mu\text{g mL}^{-1}$), m is the mass of the remaining soil
124 (g) and V is the solution volume (10 mL).

125

126 *2.4 Column movement experiments*

127 Continuous flow experiments were performed in a borosilicate column (3.5 cm long; 4.9
128 cm² cross-sectional area) where air-dried soils were packed. Soils were initially saturated
129 with a CaCl₂ 0.01 M solution. DDVP solutions at several concentrations (1, 5, and 50 μg
130 L⁻¹) were pumped from the top with a mean flow rate of 1 cm³ min⁻¹ by using a peristaltic
131 pump. Then, the applied pesticide was displaced through the column with a solution of
132 CaCl₂. Samples were collected from the end of the column at different time intervals until
133 the exit concentration equals the inlet. Studies were performed by duplicate at room
134 temperature (22 ±1 °C). The column pore volume was calculated as:

135

$$136 \quad V_p = \frac{V}{V_0} \quad (3)$$

137

138 where V is cumulative outflow volume and V₀ is the total water volume into the column.
139 This was obtained gravimetrically at the end of each displacement.

140

141 Under operating conditions, the volume samples (obtained at different times) were used
142 to construct the breakthrough curve (BTC) where the dichlorvos concentration was
143 expressed as a relative concentration, C/C₀.

144

145 *2.5 Data analysis*

146 The rate, strength, and extent of dichlorvos adsorption on soils were evaluated by using
147 kinetics and equilibrium models to obtain the physicochemical parameters involved in
148 the adsorption process.

149

150 2.5.1 Kinetic data

151 The pseudo-order and the rate adsorption were assessed fitting the experimental data to
152 the kinetics models based on the adsorbent capacity such as the Lagergren equation [21]
153 and the Ho expression [22]. The pseudo-first-order (PFO) model assumes that the rate
154 adsorption is proportional to the driving force representing by:

155
156
$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (4)$$

157

158 where k_1 is the PFO rate constant (h^{-1}), q_e ($\mu\text{g g}^{-1}$) is the adsorbed concentration of DDVP
159 in the soil particles at the equilibrium time and q_t ($\mu\text{g g}^{-1}$) is the concentration of DDVP
160 adsorbed at soil particles at the evaluated time, t. The integrated expression is:

161

162
$$q_t = q_e(1 - e^{-k_1 t}) \quad (5)$$

163

164 The pseudo-second-order (PSO) model assumes that the adsorption rate is proportional
165 to the square of the driving force [22]:

166

167
$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

168

169 where, k_2 is the pseudo-second-order sorption rate constant ($\text{g } \mu\text{g}^{-1} \text{h}^{-1}$), t is the time
170 expressed in hours and q_e and q_t were previously defined in the text. Its integrated
171 expression can be written as:

172

173
$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (7)$$

174

175 2.5.2 Equilibrium assays

176 From equilibrium experiments, adsorption/desorption isotherms of DDVP were evaluated
177 relating to the quantity of DDVP adsorbed and remained in the solution at the equilibrium
178 time. Moreover, Langmuir and Freundlich's models were used to estimate the adsorption
179 parameters related. Langmuir model assumes that the adsorption takes place forming a
180 monolayer of the solute molecules on the solid particles:

181

$$182 \quad q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (8)$$

183

184 where Q_0 (expressed as $\mu\text{g g}^{-1}$) represents the maxima coverage capacity and the
185 Langmuir constant, K_L , is related to the affinity between the DDVP molecules and the
186 adsorbent soil particles.

187

188 Data were also fitted to the Freundlich equation to estimate the equilibrium constant of
189 both adsorption and desorption processes as is suggested by the OECD normative [20].

190 For that, the exponential equation was used:

191

$$192 \quad q_e = K_F C_e^{1/n} \quad (9)$$

193

194 where K_F and $1/n$ representing the adsorption capacity (adsorption constant) and the
195 adsorption intensity, respectively.

196

197 The quantity of DDVP desorbed was calculated using the Eq. 9 where q_e^{des} is the DDVP
198 adsorbed after a cycle of desorption, q_e^{ads} is the quantity of DDVP initially adsorbed,

199 C_{aq}^{des} is the concentration of DDVP in the desorption solution, V_0 is the volume of CaCl_2
200 solution (mL) and m_{soil} is the soil mass (g).

201

$$202 \quad q_e^{des} = q_e^{ads} - \left(C_{aq}^{des} \times \frac{V_0}{m_{soil}} \right) \quad (10)$$

203

204 Additionally, the hysteresis coefficient (H) was calculated according to Eq. 10 [23]:

205

$$206 \quad H = \frac{\left(\frac{1}{n} \text{desorption} \right)}{\left(\frac{1}{n} \text{adsorption} \right)} \quad (11)$$

207

208 where $1/n$ was previously estimated from the desorption and adsorption isotherms. An H
209 < 1 value (positive hysteresis) means that DDVP molecules tend to be adsorbed whereas,
210 an H > 1 value (negative hysteresis) suggests that the desorption process is favoured.
211 Additionally, if H = 1 the hysteresis is considered to be absent and the process is
212 considered reversible [23].

213

214 *2.5 Dichlorvos measurements*

215 DDVP was determined through a high-performance liquid-chromatography (HPLC)
216 system (Shimadzu LC-20A) equipped with a UV-Vis detector. The mobile phase
217 consisted of a 65:35 volumetric mixture of 1 mM phosphoric acid and acetonitrile. The
218 used column was a Shimadzu Shim-pack VP-ODS: 25 cm x 4.6 mm, particle size 5 μm
219 which was preconditioned at 22 °C. The flow rate was set at 1.2 mL min^{-1} and the
220 detection was performed at 205 nm. All samples were previously filtered using 0.22 μm
221 nylon filters. Determined LOD and LOC were 0.025 $\mu\text{g mL}^{-1}$ and 0.076 $\mu\text{g mL}^{-1}$,
222 respectively.

223

224 *2.6 Statistical analysis*

225 Graphics and data analysis were done by using Sigma Plot 11.0 [24].

226

227 **3. Results and discussion**

228 *3.1 Soil properties*

229 The physicochemical and textural properties of collected soils are shown in Table 1.

230 **Table 1.** Properties of soils used in this study.

Properties	Soils	
	MS	9S
pH (H ₂ O)	6.95	6.46
E.C. (dS m ⁻¹)	0.17	0.11
C.E.C. (cmolc kg ⁻¹)	18.56	10.38
O.C. (% w,w)	1.81	0.67
% Clay	35	12.5
% Silt	42.5	2.5
% Sand	22.5	85.0
Textural Classification	clay loam	sandy loam

231

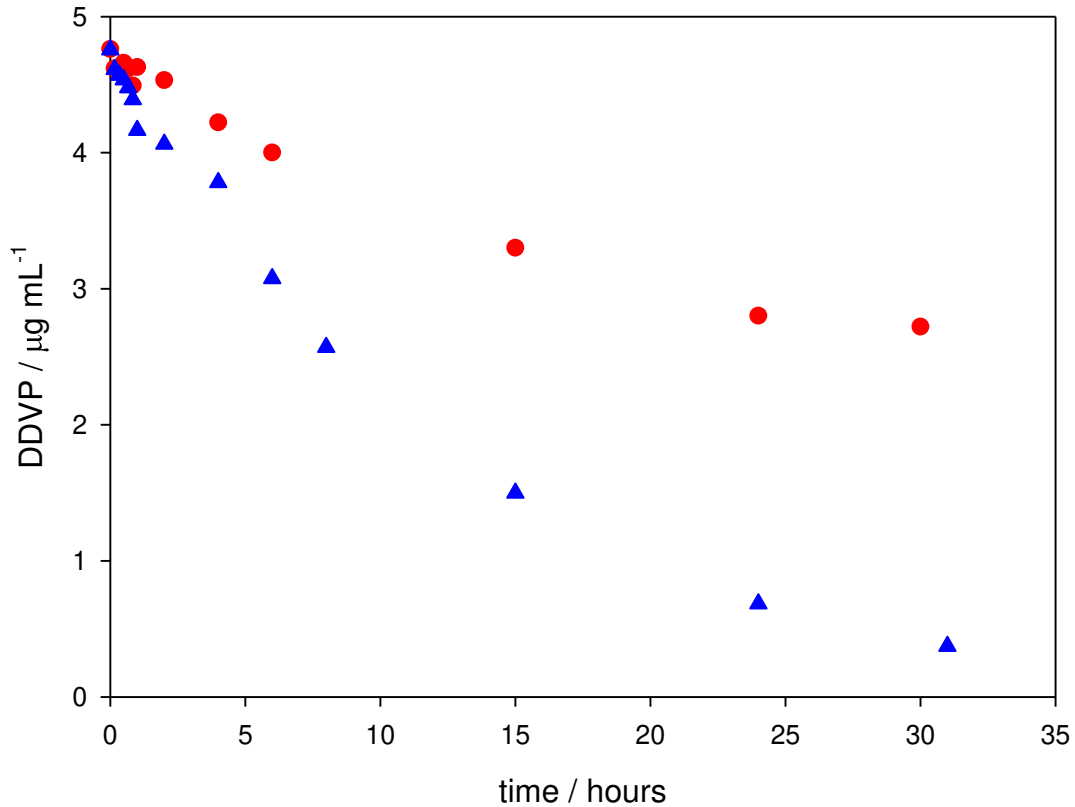
232 Samples were taken from locations where dairy farms are installed but without animal
233 occupation. Studied soils have presented different textural properties being SM clayed
234 loam while 9S soil had a higher sand content (85%). Regarding pH values, they were
235 similar although MS was slightly more alkaline. As well, the organic carbon content
236 resulted in around 2.5 times lower for 9S (0.67%).

237

238 3.2 Kinetics studies

239 Adsorption rate parameters and the equilibrium time were estimated from the analysis of

240 DDVP concentration and the time of contact with MS and 9S soils (Figure 1).



241

242 **Figure 1.** DDVP concentration as a function of contact time MS (▲) and 9S (●) soils.

243 Initial DDVP concentration: 5 µg mL⁻¹, soil dosage: 6 g L⁻¹.

244

245 The adsorption of DDVP on soil particles took place within 30 hours reaching maxima

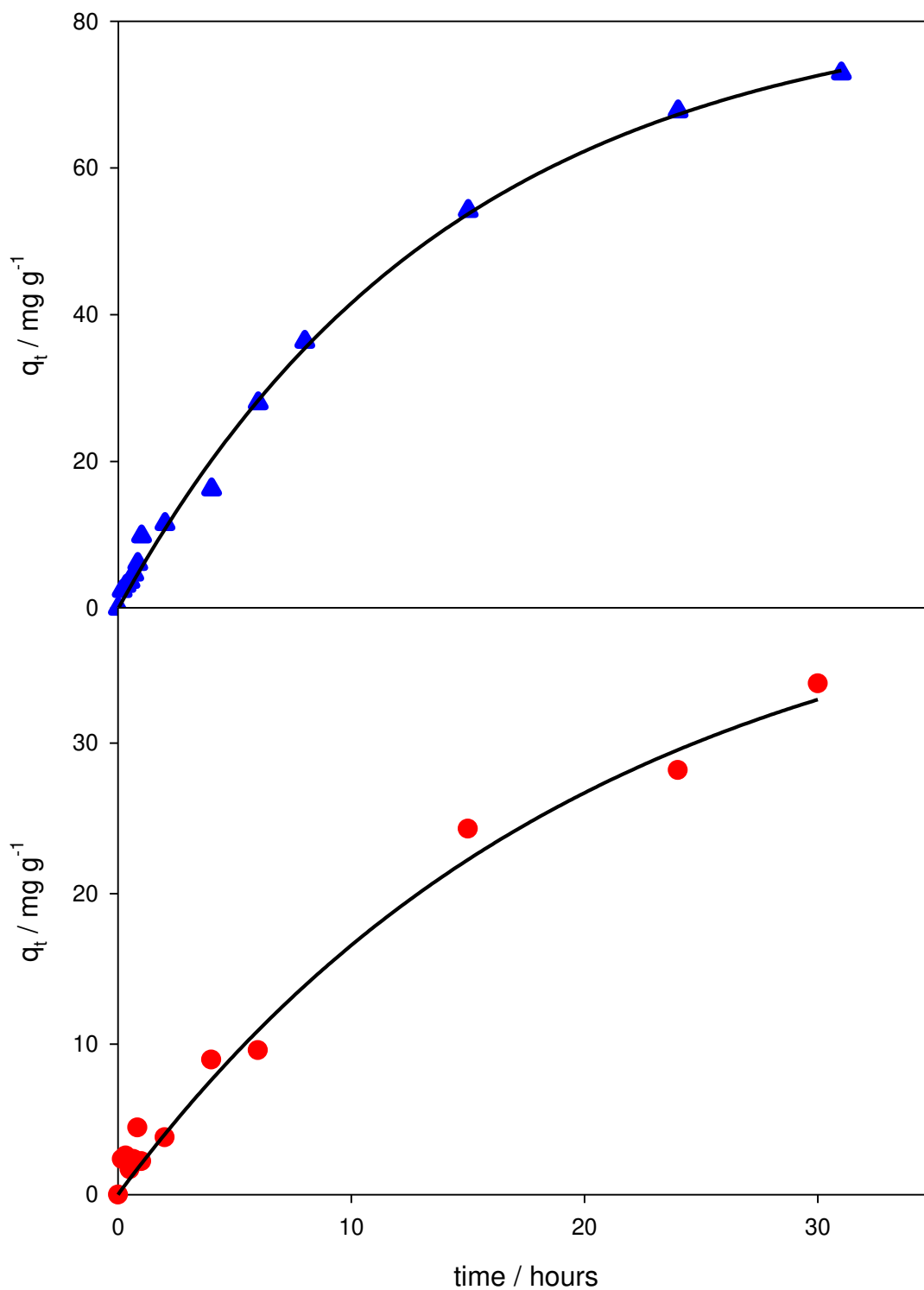
246 values of 92% and 43% for MS and 9S, respectively, from a starting concentration of 5

247 µg mL⁻¹ of DDVP. Differences between the adsorption in both soils could be related to

248 the low value of O.C. content and clay (%) in 9S regarding MS [25]. Besides,

249 experimental data were adjusted to PFO and PSO models (see Figure 2) and kinetics

250 parameters were obtained (see Table 2).



251

252 **Figure 2.** Fitting of experimental data of DDPV adsorption on soils MS (▲) and 9S (●)

253 to the PFO model (full line).

254

255 From Table 2, it is observed that experimental data adjusted very well to both proposed
 256 models being the correlation coefficients very close between them. However, the analysis
 257 of the others parameters indicated that DDVP adsorption had a better agreement with the
 258 PFO as is denoted by the coincidence between the experimental and theoretical adsorption
 259 capacities values for the two soils indicating that the DDVP adsorption processes
 260 followed a PFO law where the film diffusion is the rate-controlling of the processes.
 261 Otherwise, the parameters obtained from the fitting by PSO model were unacceptable
 262 (overestimates the adsorption capacity) suggesting that the rate-limiting step appeared not
 263 to be controlled by a chemical process [26].

264

265 **Table 2.** Kinetic parameters and q_e experimental values for the adsorption of dichlorvos
 266 onto farm soils.

	MS	9S
	$q_{e (exp)} = 72.95 \mu\text{g g}^{-1}$	$q_{e (exp)} = 33.55 \mu\text{g g}^{-1}$
PFO	$k_1 = 0.070 \pm 0.005 \text{ h}^{-1}$	$k_1 = 0.06 \pm 0.01 \text{ h}^{-1}$
	$q_{e (theo)} = 82 \pm 3 \mu\text{g g}^{-1}$	$q_{e (theo)} = 42 \pm 5 \mu\text{g g}^{-1}$
	$R^2 = 0.995$	$R^2 = 0.983$
PSO	$k_2 = 0.43 \pm 0.01 \text{ g mg}^{-1} \text{ h}^{-1}$	$k_2 = 0.64 \pm 0.02 \text{ g mg}^{-1} \text{ h}^{-1}$
	$q_{e (theo)} = 120 \pm 3 \mu\text{g g}^{-1}$	$q_{e (theo)} = 65 \pm 4 \mu\text{g g}^{-1}$
	$R^2 = 0.994$	$R^2 = 0.984$

267

268 Although DDVP has been studied for a long time, no adsorption assays have been carried
 269 out on productive soils having a lack of information regarding its adsorption properties.
 270 Until we know, only an article evaluated the rate of adsorption of DDVP on soils. Kaur
 271 and Sud [18] reported the kinetic parameters of DDVP adsorbed onto Indian soils. They

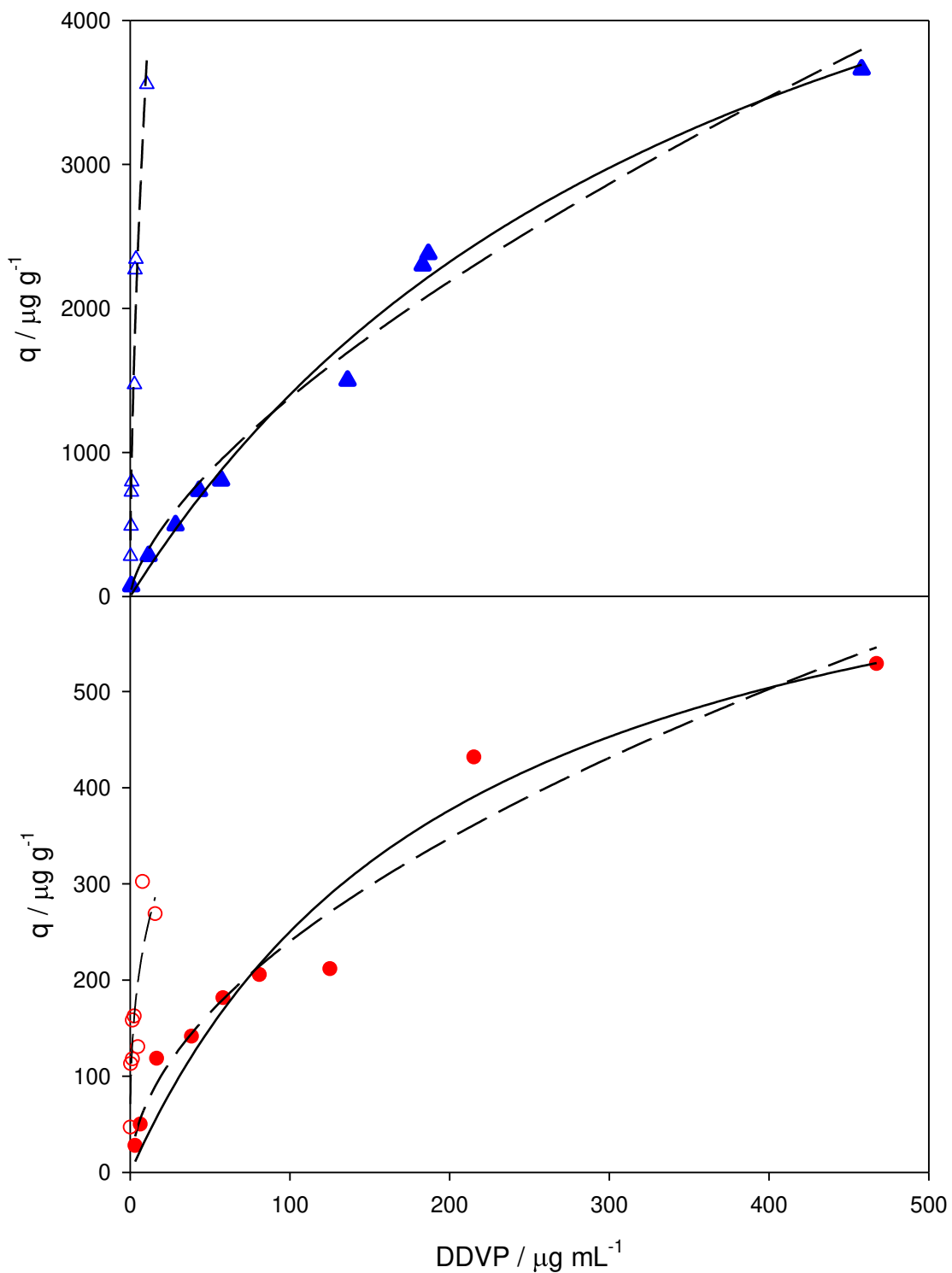
272 indicated that the adsorption followed a PSO mechanism whose rate constants ranging
273 from 6.5 to 15.77 g mg⁻¹ h⁻¹. They attribute these differences to the heterogeneous nature
274 of soil particles and its variable composition [18]. These authors have used linearized
275 equations of PFO and PSO models so the results could have differences inherent to the
276 data processing.

277

278 *3.3 Adsorption/desorption studies*

279 The analysis of partition equilibrium is relevant to discuss the fate and transport of
280 compounds in soils. The isotherms represent the quantity of substance adsorbed onto soil
281 particles as a function of the equilibrium concentration in the bulk solution.
282 Sorption/desorption isotherms of the dichlorvos are presented in Figure 3 for the studied
283 soils where the adjustment to Langmuir and Freundlich models are indicated. Moreover,
284 Table 4 summarizes the adsorption parameters estimated in this work.

285



286

287 **Figure 3.** Relation between the mass of DDVP absorbed in soil versus concentration of
 288 DDVP in the solution for MS (▲), and 9S (●). Fitting lines correspond to Langmuir (full
 289 line), Freundlich (dashed line), and desorption studies (dotted line). Dots are experimental
 290 values (full) adsorption and (empty) desorption.

291 Adsorption data have shown a good agreement with the Freundlich model within the
 292 whole range of DDVP concentrations indicating that the adsorption sites were not fully
 293 occupied (any saturation is observed). Besides, $1/n$ values are lower than the unity in both
 294 soils, suggesting a diminution in the adsorption with increasing initial concentration.
 295 Moreover, there is not a linear relationship between the adsorbed and dissolved DDVP
 296 quantities. The constant values were $90 \mu\text{g}^{(1-1/n)} \text{mL}^{(1/n)} \text{g}^{-1}$ and $21 \mu\text{g}^{(1-1/n)} \text{mL}^{(1/n)} \text{g}^{-1}$ for
 297 MS and 9S, respectively. Differences could be attributed to the soil properties such as pH,
 298 O.C., and clay fraction (Cox et al., 2000). Corrections regarding organic matter content
 299 can be done by dividing K_F by the % of O.C of each soil. Thus, K_{OC} values of $50 \mu\text{g}^{(1-1/n)}$
 300 $\text{mL}^{(1/n)} \text{g}^{-1}$ and $31 \mu\text{g}^{(1-1/n)} \text{mL}^{(1/n)} \text{g}^{-1}$ were obtained were a lower variability between them
 301 is observed.

302

303 **Table 3.** Isotherm model parameters from adsorption and desorption for DDVP in soils
 304 MS and 9S.

305

	Model	Parameter	MS	9S
Adsorption	Langmuir	$Q_0 / \text{mg g}^{-1}$	6.8 ± 0.3	006 ± 0.05
		$K_L / \text{L mg}^{-1}$	0.0043 ± 0.0008	0.005 ± 0.002
		R^2	0.989	0.941
	Freundlich	$1/n^{\text{ads}}$	0.67 ± 0.05	0.53 ± 0.03
		$K_F \mu\text{g}^{(1-1/n)} \text{mL}^{(1/n)} \text{g}^{-1}$	90 ± 22	21 ± 5
		R^2	0.984	0.969

Desorption	Freundlich	$1/n^{\text{des}}$	0.57 ± 0.06	0.31 ± 0.07
		K_F $\mu\text{g}^{(1-1/n)} \text{ mL}^{(1/n)} \text{ g}^{-1}$	1304 ± 120	120 ± 20
		R^2	0.949	0.760
	H		0.9 ± 0.1	0.6 ± 0.1

306

307 Desorption isotherms represent the quantity of DDPV that remains adsorbed per gram of
 308 soil after one desorption cycle as a function of the equilibrium concentration into the
 309 solution. In both cases, there was observed that the quantity of DDVP desorbed was lower
 310 than the total adsorbed. Thus, desorption coefficient values, K_D , were greater than the
 311 adsorption ones suggesting that the desorption process is unfavourable for DDVP on these
 312 soils (a high quantity of DDVP is retained after the desorption cycle).

313 Hysteresis calculated from Eq. 10 is associated with the reversibility of the process,
 314 comparing indirectly the forces involved in both, the adsorption and the desorption [27].
 315 In the present study, similar Freundlich desorption and adsorption coefficients were
 316 determined for MS (0.57 and 0.67, respectively) while for 9S, they were different (0.31
 317 and 0.53) suggesting a non-reversible process. The hysteresis coefficient for these soils
 318 was close to 1 (0.9) in MS, while 9S presented a positive hysteresis. As well, Barriuso et
 319 al. [23] reported a direct relationship between the adsorption constant and the hysteresis
 320 for atrazine adsorbed onto smectite. There, clay samples with low affinity by atrazine
 321 (low K_{ads}) exhibited positive hysteresis, and samples with high affinity showed negative
 322 hysteresis (passing for $H = 1$). These results are according to our findings where for 9S
 323 the K_F and the H-values were minor than the obtained for MS (see table 3).

324 Taking into account only equilibrium data could be inferred that MS and 9S had different
 325 behaviour in connection with the DDVP movement. In fact, for the maxima concentration

326 evaluated in this work, $500 \mu\text{g mL}^{-1}$, 45% is adsorbed and the rest is lixiviated for MS.
327 Moreover, from the adsorbed quantity, only 2.66% is desorbed after the first desorption
328 cycle. Otherwise, for 9S, at the same concentration, 93.6% was lixiviated and the rest
329 remains adsorbed. From this fraction, 50% is desorbed after the first cycle of desorption.
330 Lixiviation implies a risk of leaching to groundwater sources while, in the opposite, the
331 non-reversibility of the adsorption suggests a risk to surface waters by run-off. For
332 evaluating the leaching associated risk, the groundwater ubiquitous score (GUS) values
333 are normally used in the literature [28]. They are determined by the lifetime of pesticides
334 and the adsorption constant in the soil; however, any consideration is done regarding
335 equilibrium time and desorption constants or column results. For DDVP, a reported value
336 of 0.69 indicates that this compound has a low lixiviation potential [12]. However, in the
337 present article, it was demonstrated that the equilibrium time required is close to 24 hours
338 to reach the maxima adsorption. This issue is not usually considered in the leaching index
339 calculus; however, it could be underestimating the lixiviation risk for DDVP.

340

341 *3.4 Columns displacements assays*

342 The movement of pesticides through a soil column is due to convection, diffusion, and
343 mechanic dispersion processes. The differential equation to describe the movement
344 convective -dispersive of an adsorbed solute in a saturated soil under steady-state water
345 flow conditions is as follow [29]:

346

$$347 \quad R(C) \frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial x^2} - v_0 \frac{\partial C}{\partial x} \quad (12)$$

348

349 where t is time, x is soil depth, D_h is the hydrodynamic dispersion coefficient, v_0 is the
350 pore water velocity, C is the solution concentration, and $R(C)$ is the retardation factor.

351 When the adsorption reactions are instantaneous, the equilibrium state relates the
352 solution-phase and adsorbed-phase concentrations through the isotherm adsorption, and
353 then the retardation can be expressed as:

354

$$355 \quad R(C) = \left[1 + \frac{\rho K(1/n)C^{(1/n)-1}}{\theta} \right] \quad (13)$$

356

357 where ρ is the soil bulk density and θ is the volumetric soil-water content.

358

359 For non-adsorbed solutes, the adsorption coefficient is equal to zero and R becomes one.

360 Otherwise, for adsorbed solutes, $R(C)$ is greater than one, which means: solute moves slower than the
361 solvent front (retardation). Thus, larger values of $R(C)$ indicate that the mobility is
362 reduced along the soil column. Moreover, when the adsorbed and dissolved
363 concentrations relationship is not linear, ($1/n \neq 1$), this retardation is also a function of the
364 initial concentration in the inlet flow.

365 However, if the adsorption does not take place instantly, a non-equilibrium condition is
366 presented due to processes of chemical and physical nature (Rao et al., 1979). The first
367 group considers that the limiting step rate is the reaction between the solute and the
368 surface at the interphase. The second one implies that the adsorption takes place quickly,
369 but the diffusion of the solution is the slow step. The degree of non-equilibrium is related
370 to the adsorption kinetic rate constant, k , and the residence time in the column, t_r :

371

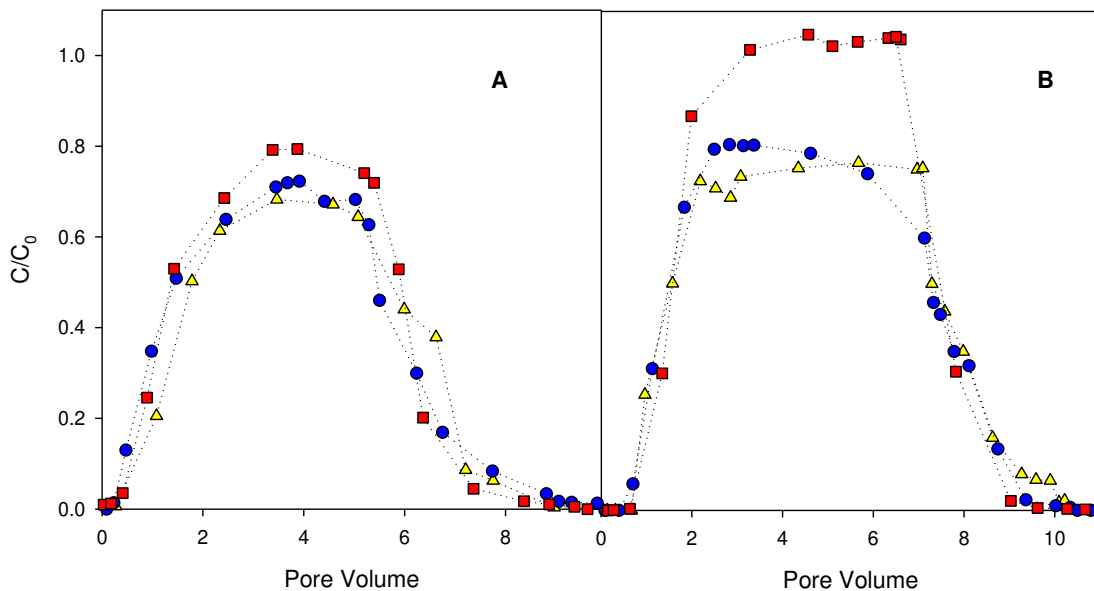
$$372 \quad \omega = k * t_r \quad (14)$$

373

374 In our experiments, this value was around 0.035 – 0.03 that is minor to the minimum
375 value to assess equilibrium conditions into the column ($\omega \geq 5$) [30]. In this context, it is

376 expected that an eluted profile shows both effects, retardation (due to adsorption
377 processes) and tailing at higher pore volumes (due to non-equilibrium adsorption
378 conditions). Moreover, equilibrium conditions would be achieved under retention time
379 greater than 71 h, which means an equilibrium column volume around 140 times greater
380 than column volumes used in our experiments. MS and 9J soil samples correspond to the
381 first soil layer (5-20 cm deep), so in field conditions, such equilibrium column volume
382 will not be composed by the same soil layer instead of deeper horizons with different soil
383 properties.

384 In this work, breakthrough curves were obtained for three DDVP concentrations (1, 5, and
385 $50 \mu\text{g ml}^{-1}$) using MS and 9S soil columns and maintaining constant the operation
386 conditions (see Figure 4 A and B). The breakthrough curves were asymmetrical in shape
387 suggesting that physical non-equilibrium processes were presented (in connection with
388 the calculated non-equilibrium degree index).



389
390 **Figure 4.** Breakthrough curves for DDVP at \blacktriangle 1 mg L^{-1} \bullet 5 mg L^{-1} and \blacksquare 50 mg L^{-1} for
391 A) Mercedes soil, B) 9 de Julio soil.

392 Additionally, the pore volume needed to obtain the maximum value of C/C_0 was around
393 3.8 and 2.5 - 3.0 for Mercedes and 9 de Julio soils, respectively. This result suggests
394 retardation in the DDVP movement [31]. Furthermore, the mobility in 9S soil is around
395 1.25 times higher than in MS that is according to the previous results presented in Table
396 3 where stronger adsorption is estimated for MS.

397 Moreover, from Figure 4A, it is observed a very short shift of BTC at 1 mg L^{-1} of DDVP.
398 Despite that, for C_0 of 5 and $50 \text{ } \mu\text{g mL}^{-1}$, the retardation effect does not seem to be a
399 function of the initial concentration. Similarly, for the sandy loam soil, 9S, no differences
400 were found between the BTC curves at the three DDVP concentrations. It is a surprising
401 result considering the previous finding regarding batch experiments showing a non-linear
402 adsorption isotherm ($1/n < 1$ in both soils, see Table 3). However, the short-range of
403 studied concentrations could be also responsible. Both soils shown a tailing at large pore
404 volumes, where the tailing observed for MS is around 1.6 more times bigger than the 9S
405 one. Tailing effects were previously related to non-equilibrium adsorption processes and
406 hysteresis effects [32]. The large time needed to reach the equilibrium condition (around
407 24 hours) makes that the time of residence is not enough to complete the adsorption
408 processes due to kinetics aspects.

409

410 **4. Conclusions**

411 Adsorption assays of DDVP onto agricultural soils have great relevance to discuss the
412 transport and environmental fate of plaguicides in agroecosystems. In this work, the
413 studies were conducted on soils belonging to Buenos Aires province (Pampa Plain).
414 Experimental adsorption data were adjusted satisfactorily to the Freundlich model being
415 MS around five times more retentive than 9J at an equilibrium stage. Moreover, from
416 desorption analysis, it was observed that the same tendency being MS eleven times more

417 retentive than 9S after a desorption cycle. Even so, DDVP adsorption was characterized
418 as a reversible process in MS but non-reversible in 9S. Regarding kinetic assays, it was
419 indicated that both soils followed the kinetics of PSO whose constants were very similar.
420 More important, it was also observed that the equilibrium state was achieved after 30
421 hours of the time of contact. In this context, column studies were necessary to explain the
422 DDVP movement in agricultural soils. Breakthrough curves indicated that DDVP
423 mobility is high in both soils being only 1.25 times faster in 9S. The eluted profile showed
424 tailing effects associated with the hysteresis and non-linear adsorption isotherms as would
425 be expected. This evidence suggests the importance of considering column studies to
426 assess the fate of contaminants in environmental matrixes. Thus, predictions based only
427 on the batch adsorption studies could underestimate the lixiviation processes.

428 In conclusion, DDVP had shown a high mobility through soil columns as was predicted by
429 the batch kinetics studies. This mobility was independent of the textural characteristics of
430 the soils studied. From these results can be stated that the principal issue to assess DDVP
431 mobility in soils is the kinetics analysis from batch and column experimental designs.

432

433 **Declarations**

434 **Availability of data and materials**

435 All data generated or analyzed during this study are available upon request.

436 **Competing interests**

437 The authors declare they have no competing interests.

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442

443 **Authors' contributions**

444 NJ Bustos carry out the experiments, processed the information, and collaborated on the
445 manuscript redaction; D. Grassi participated in the data discussion; A. Fernández Cirelli
446 supplied the necessary materials and laboratory facilities to carry out the experiments. A.
447 Iriel was responsible for the experimental design, and the redaction of this manuscript.
448 All authors read and approved the final manuscript.

449

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454

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Figures

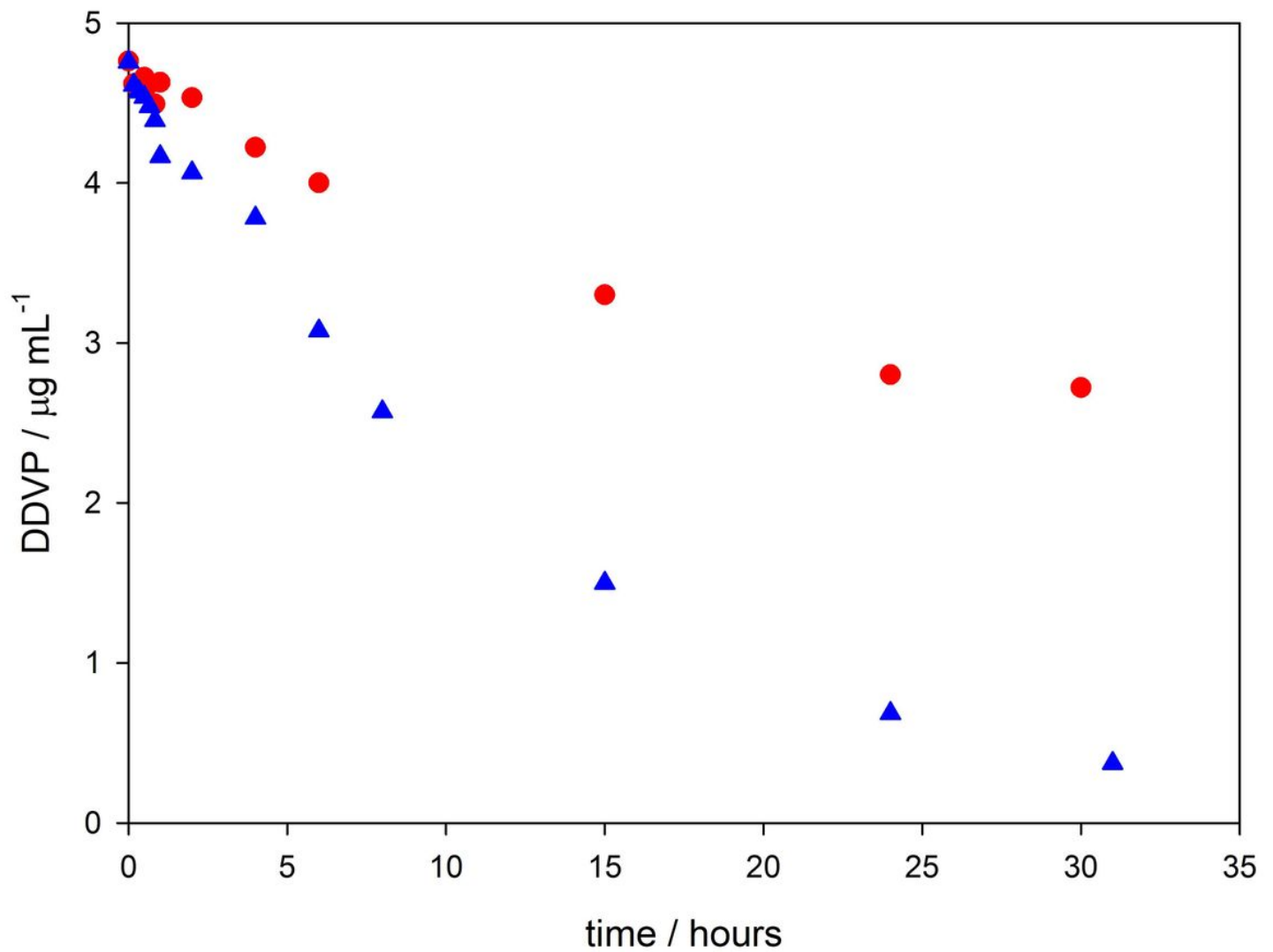


Figure 1

DDVP concentration as a function of contact time MS (●) and 9S (▲) soils. Initial DDVP concentration: 5 µg mL⁻¹, soil dosage: 6 g L⁻¹.

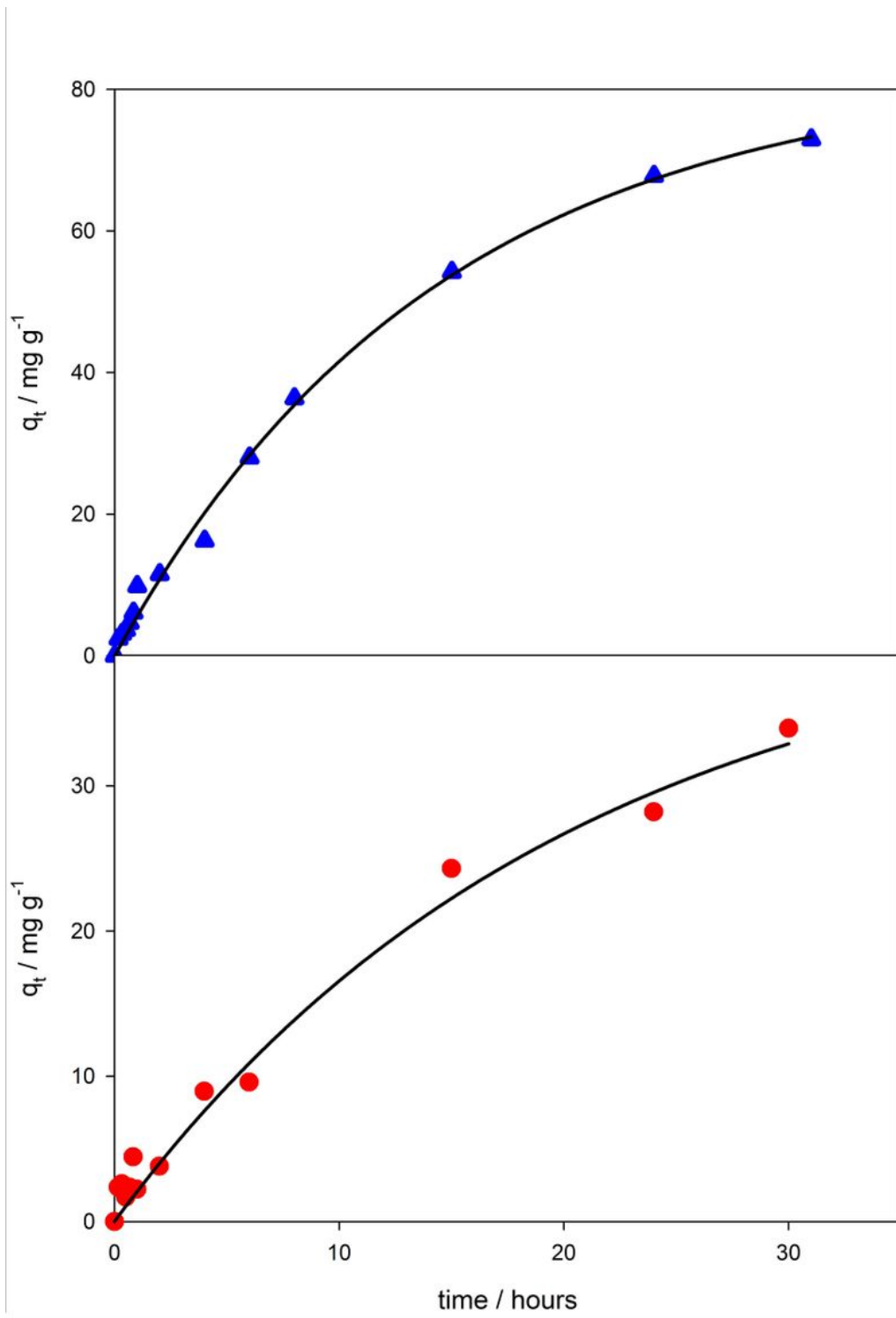


Figure 2

Fitting of experimental data of DDPV adsorption on soils MS (☒) and 9S (☒) to the PFO model (full line).

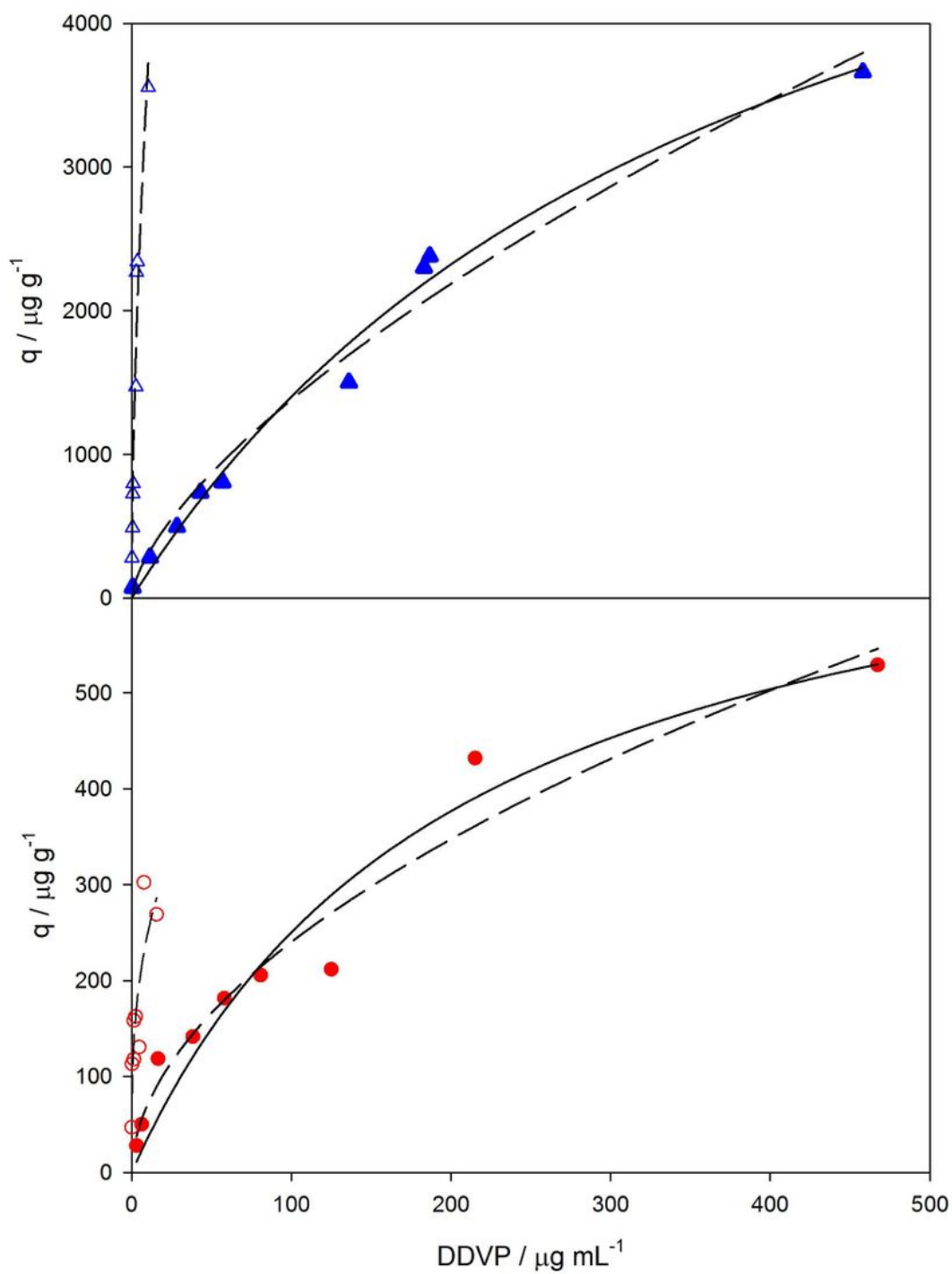


Figure 3

Relation between the mass of DDVP absorbed in soil versus concentration of DDVP in the solution for MS (☒), and 9S (☒). Fitting lines correspond to Langmuir (full line), Freundlich (dashed line), and desorption studies (dotted line). Dots are experimental values (full) adsorption and (empty) desorption.

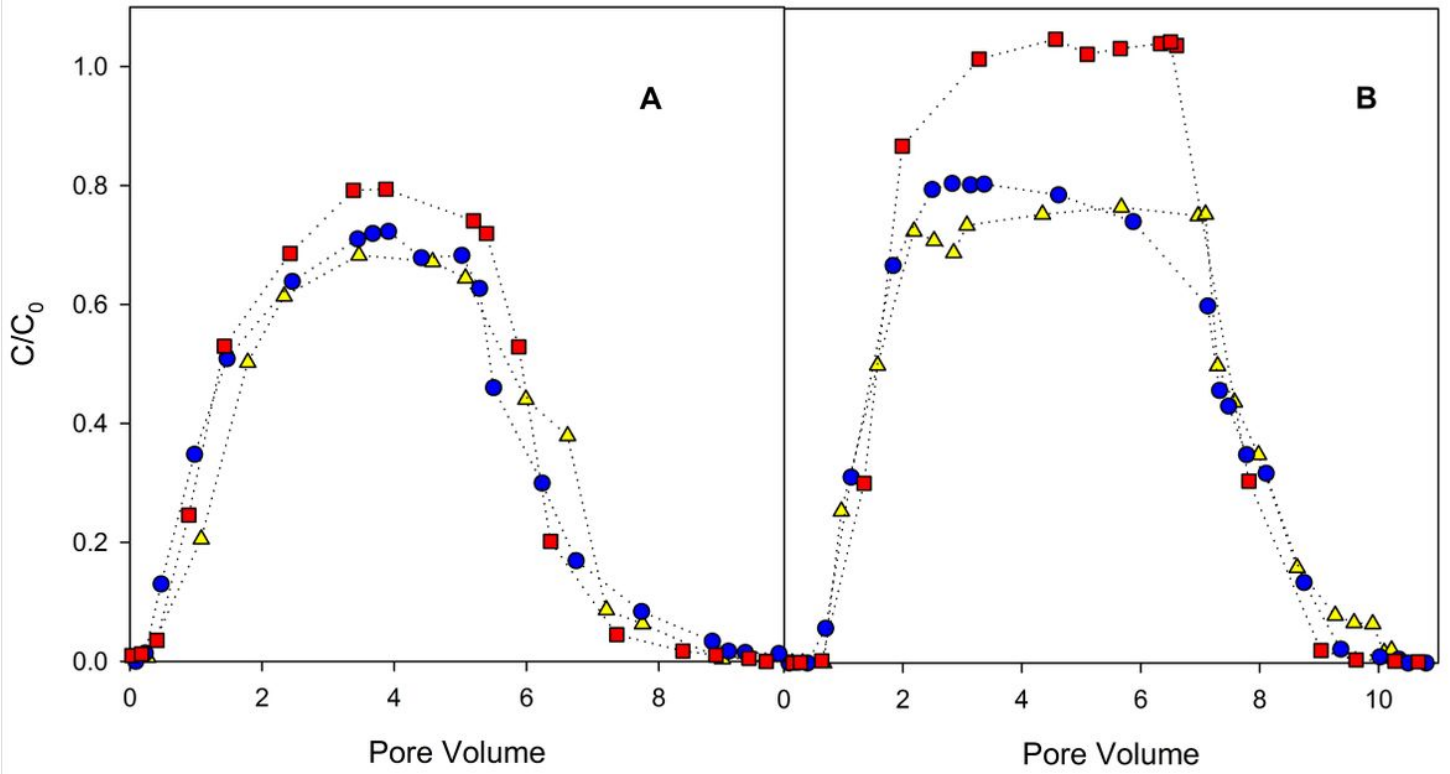


Figure 4

Breakthrough curves for DDVP at 1 mg L⁻¹, 5 mg L⁻¹ and 50 mg L⁻¹ for A) Mercedes soil, B) 9 de Julio soil.