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# Natural clay and biopolymer-based nanopesticides to control the environmental spread of a soluble herbicide

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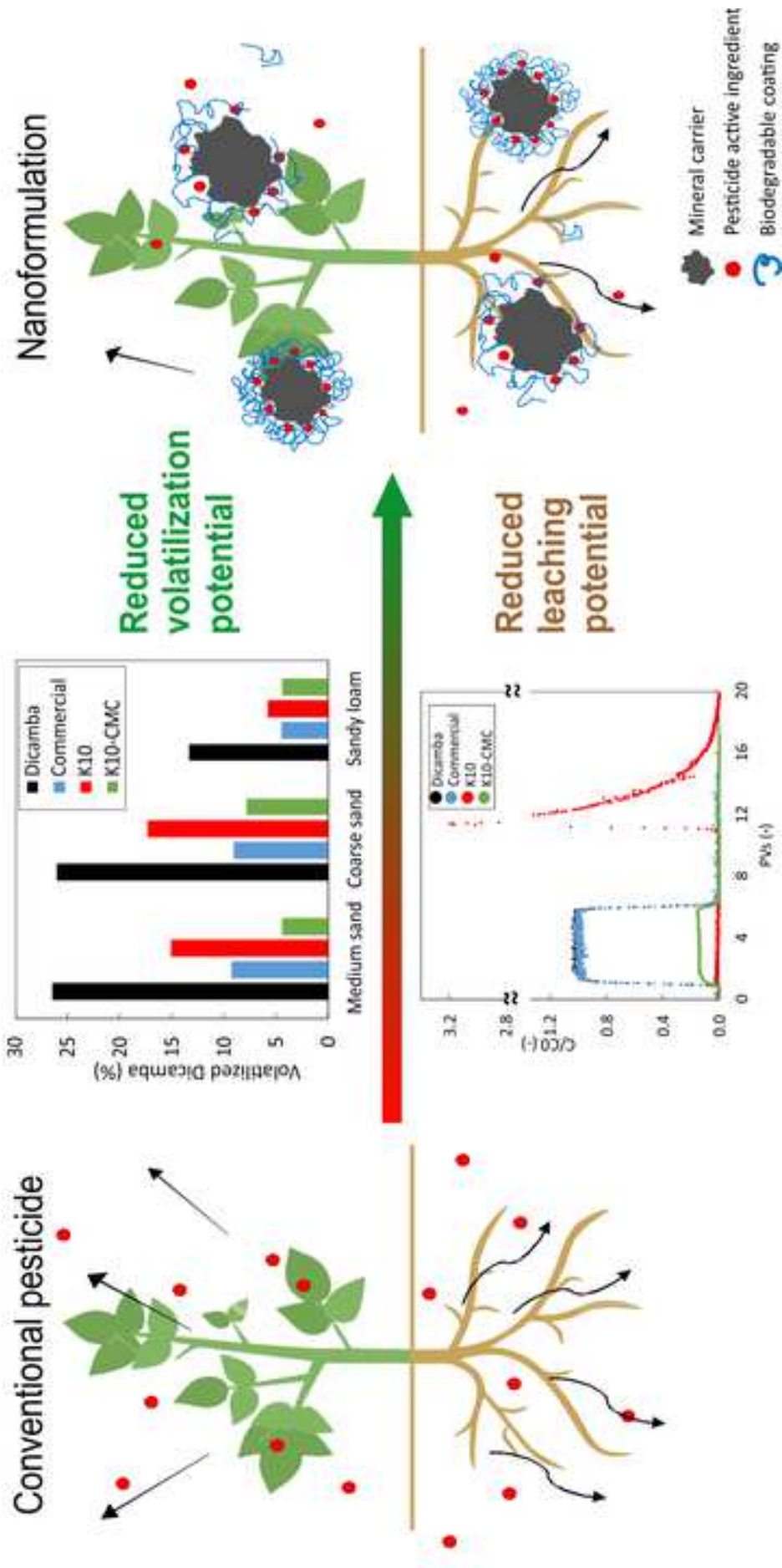
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Science of the Total Environment***

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## Highlights

natural clay and food-grade biopolymer are used in a novel nanopesticide formulation

natural clays showed effective in reduce environmental drawbacks of agrochemicals

the nanoformulation effectively encapsulated dicamba and controlled its release

the nanoformulation significantly reduced dicamba mobility in porous media

the herbicidal efficacy of dicamba was not hindered by the nanoformulation

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# Natural clay and biopolymer-based nanopesticides to control the environmental spread of a soluble herbicide

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20 **Abstract**

21 Pesticides are essential in maintaining high crop yields. Their massive use is often associated to health and  
22 ecological drawbacks particularly noticeable for soluble and volatile pesticides, which are prone to significant  
23 dispersion in the environment. In this work a novel nano-formulation is proposed to control leaching and  
24 volatilization of a broadly used herbicide, dicamba. Dicamba is subject to significant leaching in soils, due to  
25 its marked solubility, and to significant volatilization and vapor drift, with consequent risks for operators and  
26 neighbour crops. Natural, biocompatible, low-cost materials were employed to control its dispersion in the  
27 environment: a nanosized natural clay (namely, K10 montmorillonite) was selected as a carrier to adsorb the  
28 pesticide, and carboxymethyl cellulose, a food-grade biodegradable polymer, was employed as a coating  
29 agent to control herbicide release. The synthesis approach is based on direct adsorption at ambient  
30 temperature and pressure, with a subsequent particle coating to increase suspensions stability and control  
31 pesticide release. The nano-formulation showed a controlled release when diluted to field-relevant  
32 concentrations, a volatilization comparable with commercially formulated products and a markedly reduced  
33 mobility in the porous medium compared to a commercial competitor.

34

35 **Keywords**

36 Nanopesticides, dicamba, controlled pesticide leaching, nanocarrier, natural clays

37

38 **Highlights**

39 natural clay and food-grade biopolymer are used in a novel nanopesticide formulation

40 natural clays showed effective in reduce environmental drawbacks of agrochemicals

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42 the nanoformulation significantly reduced dicamba mobility in porous media

43 the herbicidal efficacy of dicamba was not hindered by the nanoformulation

## 44 1. INTRODUCTION

45 The use of agrochemicals, including pesticides and fertilizers, is unavoidable for the optimization of crop  
46 production, but has numerous drawbacks on both human health and the environment (Damalas and  
47 Eleftherohorinos, 2011). Several products have toxic effects on aquatic life and beneficial insects, and a  
48 growing number of plant protection products have been found or suspected to be toxic or carcinogenic to  
49 humans. Herbicides are particularly relevant in this sense, being the agrochemicals most frequently found in  
50 superficial waters and groundwater. Many compounds have been banned from the list of authorized  
51 pesticides in most countries, and others are currently under evaluation. In Europe, the Regulation (EC)  
52 1107/2009 has established a periodic assessment to renew the approval of active substances contained in  
53 pesticides to ensure that they continue to fulfill defined environmental and eco-toxicological criteria. In June  
54 2021, only 463 out of 1454 substances that could be potentially included in pesticides (either as active  
55 substances, safeners or synergists) were regularly approved, while 61 are still under evaluation (European  
56 Commission, 2021).

57 The persistency, hydrophilicity, volatility and more in general the affinity of the individual substance to the  
58 different environmental matrices and components ultimately control their preferred migration routes and  
59 accumulation compartments, and consequently their long-term fate and associated potential risks for human  
60 health and ecological receptors. Poorly biodegradable substances tend to progressively accumulate in deep  
61 soil, sediments and groundwater, where they remain unaltered for years or even decades (Arias-Estévez et  
62 al., 2008; Wauchope, 1978). Consequently, pesticides prohibited several years ago still represent a significant  
63 threat for health and environment: as an example, about 7% of groundwater measurement stations in EU  
64 reported values exceeding the Environmental Quality Standards (EQS) levels in 2010 - 2011 for at least one  
65 agrochemical (Cyclodiene-group and Endosulfan) (EUROSTAT, November 2017; Lapworth et al., 2006),  
66 whereas at least one pesticidal compound was found in 83% of top soil samples collected across Europe (Silva  
67 et al., 2019).

68 Highly soluble compounds show a prominent infiltration potential with rain and irrigation (and consequently  
69 transport and accumulation in deep soil and groundwater is the preferred migration route), while volatile  
70 compounds are prone to significant dispersion in the atmosphere. It has been reported that 10% to 75% of  
71 the applied pesticides do not reach the target pest species (Aktar et al., 2009; Pimentel, 2009) and the unused  
72 product can therefore migrate towards non-target crops, insects and ultimately spread in the environment  
73 (Boutin et al., 2014; Sanchez-Bayo and Goka, 2014; van den Berg et al., 1999).

74 The major routes available to reduce the environmental impact of pesticides include the development of  
75 more efficient crop management strategies (Bongiovanni and Lowenberg-Deboer, 2004; Reichenberger et  
76 al., 2007), the identification of new, less toxic and less persistent substances with pesticidal effects (Dayan et  
77 al., 2009; Lamberth et al., 2013), and the development of new formulations of existing active ingredients  
78 (AIs) (Iavicoli et al., 2017; Sopeña et al., 2009). Nanotechnology can play an important role in finding new  
79 pesticide formulations with reduced toxicity and environmental impacts (Moulick et al., 2020; Servin et al.,  
80 2015; Worrall et al., 2018), even though research is still needed to verify several aspects of the actual efficacy  
81 and convenience of nano-formulated pesticides, particularly at the field scale (Gomes et al., 2019; Kah et al.,  
82 2018a; Singh et al., 2021; Usman et al., 2020). Nanopesticides consist of nanoparticles (NPs), usually referred  
83 to as nanocarriers, containing an active ingredient dispersed in a colloidal suspension. Nanopesticides are  
84 formulated with different objectives (Adisa et al., 2019; Kah et al., 2019; Kah et al., 2018b): to promote the  
85 use of AIs that are less harmful toward non-target organisms, but whose premature degradation may need  
86 to be hindered; to optimize pest targeting; to reduce the overall amount of employed chemical substances  
87 by improving the delivery of poorly soluble AIs, or conversely by controlling and retarding the release of  
88 soluble AIs. Two main types of nano-formulations are currently used: (1) NPs that act as pesticides  
89 themselves and (2) NPs that act as a carrier for AIs with pesticidal effects, adsorbed or immobilized on them  
90 using different techniques. With respect to this second class, both organic and inorganic formulations were  
91 developed. In the last few years, organic formulations, such as nanocapsules, nano- and microemulsions, and  
92 NPs with the AI incorporated in a polymeric matrix have become the most popular (Kah and Hofmann, 2014;  
93 Kah et al., 2018a).



94 In this work a nano-to-micro-formulation, aimed at reducing environmental spreading of a highly soluble and  
95 moderately volatile herbicide, namely dicamba (3,6 dichloro-2 methoxy benzoic acid), was developed.  
96 Dicamba is an auxin-like herbicide, registered in 1967, applied in post-emergence to control annual and  
97 perennial broadleaf weeds in non-agricultural settings, lawn and turf and in different crops, such as wheat,  
98 barley, corn, oats, millet, sorghum, and asparagus (Behrens et al., 2007). The principal metabolite is 3,6-  
99 dichlorosalicylic acid (DCSA), which showed moderate persistence and medium to slight mobility in the soil.  
100 Dicamba has been established to be toxic to aquatic organisms and its metabolite was defined as harmful  
101 (Authority, 2011). Because of its high efficacy, relative inexpensiveness, relative environmental safety and  
102 low risk for weeds to develop resistance, it is used worldwide. Dicamba, as well as other auxinic herbicides,  
103 is characterized by a high solubility, in the order of 6 to 8 g/l at ambient conditions, resulting in significant  
104 infiltration and consequent mobility in soil and subsoil (Oliveira Jr et al., 2001; Sakaliene et al., 2007) and  
105 relatively high volatility, with consequent drift problems and potential risks for users (Ding et al., 2019; Egan  
106 and Mortensen, 2012).

107 Natural materials were tested in this study for the development of the nano-formulation, namely mineral  
108 carriers (montmorillonite clays and a zeolite), and carboxymethyl cellulose (CMC) as a coating agent to  
109 minimize the loss of herbicide and modulate its release over time. It is known that mineral particulate matters  
110 such as silica and clay have a good affinity with a broad set of polar or ionizable pesticides, and have been  
111 successfully proposed as carriers in the development of nano-formulations. In most cases, natural particles  
112 are chemically modified to improve their affinity to the pesticidal molecule, such as in the case of organoclays  
113 (Cabrera et al., 2016; Cornejo et al., 2008; Hermosin et al., 2001). Synthetic hollow silica particles have also  
114 been successfully employed (Bueno and Ghoshal, 2020; Gao et al., 2020; Nuruzzaman et al., 2020). Less  
115 frequently, unmodified mineral particles have been directly used, e.g. montmorillonite for hexazinone (Celis  
116 et al., 2002), simazine and 2,4-D (Cox et al., 2000). The latter approach, even if often slightly less performing  
117 in term of loading capacity, was preferred in this work due to its higher sustainability and environmental  
118 compatibility, easier implementation and reduced cost.

119 Polymers, and in particular biopolymers, are currently used in the form of capsules (Petosa et al., 2017),  
120 polymeric microbeads and as a coating of solid carriers to control the release of encapsulated pesticides and  
121 fertilizers (Joshi et al., 2020; Shasha et al., 1976), protect labile compounds (Elhaj Baddar et al., 2020), and  
122 prevent excessive volatilization (Azeem et al., 2014; Dimkpa et al., 2020). Alginate is by far the most applied  
123 biopolymer (Kenawy and Sakran, 1996), even though carboxymethyl cellulose (Kök et al., 1999), lignin (Behin  
124 and Sadeghi, 2016), starches (da Costa et al., 2019), bio-based plastics (Riggi et al., 2011) and others have  
125 been employed.

126 In this work the efficacy and efficiency of four different natural mineral carriers, namely two Na-  
127 montmorillonites, a Ca-montmorillonite and a zeolite, as well as the opportunity of using a bio-polymeric  
128 coating to control the dicamba release were evaluated through different tests. The best performing  
129 formulation was identified based on a balance between technical constraints and potential environmental  
130 effects. The ideal nano-formulation should be the one showing the highest loading capacity (evaluated in  
131 terms of mass of dicamba adsorbed per mass of carrier), the highest colloidal stability in a broad range of  
132 hydrochemical conditions (to guarantee that the formulation can be diluted in water, usually tap water in  
133 real-scale applications without an abrupt aggregation and/or sedimentation of the carriers, which would  
134 hinder its use), the lowest release of dicamba after dilution, the lowest loss of dicamba due to volatilization  
135 (which represents one of the main environmental problems of this AI), the lowest mobility in the porous  
136 medium (thus limiting as much as possible the potential spreading of dicamba, if infiltrated with rain or  
137 intense irrigation), and obviously the most efficient in controlling weeds. Clearly not all these aspects –  
138 sometimes contrasting – can be maximized, and the optimal nano-formulation was identified as the most  
139 reasonable compromise.

140

## 141 2. MATERIALS AND METHODS

### 142 2.1. Materials

143 Four carriers, all provided in the form of dry powders, were tested: a K10 Na-montmorillonite (Sigma Aldrich,  
144 labelled K10 in the following), a generic Na-montmorillonite (Indigo Herbs, UK, labelled Na-M2), a Ca-  
145 montmorillonite (PraNaturals, UK, labelled Ca-M), and a zeolite (NaturaForte, Germany, labelled ZEO). A  
146 food-grade, low-molecular-weight carboxymethyl cellulose (WALOCCEL® CRT30GA, Dow Chemical Company  
147 Ltd, US, labelled CMC) was tested as carrier coating.

148 Structure, shape and elemental composition of the carriers were investigated using SEM-EDS microscopy  
149 (JEOL, Japan) directly on the dry powders. The carrier particle size was determined using a disk centrifuge  
150 (DC24000 UHR, CPS, US). To this aim, the samples were dispersed in deionized water (DIw), allowed to  
151 hydrate, sonicated for 25 minutes prior measurement and analysed at a disc rate of 3000 rpm in the range  
152 70-0.1 microns. The zeta potential of the four carriers dispersed in DIw (following the same preparation  
153 protocol) with addition of NaCl (1 mM to 100 mM) or CaCl<sub>2</sub> (0 to 1 mM) were determined with electrophoretic  
154 measurements using dynamic light scattering DLS (Zetasizer Nano ZSP, Malvern Instrument, UK).

155 Dicamba was provided by Alfa Chemistry (US). A commercial herbicide (Mondak 21 S, Syngenta, Italy)  
156 containing dicamba (not nano-formulated) at a nominal concentration of 243.8 g/l was used as a comparison  
157 in volatilization, transport and efficacy tests.

158 The tap water (TAPw) used for release and transport tests was drawn from the municipal water supply  
159 network and chemically analysed for salts, pH, EC and TDS (data reported in Supporting Information, Table  
160 S1).

161 A medium silica sand (Dorsilit 8, Dorfner, Germany;  $d_{10}$ ,  $d_{50}$  and  $d_{90}$  equal respectively to 0.415, 0.45 and 0.5  
162 mm), was used for volatilization and column transport tests. A coarse sand (Dorsilit 5G, Dorfner, Germany;  
163  $d_{10}$ ,  $d_{50}$  and  $d_{90}$  equal respectively to 1.12, 1.58 and 1.9 mm) and a sandy loam soil (collected at DISAFA -  
164 University of Torino,  $d_{10}$ ,  $d_{50}$  and  $d_{90}$  equal respectively to 0.04, 0.065 and 0.148 mm) were used for

165 volatilization tests. For all sands, the granulometric curve (data reported in Supporting Information, Figure  
166 S1) was determined via dry sieving, while real soil undergo to wet sieving.

167

## 168 2.2.Methods

### 169 2.2.1. Nanopesticide preparation

170 The carriers were loaded with dicamba using direct adsorption. Briefly, the carrier was dispersed in a dicamba  
171 solution (in the range 0.125 g/L to 7 g/L). The suspensions were continuously mixed with a magnetic stirrer  
172 in a closed vessel with reduced headspace to minimize volatilization. Contact times of 24 h and 2 h were  
173 used. After loading, the suspensions were centrifuged and the precipitate was collected and stored as stock  
174 nano-formulation.

175 Adsorption isotherms were determined for all tested carriers and loading conditions. After centrifugation,  
176 the supernatant was filtered with a 0.45 micron syringe PTFE filter (Thermo Fisher Scientific, Waltham, USA)  
177 and the dicamba concentration in the supernatant ( $C_{w,eq}$  [ $M L^{-3}$ ]) was evaluated via Uv-vis spectrophotometry  
178 (Specord S600, Analytik Jena, Germany) at a wavelength of 280.5 nm (the calibration curve is provided in  
179 Supporting Information, Figure S2). The adsorbed concentration, or adsorption capacity, expressed as  
180 dicamba mass adsorbed per unit mass of carrier,  $C_{s,eq}$  [ $M M^{-1}$ ], was determined from  $C_{w,eq}$  measurements via  
181 mass balance.

182 In case of polymer-coated formulations, the CMC was added to the batch to reach a final polymer  
183 concentration of 0.5 g/l. Polymer adsorption onto the loaded carrier was promoted via stirring for 2h.

184

## 185 2.2.2. Release tests

186 Release tests were conducted on all uncoated nano-formulations and on selected coated ones. All tested  
187 stock samples were obtained via loading of the carrier in a 7 g/L dicamba solution and with a contact time of  
188 24 h, following the procedure described above.

189 The stock nano-formulation was dispersed in DIw or TAPw, depending on the tested condition, at a  
190 concentration of 5 g/L (1g of nano-formulation in 200 ml). The suspension was maintained in agitation with  
191 a magnetic stirrer at 200 rpm in a beaker sealed with parafilm, with reduced headspace to minimize  
192 volatilization, for at least 6 hours. Selected tests were prolonged to 30 h. A sample was periodically collected,  
193 filtered with a PTFE syringe filter to remove the carrier and analysed via spectrophotometry to determine  
194 the concentration of dicamba released from the nano-formulation.

195 The fraction of herbicide retained on the carrier at a given time,  $R(t)$ , was evaluated as:

$$196 R(t) = 1 - \frac{C_w(t) \cdot V_w(t)}{C_{s,eq} \cdot M_{s,c}} \quad (\text{eq. 1})$$

197 where  $C_w(t)$  is the dicamba concentration measured in the water sample collected at time  $t$  [ $M L^{-3}$ ],  $V_w(t)$  is  
198 the dispersion volume at time  $t$  [ $L^3$ ],  $C_{s,eq}$  is the adsorbed concentration at the beginning of the test, and  $M_{s,c}$   
199 is the dry mass of carrier present in the system at the beginning of the test [ $M$ ].

200

## 201 2.2.3. Volatilization tests

202 Volatilization tests were performed for uncoated and CMC-coated K10 nano-formulations (labelled  
203 respectively K10 and K10-CMC) and compared with a pure dicamba solution and with the commercial  
204 product. All samples were diluted in DIw in order to reach the same concentration of the AI (3 g/l).

205 In pre-screening tests, direct volatilization from the solution/suspension was assessed. Each sample was  
206 exposed to ambient air on a petri dish (Mueller, 2015; Strachan et al., 2010), which was periodically weighted  
207 for 30 hours. Tests were run at least in duplicate, at ambient temperature. After 30 hours the remaining mass

208 of dicamba was determined via solvent extraction method: acetonitrile and water at a mass ratio of 7:3 were  
209 added and kept in agitation for 24h in a closed vial with minimal headspace; the solution/suspension was  
210 then filtered using a PTFE syringe filter and analysed with UV-vis spectrophotometry. Two blank sets of tests  
211 containing only K10 and one with only water were run to check possible releases from sand and carriers that  
212 may interfere with the UV-vis analysis (no interference was observed).

213 Volatilization from dicamba-sprayed soil was then assessed in a second set of tests. The coarse and medium  
214 sands and the sandy loam soil were air-dried; the soil was sieved to remove particles and conglomerates  
215 larger than 2mm. 15 g of soils were added to each petri dish, sprayed and treated similarly to the pre-  
216 screening tests. Blank tests that included soil only (no spray), soil sprayed with water only and soil sprayed  
217 with K10 suspension (no dicamba) were run in parallel.

218

#### 219 2.2.4. Column transport tests

220 Column transport tests in saturated conditions, aimed at mimicking carrier and pesticide transport in  
221 groundwater, were performed for K10 without pesticide loading (with or without polymeric coating),  
222 pesticide-loaded K10 (with or without coating), pure dicamba solution and the commercial product. Pre-  
223 screening tests with carrier only (with and without coating) were also run.

224 A Plexiglas column with adjustable ends and internal diameter of 1.6 cm was wet-packed with 36.5 g of  
225 Dorsilit 8 sand to an average length of 11.61 ( $\pm 0.15$ ) cm. The sand was hydrated and degassed prior packing  
226 to remove residual air microbubbles. A polypropylene filter with 120  $\mu\text{m}$  mesh was placed at the top and  
227 bottom of the column to avoid sand from entering inlet and outlet tubing. The solutions/suspensions were  
228 injected in saturated conditions with a peristaltic pump (ISMATEC REGLO Analog MS-4/8, Cole-Parmer,  
229 Germany) at a constant flow rate of  $1.46 \cdot 10^{-8} \text{ m}^3/\text{s}$ , corresponding to a Darcy velocity of  $7.26 \cdot 10^{-5} \text{ m/s}$ . Inflow  
230 and outflow concentration of solutes and suspensions was monitored via optical density measurements using  
231 the UV-vis spectrophotometer equipped with from-through quartz cells with 5 mm lightpath (Hellma,

232 Germany). Monitoring wavelengths of 198.5 nm, 280.5 nm and 350 nm were adopted for NaCl, dicamba and  
233 carriers, respectively (calibration curves in Supporting Information, Figures S2 and S3). For tests involving the  
234 nano-formulations, outflow samples were also manually collected, filtered and analysed to reconstruct the  
235 breakthrough curve of free dicamba.

236 The nano-formulations were injected at a carrier concentration of 0.9 g/l, corresponding to a dicamba  
237 concentration of approximately 50 mg/l (the actual concentration slightly varied based on the specific tested  
238 formulation). This concentration corresponds to approximately 10% of the typical recommended  
239 concentration for dicamba-based products when applied on weeds: after field applications the most  
240 commonly detected dicamba concentration in leaching water is 3% to 10% of the applied one (Sakaliene et  
241 al., 2007; Tindall and Vencill, 1995), and consequently the most severe expected scenario for groundwater  
242 contamination was adopted.

243 Preliminary transport tests of K10 alone (without dicamba loading), with and without CMC coating, followed  
244 this protocol:

- 245 1. Pre-equilibration with DIw for at least 5 pore volumes (PVs)
- 246 2. Tracer injection (NaCl 30 mM) for 5 PVs
- 247 3. Flushing with DIw for 5 PVs
- 248 4. Injection of K10 dispersed in DIw for 5 PVs
- 249 5. Post-flushing with DIw for at least 5 PVs

250 The injection protocol for pesticide transport tests (including dicamba solution, nano-formulations and  
251 commercial herbicide) included the following steps:

- 252 1. Pre-equilibration with DIw for at least 5 PVs
- 253 2. Pre-flushing with background electrolyte solution (NaCl 30 mM) or TAPw (depending on the specific  
254 test) for 5 PVs
- 255 3. Injection of the dicamba solution/nano-formulation (dispersed in NaCl 30 mM solution or in TAPw)  
256 for 5 PVs

257 4. Post-flushing with NaCl 30 mM solution or TAPw for 5 PVs

258 5. Second post-flushing with DIw for at least 5 PVs

259 The porosity and the dispersivity coefficient of the sand-packed columns were determined for each transport  
260 tests by least-squares fitting the NaCl breakthrough curve (i.e. steps 1 and 2 of the injection protocols) to the  
261 classic advection-dispersion partial differential equation for conservative solutes:

$$262 \quad \varepsilon \frac{\partial C_t}{\partial t} = -q \frac{\partial C_t}{\partial x} + \alpha_x \frac{\partial^2 C_t}{\partial x^2} \quad (\text{eq. 2})$$

263 where  $C_t$  is the tracer concentration [ $M L^{-3}$ ],  $q$  is Darcy velocity [ $L T^{-1}$ ],  $\varepsilon$  is the effective porosity [-] and  $\alpha_x$  is  
264 the dispersivity coefficient [L] of the porous medium.

265 The transport of the carriers was modelled using the modified advection-dispersion-deposition equation  
266 usually adopted to describe colloid transport in saturated porous media:

$$267 \quad \begin{cases} \varepsilon \frac{\partial C}{\partial t} - \sum_i \rho_b \frac{\partial S_i}{\partial t} = -q \frac{\partial C}{\partial x} + \alpha_x \frac{\partial^2 C}{\partial x^2} \\ \rho_b \frac{\partial S_i}{\partial t} = \varepsilon k_{a,i} \left( 1 + A_i S_i^{\beta_i} \right) C - \rho_b k_{d,i} S_i \end{cases} \quad (\text{eq.3})$$

268 where  $C$  is the carrier concentration in water [ $M L^{-3}$ ],  $S_i$  is the concentration of carrier particles retained on  
269 the solid grains due to the  $i$ -th retention mechanism [ $M M^{-1}$ ],  $\rho_b$  is the bulk density of the porous medium [ $M$   
270  $L^{-3}$ ],  $k_{a,i}$  is the carrier attachment rate due to the  $i$ -th retention mechanism [ $T^{-1}$ ],  $k_{d,i}$  is the corresponding  
271 detachment rate [ $T^{-1}$ ],  $A_i$  and  $\beta_i$  are empirical coefficients specific to the deposition mechanism [-]. The first  
272 equation refers to particle transport in water and the second one describes the deposition mechanism(s).  
273 The parenthesis in the second equation is the generic formulation for particle retention mechanisms  
274 proposed by Tosco and Sethi (Tosco and Sethi, 2010). For linear attachment,  $A_i = \beta_i = 1$ ; for blocking,  $\beta_i = 1$   
275 and  $A_i = -1/S_{\max,i} < 0$  (where  $S_{\max,i}$  is the maximum concentration of particles retainable on the solid matrix  
276 due to the  $i$ -th retention mechanism); for ripening,  $A_i > 0$  and  $\beta_i > 0$ . In case of irreversible deposition, the  
277 second term vanishes being  $k_{d,i} = 0$ .

278 In this work the following two-site deposition model was adopted:



$$\begin{cases}
 \varepsilon \frac{\partial C}{\partial t} - \rho_b \frac{\partial S_1}{\partial t} - \rho_b \frac{\partial S_2}{\partial t} = -q \frac{\partial C}{\partial x} + \alpha_x \frac{\partial^2 C}{\partial x^2} \\
 \rho_b \frac{\partial S_1}{\partial t} = \varepsilon k_{a,1} C \\
 \rho_b \frac{\partial S_2}{\partial t} = \varepsilon k_{a,2} (1 + A_2 S_2^{\beta_2}) C
 \end{cases}
 \quad (\text{eq. 4})$$

280 The breakthrough curves of tracer and particles were inverse-fitted to the respective transport equations  
 281 using the software MNMs 2018 (Micro-and Nanoparticle transport, filtration and clogging Model - Suite)  
 282 (Bianco et al., 2016; Mondino et al., 2020; Velimirovic et al., 2020). A porosity of 0.31 ( $\pm 0.02$ ) and dispersivity  
 283 of  $1.84 \cdot 10^{-4} (\pm 3 \cdot 10^{-7})$  m were obtained from tracer tests, and were assumed valid also for particle transport,  
 284 since no evidence of particle early breakthrough was observed.

285 Dicamba adsorption/desorption onto/from the carriers was not modeled since all nano-formulations were  
 286 prepared for injection a few hours in advance, thus allowing the complete release of the pesticide before  
 287 injection into the column.

288

#### 289 2.2.5. Weed control efficacy tests

290 Weed control efficacy of the commercial dicamba, K10 and K10-CMC was evaluated in greenhouse on  
 291 *Solanum nigrum* and *Amaranthus retroflexus*, two dicamba sensitive weeds, grown in pot filled with  
 292 commercial potting mix. Each pot contained 5 seeds of a single weed species and 4 replicate pots were  
 293 prepared for each combination of herbicide formulation, dose and species. The experiment was repeated  
 294 twice, in May and August 2019. When weeds reached a two to three leaf stage, they were sprayed with the  
 295 following equivalent dose of dicamba: 0 (untreated control), 146.3, 195.0, 219.4, 243.8, 268.2 and 292.6 g Al  
 296  $\text{ha}^{-1}$ , corresponding to the following volume of commercial dicamba: 0, 0.6, 0.8, 0.9, 1 (field rate), 1.1. and  
 297 1.2 L  $\text{ha}^{-1}$ . Seedrape oil (Codacide, Corteva) used at 1 L  $\text{ha}^{-1}$  as an adjuvant was added to all the spray solutions.  
 298 Herbicide treatment was performed using a cabinet sprayer equipped with a single flat fan nozzle (Teejeet  
 299 AI11002-VS), calibrated to deliver 300 L  $\text{ha}^{-1}$  at a pressure of 203 kPa. After treatment, pots were randomly  
 300 arranged in greenhouse benches until the study ended. At 21 days after treatment the fresh biomass of  
 301 treated plants was weighted by cutting them just above the soil level. Treatment efficacy was expressed as

302 percentage of fresh aboveground weight relative to the untreated control (relative weight %). Values of  
303 relative weight may range from 0% (complete plant desiccation) to 100% (fresh weight of untreated plants).  
304 A dose-response curve was built for each herbicide formulation, averaging between experiments, separately  
305 per weed species. The percentage of relative weight of treated plants was fit against herbicide rates  
306 according to a three-parameter log-logistic regression model (Equation 5):

$$307 \quad Y = \frac{d}{1 + \exp\{b[\log(x) - \log(e)]\}} \quad (\text{eq. 5})$$

308

309 where  $Y$  is the relative weight of treated plants,  $x$  is the herbicide rate expressed in  $\text{g AI ha}^{-1}$ ,  $d$  is the upper  
310 limit, and  $b$  is the relative slope at the point of inflection  $e$ . Model fitting was performed using the *drm*  
311 function of the DRC add-on package of the open-source program R (Fogliatto et al., 2021; Team, 2019). The  
312 effective herbicide dose required to reduce plant relative weight by 50% ( $ED_{50}$ ) and 90% ( $ED_{90}$ ) compared  
313 with the values observed at  $0 \text{ g AI ha}^{-1}$  were calculated from the fitted model using the *ED* function of the  
314 DRC package.

315

## 316 3. RESULTS AND DISCUSSION

### 317 3.1. Carrier characterization

318 Information on particle size, zeta potential and fraction of retained herbicide after dilution was used to  
319 identify the best performing carrier and coating, to be further assessed in the following steps of the study.

320 The particle size distribution was measured for the carriers dispersed in deionized water using a disk  
321 centrifuge (Supporting Information, Figure S4). Table 1 reports the  $D_{10}$ ,  $D_{50}$  and  $D_{90}$  values obtained for all  
322 samples from the cumulated particle size distribution.  $D_{50}$  is in the range  $0.5 - 2.5 \mu\text{m}$  for all samples. The  
323 particles are broadly distributed, with uniformity coefficient above 4 in all cases, and show a dominant

324 fraction in the micrometer range, and a secondary fraction in the nanometer range. In particular, a wide peak  
325 in the range 2 - 4  $\mu\text{m}$  was observed for all materials except the zeolite (ZEO), which showed a wider peak in  
326 the range 3 - 10  $\mu\text{m}$ . Only the Na-M2 sample showed a clear second peak, around 200 nm.

327 The zeta potential (Supporting Information, Figure S5) of the carriers was negative in all explored conditions,  
328 as expected for clays and zeolites. More negative values were measured for particles dispersed in DIw; when  
329 particles were dispersed in NaCl or CaCl<sub>2</sub> solutions at a high salinity, the zeta potential approached zero,  
330 suggesting lower colloidal stability. It is worth to highlight that Ca-M particles showed, in all solutions, zeta  
331 potential values closer to neutrality compared to the other particles, suggesting that they may be more prone  
332 to aggregation. This was confirmed by a general tendency of Ca-M to sediment faster when dispersed in  
333 solutions other than DIw (including tap water). Such a fast sedimentation rate, visible even by eye, cannot be  
334 attributed to a difference in size of primary particles nor to a higher density. This behaviour compromised  
335 the use of Ca-M in some tests, as discussed in the following paragraphs.

336

### 337 3.2. Adsorption and release tests

338 The capability of the four candidate carriers to adsorb the pesticide was evaluated first based on adsorption  
339 isotherms. To this aim, carriers were loaded with dicamba, in the absence of polymeric coating, in a broad  
340 range of herbicide concentration (0.125 g/L to 7 g/L). The upper concentration limit was selected close to the  
341 dicamba solubility (8 g/L at pH 1.9).

342 A contact time of 24 h was first selected based on the literature (Azejjel et al., 2009; Carrizosa et al., 2001).

343 The adsorption isotherms (Figure 1) showed a linear relationship between adsorbed and dissolved herbicide  
344 concentration (respectively  $C_{s,eq}$  and  $C_{w,eq}$ ) in the explored concentration range. Thus, experimental data were  
345 fitted with a linear isotherm,  $C_{s,eq} = K_d \cdot C_{w,eq}$ . All carriers reached the highest loading capacity for the highest  
346 tested concentration. Comparing carriers, the calcium montmorillonite (Ca-M) and one of the sodium  
347 montmorillonites (Na-M2) reached the highest loading capacities, corresponding to adsorbed concentrations

348 of approximately 120 mg of dicamba per gram of carrier in both cases. The fitted partition coefficients are,  
349 respectively, 0.0251 L/g ( $R^2 = 0.9759$ ) and 0.0216 L/g ( $R^2 = 0.9966$ ). The K10 sodium montmorillonite reached  
350 a maximum of 80 mg/g, with  $K_d = 0.0124$  L/g ( $R^2 = 0.9612$ ); the lowest loading capacity was registered for the  
351 zeolite (ZEO), which showed a maximum retained dicamba mass of 62 mg/g, with  $K_d = 0.0122$  L/g ( $R^2 =$   
352 0.9893).

353 A shorter contact time (2 h) was also tested in view of a possible optimization of the loading procedure.  
354 However, the results were not univocal (Supporting Information, Figure S7), showing for Ca-M a loading  
355 capacity comparable to the one obtained in 24 h, a slightly higher  $C_{s,eq}$  for K10, and lower for Na-M2 and ZEO.  
356 The results were only partly reproducible, thus suggesting that for at least some carriers a contact time of 2  
357 hours does not guarantee equilibrium between phases. In particular, the structure of zeolite, characterized  
358 by cages and channels between the structural tetrahedral that form the primary porosity, is likely responsible  
359 for the lowest performance of the ZEO sample at short contact time (Rhodes, 2010; Stocker et al., 2017).  
360 Based on adsorption isotherms, a contact time of 24 h was therefore adopted for the following steps of the  
361 study, for all carriers.

362 Release tests were carried out diluting the nano-formulations in DIw or TAPw, the latter to simulate  
363 conditions similar to real pesticide application in the field. The nano-formulation concentration after dilution  
364 (5 g/l) corresponded to a dicamba concentration of 0.42, 0.58, 0.55 and 0.34 g/l, respectively for K10, Na-  
365 M2, Ca-M, ZEO (compare to adsorption isotherms). This dilution ratio was selected appropriately to  
366 guarantee a dicamba concentration in the range of recommended application rate of the commercial  
367 products (namely 0.12-1.46 g/l of dicamba, depending on the specific crop).

368 Release tests in DIw (Figure 2a) were used as a screening for the selection of the best candidate carrier, in  
369 combination with adsorption and characterization results. When the uncoated nano-formulations were  
370 diluted in DIw, Na-M2 showed the lowest percentage of retained pesticide, both on the short term (less than  
371 1 hour) and on a longer time frame (60 hours and later). The highest release was observed in less than 1 hour,  
372 with a subsequent partial re-adsorption on later stages. A final percentage of approximately 30% of dicamba  
373 retained on the Na-M2 carrier after dilution was registered for the uncoated carriers, and similar results were

374 obtained also for the CMC-coated carrier (data not reported). This result indicates that Na-M2, even if  
375 capable to perform better than other carriers in terms of adsorption capacity, is not a suitable candidate for  
376 the dicamba nano-formulation. Even if a high release in a short time could be desirable for applications where  
377 an initial higher herbicide quantity is required, in light of the high dicamba volatility a Na-M2 based nano-  
378 formulation would not be the optimal choice because of the high risk of pesticide losses in air.

379 Ca-M showed the highest percentage of retained pesticide after dilution in DIW (approximately 80%).  
380 However, a peculiar behaviour was observed for this carrier: a fast, significant release was registered on a  
381 short time frame (1 h), leading to a retained percentage of 65%. In a longer time frame, part of the pesticide  
382 was re-adsorbed, leading to a final percentage of 80% retained dicamba approximately two hours after  
383 dilution. Based on high retention only, Ca-M would have been the best candidate carrier for the development  
384 of the nano-formulated dicamba. However, the high variability over time of the retained dicamba may lead  
385 to a partly unpredictable behaviour at the field scale: it is not possible to assume a priori how much time  
386 would it take for a farmer to start the field application of the pesticide after its dilution. If this time is shorter  
387 than one hour, it is possible that a high fraction of AI is dissolved in water, and therefore prone to  
388 volatilization and/or free infiltration in the subsoil. Moreover, its relatively poor colloidal stability, highly  
389 sensitive to salt content even in the presence of a polymeric coating, weakens its suitability for real-scale  
390 applications, where ionic strength and salt composition of natural or tap water used for pesticide dilution is  
391 not under control and highly variable. In light of these considerations, Ca-M was not further considered in  
392 the development of the dicamba nano-formulation.

393 ZEO and K10 showed similar behaviours, with approximately 55% of dicamba remaining adsorbed on the  
394 carrier 6 hours after dilutions, therefore resulting suitable candidate carriers. However, due to the higher  
395 adsorption capacity of K10 compared to the zeolite, K10 was selected as the best candidate for the next steps  
396 of the study. It is also worth to mention that the K10 carrier showed the most constant trend in dicamba  
397 release, with an initial fast release in the first 10 minutes, followed by a fast stabilization.

398 The polymeric CMC coating helped reducing the dicamba release from K10: CMC-coated particles diluted in  
399 DIW (Figure 2b) showed a fast (less than 10 mins) stabilization on a plateau corresponding to approximately

400 80% of retained dicamba, comparable with uncoated Ca-M, with an overall increase of retained AI of  
401 approximately 25% with respect to the uncoated K10. The coating is expected to primarily act by hindering  
402 the herbicide desorption, increasing the diffusive path toward the bulk fluid (Rashidzadeh et al., 2017).  
403 Conversely, when the nano-formulations were diluted in TAPw, the effect of the CMC coating on the release  
404 was reduced (Figure 2b), particularly on the long term: the released dicamba was 28% after 6h from both  
405 formulations, with a slightly higher release for the coated formulation in the first 3 hours. The major elements  
406 expected to influence the release behaviour are pH and salt content. The pH of the formulations diluted in  
407 tap water was 8.4 and, since dicamba has a very low  $pK_a$  ( $pK_a=1.95$ ), in this alkaline environment the herbicide  
408 is present primarily as a deprotonated species; the presence of ionic species in water, such as  $HCO_3^-$  and  $PO_3^-$ ,  
409 could inhibit the release from the clay surface when coating is not present.

410

### 411 3.3. Volatilization tests

412 Pre-screening volatilization tests were performed exposing to ambient air the diluted K10-based nano-  
413 formulations (K10 and K10-CMC), pure dicamba solution and diluted commercial product on petri dishes,  
414 without soil. The results (Supporting Information, Figure S8) showed a marked volatilization of pure dicamba:  
415 after 24 hours about 30% of the AI was lost via volatilization, indicating a moderate attitude of the AI to pass  
416 in air phase. Volatilization from the commercial product was negligible, with 99.7% of the pesticide mass  
417 remaining after 24 hours, likely thanks to the co-formulants, aimed, among other purposes, at increasing  
418 wettability and adhesive performance of the formulated dicamba, thus reducing water-air mass exchange.  
419 The uncoated K10 formulation, despite the high amount of AI released in water, limited the volatilization  
420 losses to 7.6% of the initial dicamba mass. Interestingly, a simple mass balance suggests that the presence of  
421 the K10 particles in the solution inhibits also the volatilization of the freely dissolved dicamba: for uncoated  
422 nano-formulations diluted in DIw, approximately 45% of the dicamba initially adsorbed on the carrier is  
423 expected to be released after dispersion in DIw (based on release tests), 30% of which should in principle be  
424 lost via volatilization (based on pure dicamba volatilization results). However, this would correspond to an

425 overall volatilization of 13.5% of the initial dicamba mass, while only 7.6% was observed here. This could be  
426 linked to the specific experimental configuration (i.e. concentrated formulation applied on a petri dish): the  
427 rapid water evaporation (expected to occur the first 1h of the test) may have left the AI in contact with the  
428 air phase, with higher mass exchange in the first phase of the test; later on, tortuous paths can have formed  
429 through the clay film over the petri dish while water was evaporating, with an overall reduced contact  
430 between dissolved dicamba and air. However, more interestingly, it is also possible that, during water  
431 evaporation, part of the dissolved dicamba re-adsorbed onto the clay particles due to the altered equilibrium  
432 between the phases (Sciumbato et al., 2004; Strachan et al., 2010). At this stage it is not possible to  
433 discriminate between the two processes and, likely, the observed results are obtained as a combination of  
434 both. For the CMC-coated formulation a similar trend was observed, with even more limited volatilization,  
435 resulting in an overall loss of 4.6% of the initial dicamba mass after 30 hours, thus confirming the usefulness  
436 of the polymeric coating also to prevent volatilization(Rashidzadeh et al., 2017).

437 The dicamba formulations applied to soils evidenced similar volatilization trends (Figure 3). As a general rule,  
438 dicamba alone showed the highest losses: in medium and coarse sand the volatilization was very similar, with  
439 approximately 26% of AI losses in 24h; in sandy loam, the volatilization rate was lower (13.4%). Also for the  
440 commercial formulation and for the two nano-formulations, the volatilization was more pronounced in the  
441 sand samples and reduced in the sandy loam, suggesting a partial affinity of the compound to the fine fraction  
442 of the soil. Contrary to the preliminary volatilization tests performed assessing direct volatilization from the  
443 solution, when applied to soils the commercial formulation and the CMC-coated nano-formulation showed  
444 comparable volatilization rates. In coarse sand and sandy loam the AI loss is respectively close to 8% and  
445 4.5%, while in medium sand the coated nano-formulation performed significantly better than the commercial  
446 dicamba-based product, showing a loss of 4.5% versus 9.3%. It is finally worth to highlight that in all cases,  
447 but particularly in the two sand samples, the presence of the CMC coating significantly reduced the dicamba  
448 volatilization (from 15.1% to 4.5% in medium sand, from 17.4% to 7.9% in coarse sand, and from 5.8% to  
449 4.5% in sandy loam), thus confirming the key role of the polymeric coating in controlling the release of  
450 dicamba from the montmorillonite carrier.

451

### 452 3.4. Transport in the porous medium

453 Preliminary transport tests were performed injecting the K10 carrier with and without the polymeric coating  
454 in sand-packed columns to assess the potential role of the polymeric shell in modifying particle transport. In  
455 DLW the presence of the CMC coating is not expected to play a significant role in particle transport. The zeta  
456 potential of both coated and uncoated particles is strongly negative ( $-25.2 \pm 0.46$  mV for uncoated K10, -  
457  $38.4 \pm 0.89$  mV for CMC coated K10). To help understanding transport-controlling processes, DLVO  
458 interactions were estimated (Elimelech, 1995). Both particle-particle and particle-sand DLVO interaction  
459 profiles are repulsive without secondary minima, which could suggest mild aggregation and/or deposition  
460 (Supporting Information, Figures S9a and S10a). Coherently, the particle breakthrough curves (BTCs)  
461 obtained from column transport tests (Figure 4) show a non-negligible mobility of both coated and uncoated  
462 carrier. In both cases the breakthrough concentration approached 60% of the injected one, showing minimal  
463 influence of the coating. The mass balance (Table 2) indicates a slightly higher mobility for the CMC-coated  
464 particles, coherently with slightly more repulsive particle-particle and particle-collection DLVO profiles:  
465 67.22% of the injected mass of coated K10 was eluted at the end of the test, while 63.09% was recovered at  
466 column outlet for bare K10. Based on the measured zeta potential values and the clearly repulsive DLVO  
467 interaction it is possible to attribute the carrier retention in the porous medium mainly to physical  
468 mechanisms, above all to mechanical filtration: the K10 particles, even if stably dispersed in the injected  
469 suspension, are sufficiently large to partly interact with the porous medium; the ratio of K10  $d_{90}$  ( $3.746 \mu\text{m}$ )  
470 to sand  $d_{10}$  ( $370 \mu\text{m}$ ) approaches the critical ratio of 1% above which a partial mechanical filtration of particles  
471 can be observed (Luna et al., 2015; Xu et al., 2006). The experimental breakthrough curves were modelled  
472 using a dual deposition site attachment/detachment model (eq. 4) with a linear irreversible deposition site  
473 (representing mechanical filtration) and a linear reversible deposition site (representing physical-chemical  
474 interactions, obtained imposing  $A_2 = 0$  in the model equation). They showed a good agreement between  
475 simulated and measured BTCs. The fitted coefficients are reported in the first two columns of Table 2. The



476 first interaction site is dominant, thus reflecting the dominance of mechanical filtration as retention  
477 mechanism. The particle retention observed in these tests can be assumed to be the minimum to be  
478 reasonably expected in all experimental conditions, due to the clearly repulsive interactions.

479 When comparing the different dicamba-based formulations dispersed in NaCl 30 mM solutions (Figure 5), a  
480 significant discrepancy between nano-formulated and not nano-formulated suspensions is observed. Pure  
481 dicamba and the commercial product, as it can be denoted from their breakthrough curves, were transported  
482 similarly to a trace. They reached  $C/C_0 = 1$  with no evident delay (thus indicating the absence of any relevant  
483 adsorption phenomenon onto the silica sand) and all injected mass is recovered at column outlet at the end  
484 of the test (recovered mass of 99.35% for pure dicamba and 98.44% for the commercial product).

485 The K10-formulated dicamba, both in presence and absence of coating, showed a remarkably limited mobility  
486 compared to pure and commercial dicamba. During the injection and subsequent flushing at constant NaCl  
487 concentration (i.e. in PVs 1 to 10), the uncoated formulation did not show any appreciable breakthrough,  
488 while the CMC-coated formulation reached a maximum outflow concentration equal to 15.3% of the injected  
489 one (Figure 5, respectively red and green curves). In terms of mass balance, this corresponds to 1.74% of  
490 injected uncoated K10 nano-formulation reaching the column outflow and 14.45% of the coated one in the  
491 first PVs. The breakthrough curves of the two carriers were successfully fitted with eq. 4 (Supporting  
492 Information, Figure S11). In this case the fitted attachment coefficients for site 1 (linear irreversible  
493 attachment) are approximately one order of magnitude higher than those obtained for the carriers in DIw,  
494 both for coated and bare K10, indicating that a stronger physical retention was occurring for the nano-  
495 formulations dispersed in the NaCl solution compared to the carriers dispersed in DIw. As for the second  
496 interaction site, for the CMC-coated K10, a linear reversible interaction ( $A_2 = 0$ ) was adequate to represent  
497 the physical-chemical interaction, while for the bare particles a ripening mechanism ( $A_2 > 0$ ) correctly  
498 described the particle physical-chemical interactions occurring in the porous medium. This is in agreement  
499 with the predicted DLVO interaction profiles (Supporting Information, Figures S9b and S10b): for the CMC-  
500 coated nano-formulation, a weakly repulsive profile is obtained for particle-particle interaction, with a  
501 shallow secondary attractive minimum and a very limited energy repulsive barrier ( $\sim 0.2$  KT), suggesting that

502 aggregation may partly occur in the suspension. Conversely, for the uncoated K10 formulation, an entirely  
503 attractive profile is obtained, indicating that particles are attracting each other and agglomerating. As for  
504 particle-collector interaction, on the contrary, repulsive profiles are observed, even though the repulsive  
505 energy barrier against deposition is of limited extent ( $\sim 2-4$  kT). In terms of particle transport, this  
506 suggests that, for the uncoated formulation, particles are partly aggregated, thus prone to a more  
507 pronounced mechanical filtration (represented by the first interaction site) with respect to the carrier in DIw,  
508 and deposited particles are attracting suspended ones, thus resulting in a strong ripening (reflected by the  
509 second interaction site). For the coated nano-formulation, the CMC shell prevents excessive aggregation,  
510 mechanical filtration is more limited and ripening does not occur, at least on the time scale and travel path  
511 explored in these tests.

512 It is worth to recall that, when the nano-formulations are diluted in water, a fraction of dicamba is released  
513 and therefore is present as freely dissolved compound in the injected suspensions; in these tests this fraction  
514 corresponded approximately to 25% of the total dicamba for uncoated K10 and 20% for CMC-coated K10  
515 (compared with release tests). The breakthrough curves for the free fraction of dicamba (Supporting  
516 Information, Figure S12) show that, for both nano-formulations, the free compound is transported through  
517 the sand-packed column similarly to a tracer, with no evidence of any retention. Based on this additional  
518 information, it is possible to draw a mass balance for the total dicamba (i.e. both freely dissolved and  
519 embedded in the carrier), which indicates that, at the end of the first 10 PVs, for the uncoated carrier 10% of  
520 the injected dicamba has been eluted from the column, and 20.73% has been eluted for the CMC-coated  
521 carrier. This finding suggests that, even though the polymeric coating helps preventing excessive release and  
522 volatilization of the AI from the carrier, it slightly enhances mobility compared to bare K10 particles.  
523 However, in the second part of the transport tests (PVs 10 to 20), when the columns were flushed with DIw,  
524 the abrupt change in ionic strength generated a markedly different response of bare and CMC-coated  
525 carriers. The uncoated nano-formulation was strongly mobilized by the step change in ionic strength,  
526 resulting in the remobilization of most formulation previously retained in the column (79.68% of the K10  
527 carrier and 88.43% of the total injected dicamba was eluted at the end of the test). Conversely, the

528 mobilization of the CMC-coated nano-formulation was minimal, resulting in an overall elution of 15.35%  
529 of the injected carrier, corresponding to 24.52% of the total injected dicamba. This last finding remarkably  
530 suggests that, even though the CMC coating imparts a slightly higher mobility to the nano-formulation, it also  
531 reduces the effects of changes in ionic strength. In particular, it decreases the possibility of the retained nano-  
532 formulation re-mobilization in case the salt concentration is reduced, for example, due to intense infiltration  
533 of rain.

534

### 535 3.5. Weed control efficacy tests

536 The dose-response curve highlighted a relative weight reduction of the treated weeds at increasing herbicide  
537 rates (Figure 6 and Table S2 in Supporting Information). All the herbicide formulations showed higher efficacy  
538 on *S. nigrum* than against *A. retroflexus*. However, the efficacy was consistent between herbicides in the two  
539 species, highlighting a higher relative weight reduction with K10-CMC, followed by commercial dicamba and  
540 K10. The herbicide rate able to reduce weed biomass by 50% showed higher differences between herbicides  
541 with K10-CMC always displaying the lowest rates: 1.5 g Al/ha for *S. nigrum* and 33 g Al/ha for *A. retroflexus*.  
542 At 90% weight reduction (corresponding to a relative weight of 10% in comparison to control) all the  
543 herbicides acted similarly, particularly in the case of *A. retroflexus*, in which values of herbicide rates higher  
544 than 100 g Al/ha were necessary to obtain a similar efficacy level. In the case of *S. nigrum*, 90% weight  
545 reduction was obtained at about 50 g Al/ha, value much smaller than that required for commercial and K10.

546

## 547 4. CONCLUSIONS

548 In this work a novel approach based on the use of natural clays to reduce the environmental mobility of  
549 dicamba was proposed. Four candidate carriers (namely, two Na-montmorillonites, a Ca-montmorillonite  
550 and a zeolite) were tested, and all proved to be effective in adsorbing the herbicide. However, not all of them

551 guaranteed easy applicability or reduced release in water when the formulations were diluted (i.e. mimicking  
552 the preparation of the product prior field application). A key role was played by the polymeric coating, formed  
553 by carboxymethyl cellulose, a food-grade biodegradable polymer used in a broad range of applications, from  
554 food industry to enhanced oil recovery to pharmaceuticals. The best performing formulation, namely CMC-  
555 coated Na-montmorillonite K10, was identified as the most advantageous compromise between technical  
556 constraints and potential environmental effects. From the technical point of view, it showed a good control  
557 of dicamba release after dilution and good colloidal stability, which allows its application using conventional  
558 pesticide spraying equipment. Its efficacy in the greenhouse tests against target weeds was similar or  
559 sometimes higher than that of commercial dicamba formulation, and showed promising prospects for  
560 improvements, which will be the focus of upcoming work.

561 Compared to other approaches previously proposed in the literature, based on organoclays and, more in  
562 general, of chemically modified adsorbing carriers, in this work the focus was on the use of natural  
563 unmodified materials as carriers, and on the development of a simple and low-impact preparation method,  
564 applicable at room temperature and pressure without addition of chemicals. The loading capacity obtained  
565 in this study is comparable or lower than those reported in the literature for organoclays (e.g. (Carrizosa et  
566 al., 2001)), but the CMC-coated K10 showed a good control of the major environmental criticalities of  
567 dicamba, namely volatilization and mobility in the subsoil. In particular, the CMC-coated K10 allowed a  
568 control of volatilization losses comparable to a commercial dicamba-based product, even in the absence of  
569 specific co-formulants, which are present in the commercial formulation but were not included in the nano-  
570 formulations.

571 Concerning the mobility in the subsoil, in this work a preliminary assessment was performed focusing on the  
572 saturated zone, a potential major route for dicamba migration in the subsoil. The remarkable mobility of pure  
573 and commercially formulated dicamba observed in transport tests, both in synthetic and real water indicates  
574 that, in case dicamba reaches an aquifer system as a free compound, it is expected to be highly mobile  
575 without any significant attenuation (except obviously for degradation processes, which are not appreciable  
576 on the short time scale of the experiments performed in this study). Conversely, the use of a mineral carrier

577 significantly reduced the potential mobility, in all explored conditions. Also in this case, the polymeric coating  
578 played a key role. Even though it imparted a slightly higher mobility to the nano-formulations, compared to  
579 bare carriers, it also significantly reduced the risk of re-mobilization when abrupt hydrochemical  
580 perturbations were applied, namely, when the columns were flushed with deionized water. Even if this  
581 condition is clearly unrealistic in a field-scale scenario, it has been adopted here as an extremized simulation  
582 of intense rain events: in this case the precipitation, characterized by a significantly lower salinity than  
583 groundwater, may infiltrate and, particularly for shallow aquifer systems, can significantly reduce the local  
584 groundwater salinity, with the risk of local re-mobilization of the nano-formulation. Clearly an in-depth study  
585 of the potential mobility of the new nano-formulations in the subsoil requires the assessment of a broader  
586 range of experimental conditions, and a detailed investigation focused on the top soil, which is beyond the  
587 scope of this paper. More in general, deeper investigation is needed on several other aspects touched in this  
588 work, including for example a further optimization of the preparation procedure, and a more detailed  
589 evaluation of the nano-formulation efficacy toward target weeds. However, the authors believe that even  
590 the preliminary results presented here already provide a first insight on the potentialities of natural clays as  
591 a low-impact solution to reduce environmental drawbacks of critical agrochemicals.

592

## 593 5. CITED LITERATURE

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761 ***Conflicts of interest***

762 There are no conflicts to declare

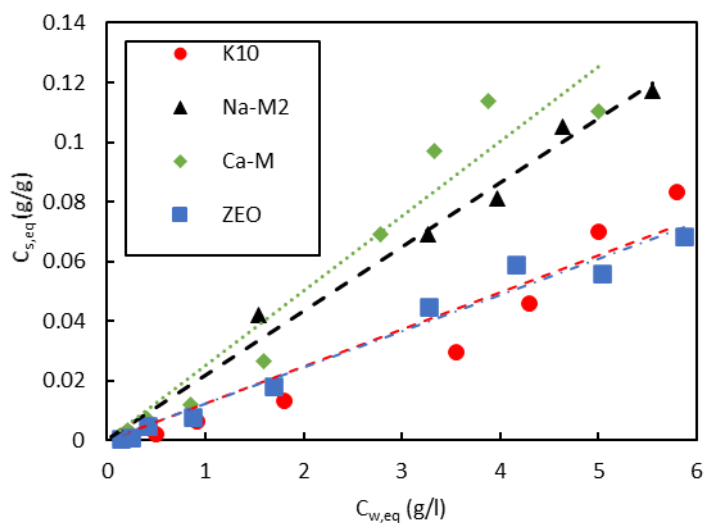
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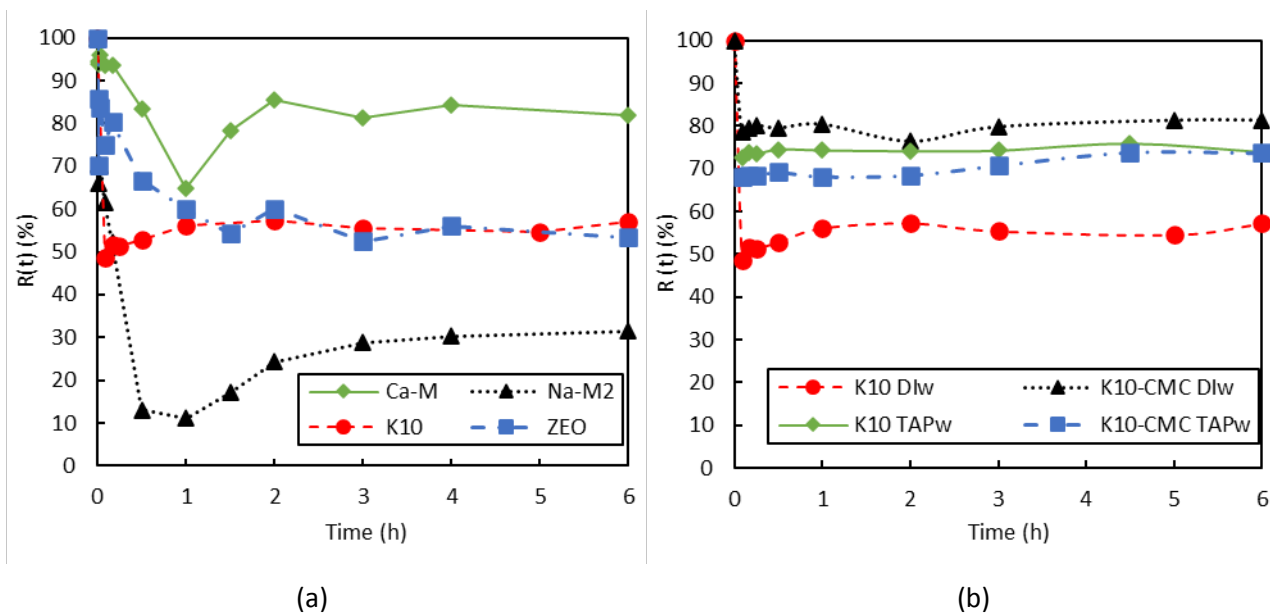
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771 *Figure 1 Adsorption isotherms for the four candidate carriers (K10, Na-M2, Ca-M, ZEO) obtained for a contact time of*  
 772 *24 hours. Experimental data (dots) and least-squares fitted linear isotherms (lines).*

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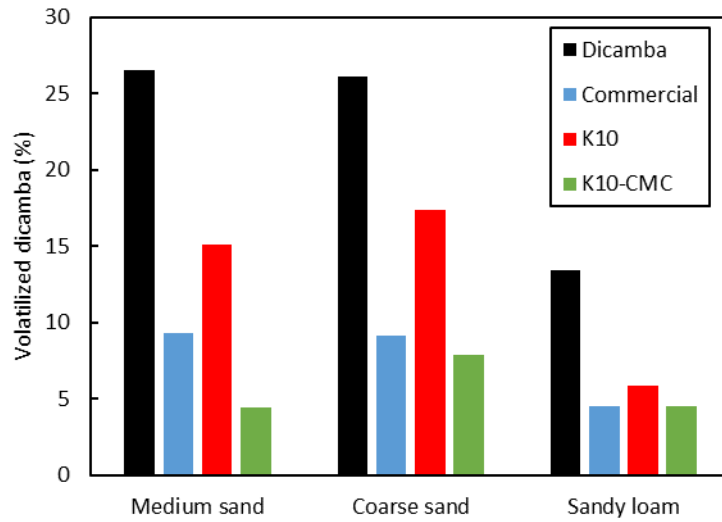


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776 *Figure 2 Release tests: retained dicamba R(t) expressed as a percentage for the four carriers (ZEO, Na-M2, Ca-M, ZEO),*  
 777 *after dilution in deionized water (DIw), without CMC coating (a), and on K10, after dilution in deionized water (DIw) or*  
 778 *in tap water (TAPw), with and without CMC coating (b)*

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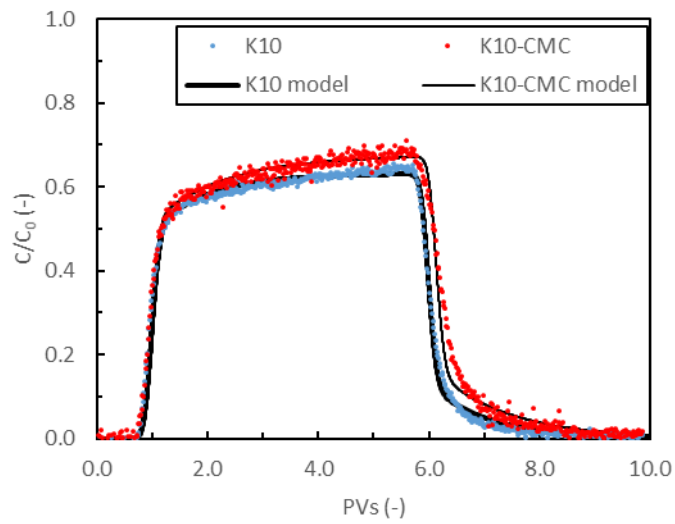
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Figure 3 Volatilization from soils: dicamba loss 24 h after application to different soils, reported as percentage of volatilized mass with respect to applied mass

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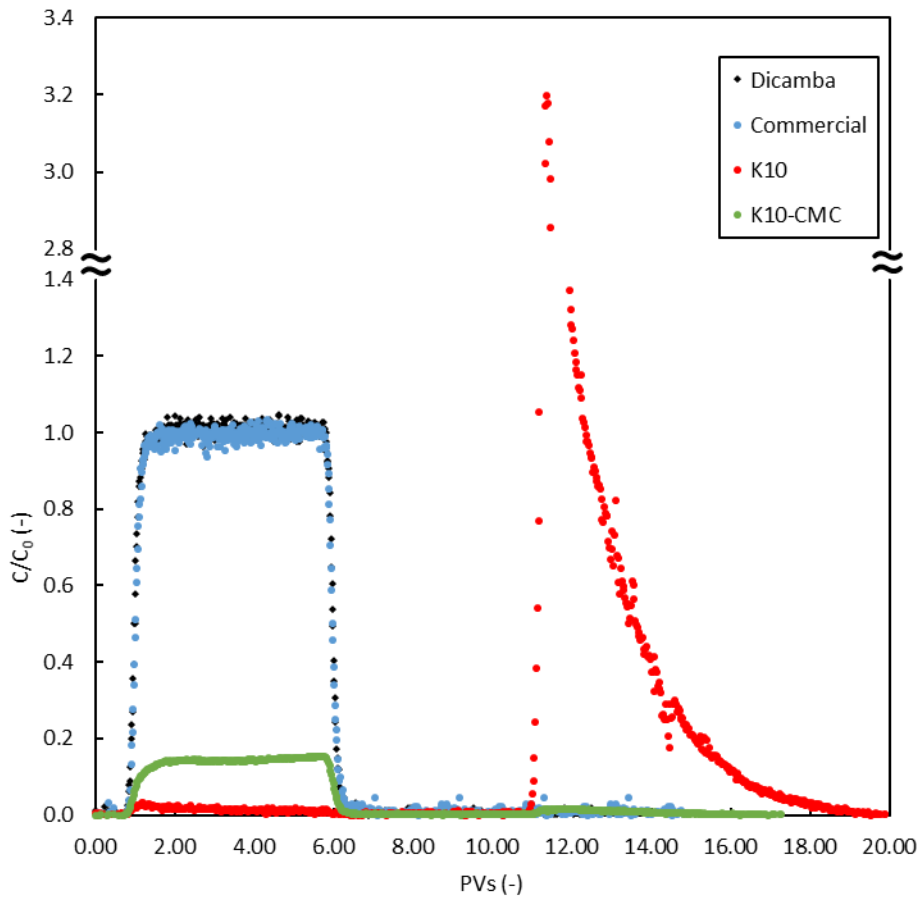
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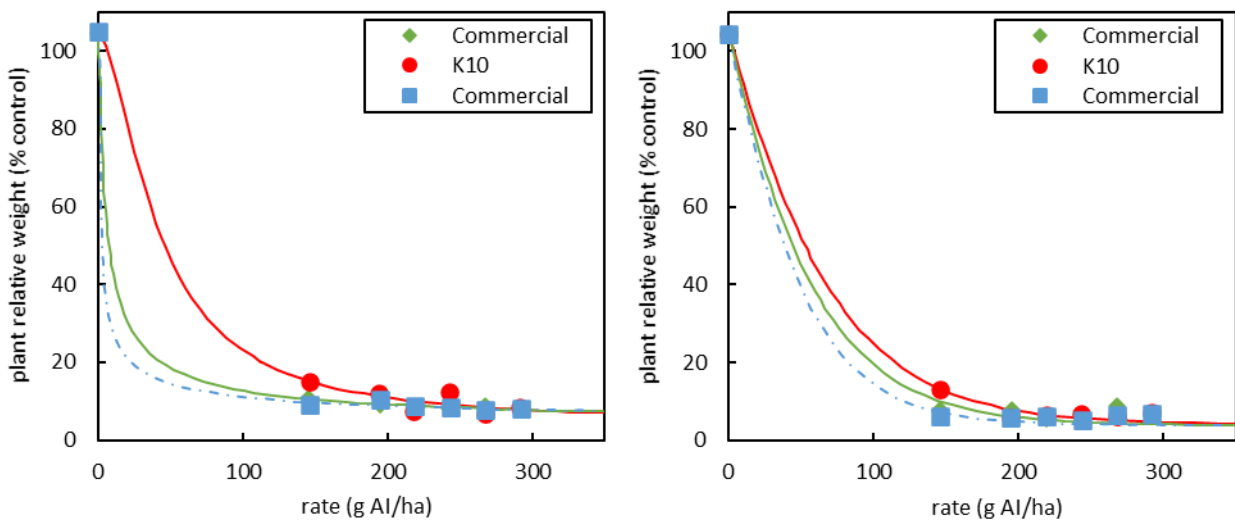
Figure 4: Breakthrough curves for uncoated (blue) and CMC-coated (red) K10 carrier, without dicamba. Experimental data (coloured dots) and least-squares model curves (black lines) are reported.

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789 *Figure 5 Breakthrough curves for non-formulated dicamba (black), commercial formulation (blue) and*  
 790 *CMC-coated (green) nano-formulations. All formulations were dispersed in NaCl 30 mM solution (injection: pore*  
 791 *volumes 0 to 5); the first flushing (pore volumes 5 to 10) was performed injecting pesticide-free 30 mM NaCl solution;*  
 792 *the second flushing (pore volumes 10 to 20) was performed with DIw.*



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795 *Figure 6 Dose-response curves between Solanum nigrum (a) and Amaranthus retroflexus (b) plant relative weight and*  
 796 *herbicide dose of K10-CMC, commercial dicamba and K10 formulations.*

797 **Tables**798 *Table 1 Size and zeta potential in DIW and their variation in NaCl different ionic strength*

	Particle size distribution ( $\mu\text{m}$ )				Zeta potential (mV)		
	D <sub>10</sub>	D <sub>50</sub>	D <sub>90</sub>	U=D <sub>60</sub> /D <sub>10</sub>	in DIW	in NaCl 100 mM	in CaCl <sub>2</sub> 2mM
<b>K10</b>	0.287	1.561	3.746	6.49	-18.9 $\pm$ 2.0	-14.2 $\pm$ 0.7	-6.2 $\pm$ 0.5
<b>Na-M2</b>	0.154	0.570	2.834	6.06	-26.5 $\pm$ 2.6	-14.6 $\pm$ 2.8	-13.2 $\pm$ 1.1
<b>Ca-M</b>	0.180	0.656	2.262	4.93	-14.3 $\pm$ 0.9	-10.2 $\pm$ 0.1	-8.0 $\pm$ 0.6
<b>ZEO</b>	0.674	2.525	2.525	4.39	-18.2 $\pm$ 0.5	-8.7 $\pm$ 0.3	-12.3 $\pm$ 1.0

799

800 *Table 2 Mass balance and fitted model parameters for the transport of carriers and formulations in the porous medium*

			K10 carrier only		Dicamba formulations			
			K10	K10-CMC	Dicamba	Commercial	K10	K10-CMC
<b>Mass balance</b>	Carrier	Eluted mass @10 PVs	63.09%	67.22%	n.a.	n.a.	1.74%	14.45%
		Eluted mass @20 PVs	n.a.	n.a.	n.a.	n.a.	79.68%	15.35%
	Free dicamba	Eluted mass @10 PVs	n.a.	n.a.	99.35%	98.44%	99.77%	100.00%
		Eluted mass @20 PVs	n.a.	n.a.	99.35%	98.44%	10.06%	20.73%
	Total dicamba	Eluted mass @10 PVs	n.a.	n.a.	n.a.	n.a.	88.43%	24.52%
<b>Modeling</b>	Site 1	k <sub>a,1</sub> (1/s)	6.99·10 <sup>-4</sup>	6.32·10 <sup>-4</sup>	n.a.	n.a.	4.00·10 <sup>-3</sup>	4.48·10 <sup>-3</sup>
	Site 2	k <sub>a,2</sub> (1/s)	3.53·10 <sup>-4</sup>	4.32·10 <sup>-4</sup>	n.a.	n.a.	6.40·10 <sup>-3</sup>	9.70·10 <sup>-4</sup>
		k <sub>d,2</sub> (1/s)	1.68·10 <sup>-3</sup>	1.38·10 <sup>-3</sup>	n.a.	n.a.	2.68·10 <sup>-5</sup>	6.07·10 <sup>-3</sup>
		A <sub>2</sub> (-) (*)	0	0	n.a.	n.a.	998.1	0
		$\beta_2$ (-) (**)	1	1	n.a.	n.a.	1	1
	Fitting	R <sup>2</sup>	0.9963	0.9937	n.a.	n.a.	0.8384	0.9956

801 (\*) fitted only for dicamba nano-formulations

802 (\*\*) not fitted

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**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: