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1 INFLUENCE OF COMMERCIAL FORMULATION ON  
2 LEACHING OF FOUR PESTICIDES THROUGH SOIL

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11

## 12 **Abstract**

13 Studies with small soil columns (2 cm i.d. x 5.4 cm depth) compared leaching of four  
14 pesticides added either as technical material or as commercial formulations. Pesticides were  
15 selected to give a gradient of solubility in water between 7 and 93 mg L<sup>-1</sup>, comprising  
16 azoxystrobin (emulsifiable concentrate, EC, and suspension concentrate, SC), cyproconazole  
17 (SC), propyzamide (SC) and triadimenol (EC). Columns of sandy loam soil were leached  
18 with 6 pore volumes of 0.01M CaCl<sub>2</sub> either 1 or 7 days after treatment. Separate experiments  
19 evaluated leaching of triadimenol to full breakthrough following addition of 18 pore volumes  
20 of 0.01M CaCl<sub>2</sub>. The mass of pesticide leached from columns treated with commercial  
21 formulation was significantly larger than that from columns treated with technical material  
22 for all compounds studied and for both leaching intervals (two-sided t-tests, p<0.001). This  
23 difference was conserved when triadimenol was leached to full breakthrough with 79 ± 1.2  
24 and 61 ± 3.1% of applied triadimenol leached from columns treated with formulated and  
25 technical material, respectively. There were highly significant effects of formulation for all  
26 pesticides (two-way ANOVA, p<0.001), whereas leaching interval was only significant for  
27 azoxystrobin EC formulation and cyproconazole (p <0.001 and 0.021, respectively) with  
28 greater leaching when irrigation commenced 1 day after treatment. Leaching of azoxystrobin  
29 increased in the order technical material (6.0% of applied pesticide) < SC formulation (8.5-  
30 9.1% of applied) < EC formulation (15.8-21.0% of applied). The relative difference between  
31 leaching of formulated and technical pesticide increased with pesticide solubility in water,  
32 increasing from a factor of 1.4 for the SC formulation of azoystrobin to 4.3 for the SC  
33 formulation of triadimenol. Experimental systems differ markedly from field conditions  
34 (small columns with intense irrigation). Nevertheless, results indicate the need to consider  
35 further the influence of co-formulants in pesticide formulations on behaviour of the active  
36 ingredient in soil.

37 **Keywords:** Co-formulants, contaminant, environmental fate

38

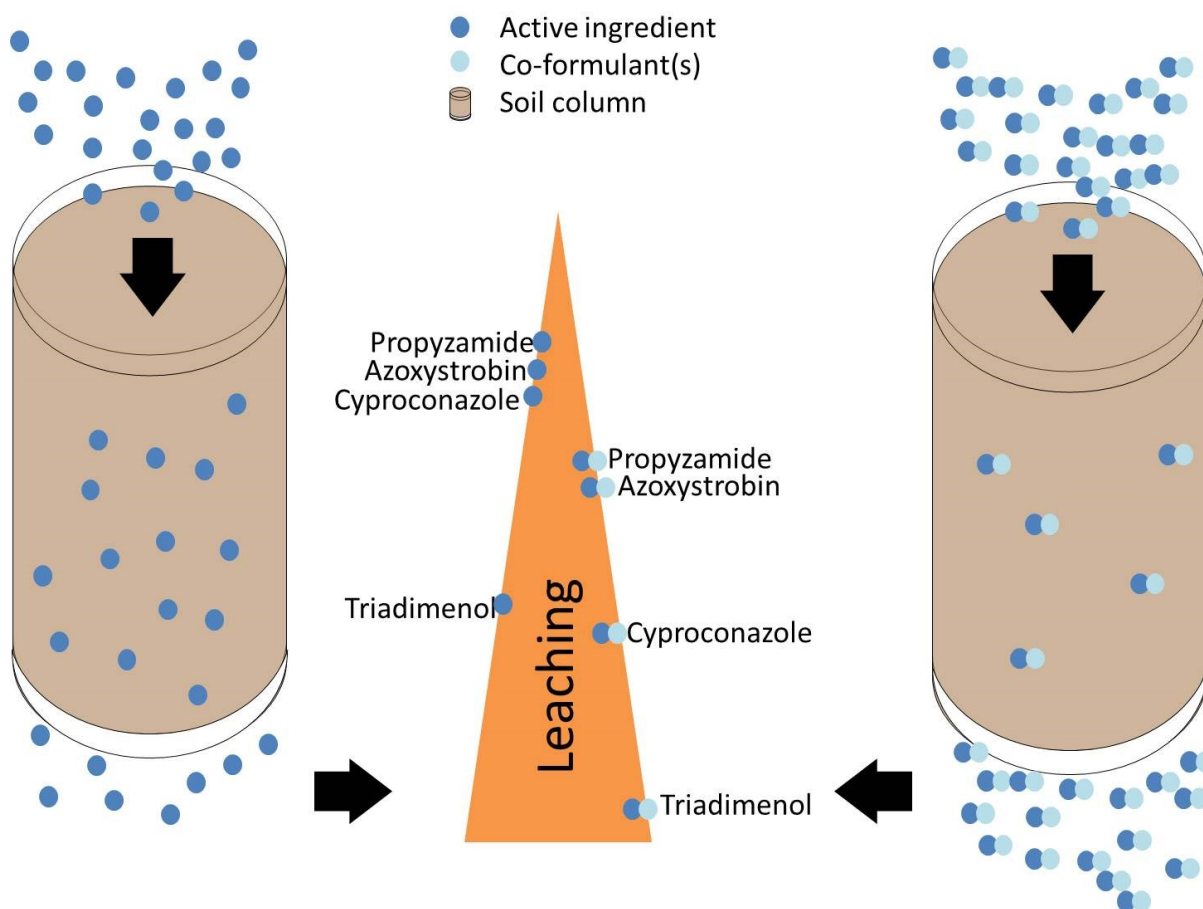
39 **Highlights**

- 40 • Greater pesticide leaching from commercial formulations versus technical material
- 41 • Emulsifiable concentrate of azoxystrobin leached more than suspension concentrate
- 42 • Effect of formulation on leaching increased with solubility of the active substance
- 43 • Assessments of pesticide fate that ignore co-formulants may be over-simplified

44

45 **Graphical abstract**

46



47

48

## 49 **1. Introduction**

50 Leaching of pesticides through soils may result in contamination of groundwater via  
51 transport to depth and surface water via either direct interception by subsurface drains or  
52 transfer through the saturated zone as river baseflow. Factors influencing leaching have been  
53 investigated over many years and include properties of the pesticide as well as factors relating  
54 to soil, hydrogeology, weather and agronomy (Flury, 1996). Given the huge amount of work  
55 reported in the literature, it is surprising that the influence of formulating pesticides as  
56 commercial products has not received greater attention to date. We previously compared  
57 leaching of the herbicide propyzamide through small soil columns when added at the surface  
58 either as technical grade pesticide or the commercial product Kerb® Flo which is formulated  
59 as a suspension concentrate (Khan & Brown, this issue). We demonstrated enhanced  
60 availability in pore water and greater leaching of the commercial formulation in two soils and  
61 for intervals between treatment and leaching of 1 to 28 days. Here, we extend the  
62 investigation to compare the effect of commercial formulation on leaching of three additional  
63 pesticides.

64 The literature reports a large number of studies that investigate the effect on leaching  
65 of incorporating pesticides into controlled-release formulations including manufactured  
66 polymers as well as starch, lignin and alginate-based systems (Dubey et al., 2011). This  
67 formulation type allows for the slow release of the active substance over time and many  
68 experiments compare leaching of controlled-release formulations with that of either technical  
69 pesticides or sprayable formulations of pesticides. Generally, it has been shown that  
70 controlled-release formulations restrict pesticide leaching by reducing the concentration of  
71 the chemical in the bulk soil that is available for leaching (Flury, 1996). There are exceptions  
72 in the literature, and controlled-release formulations can extend the period during which  
73 pesticide is present in soil and increase leaching when this occurs at longer periods after

74 application (Buhler et al., 1994). Setting aside this exception of controlled-release  
75 formulations, it has often been assumed for other formulation types that the active substance  
76 separates from any co-formulants upon entry into the soil and that pesticide fate in soil is  
77 unchanged relative to that of the pure active substance (Flury, 1996).

78         A few recent studies have investigated formulation types other than controlled-  
79 release, undertaking batch experiments that compare sorption of pesticides in soil slurry  
80 systems when added as pure substances or as commercial formulations (e.g. Beigel &  
81 Barriuso, 2000; Pose-Juan et al., 2010; Földényi et al., 2013). We have shown that such  
82 experiments will not always capture formulation effects and proposed that a centrifugation  
83 methodology provides a better measure of any influence of formulation under natural soil  
84 conditions (Khan & Brown, this issue). Where sorption of pesticides has been shown to be  
85 less for commercial formulations than for technical material, it has been hypothesised that co-  
86 formulants act either to solubilise the active substance or to hold it in solution by formation of  
87 relatively stable micelles through the action of surfactants and/or oils (Beigel and Barriuso,  
88 2000; Pose-Juan et al., 2011); in either case, the effect is to retard sorption by holding a  
89 greater proportion of the active substance in soil solution. Alternative behaviours have been  
90 observed and Pose-Juan *et al.* (2010) reported greater sorption of penconazole from a  
91 commercial water-oil emulsion formulation of penconazole compared to technical grade  
92 material in batch experiments. They hypothesised that the presence of oil-surfactant mixture  
93 in the commercial formulation influenced sorption of penconazole through either enhanced  
94 penetration of the active substance onto the less polar sites of the soil organic matter, or by  
95 co-adsorption of the active substance within the oil-surfactant mixture.

96         There are far fewer studies that compare leaching of sprayable formulations with that  
97 of the technical material. Wybieralski (1992) carried out column leaching experiments to  
98 investigate the kinetics of leaching of propoxur and reported fastest leaching of the

99 compound from an emulsion form, intermediate leaching kinetics for a suspension form and  
100 slowest leaching from pure active substances in five different arable soils. Sharma et al.  
101 (2013) compared leaching of hezaconazole under saturated conditions for four soil types;  
102 they included a comparison between technical material and a 5% emulsifiable concentrate  
103 formulation and reported that leaching results were similar. Any impact of formulation may  
104 be particularly significant under conditions of macropore flow, where pesticide can be  
105 transferred into infiltrating water close to the soil surface and transported rapidly to depth.  
106 Where chromatographic flow through the soil matrix is dominant, the timescales involved  
107 may be much longer providing a much greater opportunity for separation of the active  
108 substance from any co-formulants.

109 It is well established that hydrophobic partitioning is an important component of  
110 pesticide sorption for low-solubility, non-polar pesticides. This is not an active sorption  
111 mechanism, but rather involves a partitioning between soil aqueous phase and a non-specific  
112 surface of a solute introduced into the soil environment (Gevao *et al.*, 2000; Kah and Brown,  
113 2006). Hydrophobic bonding may also be regarded as solvent-motivated sorption where a  
114 hydrophobic solute is expelled from the water and becomes associated with the soil organic  
115 matrix. By changing the microenvironment surrounding a hydrophobic pesticide in soil  
116 solution, co-formulants could be expected to affect a change on sorption to soil constituents,  
117 and it might further be expected that the extent of this effect would be different for chemicals  
118 with different solubility in water. Here, we investigate the effect of commercial formulation  
119 on leaching of three pesticides through small soil leaching columns and compare results with  
120 those generated previously for propyzamide. Experiments aim to determine whether the  
121 observation of enhanced leaching of propyzamide from a commercial formulation compared  
122 to the technical grade pesticide can be generalised and whether any effect varies as a function  
123 of pesticide solubility in water.

124

## 125 **2. Materials and methods**

### 126 *2.1. Test materials*

127 A sandy loam soil (62% sand, 37% silt, 1% clay) of the Blackwood association was  
128 collected from the upper 5-15 cm of an arable field margin in York, UK (national grid  
129 reference 4648 4478). The soil has pH in water of 5.1, organic matter content of 2.7%, and  
130 water contents at 100 cm water tension and maximum water holding capacity of 0.22 and  
131 0.37 g g<sup>-1</sup>, respectively. Soil was air dried at room temperature, passed through a 2-mm mesh  
132 sieve, and stored at <5°C in the dark prior to use.

133 Pesticides used in this study were chosen to provide a gradient from low to moderate  
134 solubility in water whilst maintaining similar sorption characteristics and being stable to  
135 aqueous photolysis and relatively persistent in soil. Physico-chemical properties of the  
136 pesticides studied are summarised in Table 2. Analytical grade propyzamide, azoxystrobin  
137 and triadimenol (purity 99.6, 99.9 and 98.7%, respectively) were purchased from Sigma-  
138 Aldrich Ltd (Dorset, UK), while cyproconazole (racemic mixture of diastereomers A and B;  
139 purity 99.7%) was acquired from Alfa Aesar (UK). The commercial products Kerb® Flo  
140 (suspension concentrate (SC), 400 g L<sup>-1</sup> (35.3% w/w) propyzamide), Priori Xtra® (SC  
141 mixture of 200 g L<sup>-1</sup> azoxystrobin and 80 g L<sup>-1</sup> cyproconazole), Headway™ (emulsifiable  
142 concentrate (EC) mixture of 62.5 g L<sup>-1</sup> azoxystrobin and 104 g L<sup>-1</sup> propiconazole) and Veto®  
143 F (EC mixture of 75 g L<sup>-1</sup> triadimenol and 225 g L<sup>-1</sup> tebuconazole) were supplied by the Food  
144 and Environment Research Agency York, UK. Information on the co-formulants declared on  
145 the product labels are given in Table 2.

146 Deionised water was used to make up CaCl<sub>2</sub> solution for leaching experiments. All  
147 solvents used throughout and water used in pesticide extraction procedures were HPLC  
148 grade.

149

## 150 2.2. Leaching experiments

151 Leaching experiments were carried out in PVC columns (2 cm i.d. x 10 cm length).  
152 Each column was manually packed with 20 g of soil on an oven-dry weight basis with glass  
153 wool at the bottom to prevent loss of soil. Four replicate columns were prepared per treatment  
154 and for each leaching event. Soil was added to the columns in steps followed by gentle  
155 tapping to ensure uniform packing and achieve the same height of soil within each column  
156 (ca. 5.4 cm). Columns were then saturated from the base with 0.01M CaCl<sub>2</sub> and allowed to  
157 drain freely for 24 h under gravity. After this time, water held within the glass wool plug was  
158 evacuated by applying a small suction to the base of the column using a plastic syringe. The  
159 bulk density of the packed column was 1.18 g cm<sup>-3</sup> and this value was used to determine total  
160 porosity of 0.54 cm<sup>3</sup> cm<sup>-3</sup> based on an assumed particle density for topsoil of 2.55 g cm<sup>-3</sup>  
161 (Avery and Bascomb, 1982). One pore volume for each soil column was thus equivalent to  
162 9.20 cm<sup>3</sup>.

163 Eight soil columns each were treated with either technical or formulated material for  
164 azoxystrobin (EC and SC formulations), cyproconazole, propyzamide, and triadimenol,  
165 giving a total of 72 treated columns. A further four columns were untreated to act as controls.  
166 Each treated column received 100 µg of the respective pesticide. This is equivalent to 3.2 kg  
167 a.s. ha<sup>-1</sup> which is larger than typical field application rates and was selected to facilitate  
168 analysis for pesticides in leachate. Columns receiving technical pesticide were treated with  
169 0.1 mL of a 1000 µg mL<sup>-1</sup> solution in acetone; the solvent was allowed to evaporate before  
170 the addition of 0.5 mL deionised water. Columns receiving formulated pesticide were treated  
171 with 0.5 mL of a 200 µg active substance mL<sup>-1</sup> solution of the formulated material in  
172 deionised water. Immediately after treatment, a 1-cm layer of acid-washed sand was added to  
173 the top of each column. All columns were incubated in the dark and at <5°C until leaching.

174 Separate columns were leached either 1 or 7 days after pesticide application. At each  
175 leaching event, one set of four replicates from each treatment together with two control  
176 columns were irrigated with a total of six pore volumes (55.2 mL) of 0.01M CaCl<sub>2</sub> solution  
177 using a 323S Watson Marlow peristaltic pump at the rate of 12.6 mL hr<sup>-1</sup>. Rate of irrigation  
178 was equivalent to 40.1 mm hr<sup>-1</sup> which is at the upper end of natural rainfall intensities in  
179 temperate maritime climates such as that in the UK. Irrigation did not result in a continuous  
180 layer of water on the soil surface. Leachate was collected as a single fraction at the bottom of  
181 each column, weighed and stored in the fridge pending analysis.

182 A separate column leaching experiment was carried out with triadimenol to generate  
183 complete breakthrough curves for this compound. The aim was to determine whether the  
184 effect of pesticide formulation was to induce only a change in the timing of breakthrough or  
185 whether the total loss of pesticide in leachate was also changed. Eight soil columns were  
186 prepared and treated as described above, with four each treated with either technical or  
187 formulated triadimenol. All columns were leached 24 hours after pesticide application with a  
188 total volume of 165.6 mL of 0.01M CaCl<sub>2</sub> solution, equivalent to 18 pore volumes (323S  
189 Watson Marlow peristaltic pump at a rate of 12.6 mL hr<sup>-1</sup>). Leachate was collected in 10-mL  
190 fractions for separate analysis.

191

### 192 *2.3. Sample preparation for analysis*

193 For analysis of propyzamide in leachate, a 1-mL aliquot of each leachate sample was  
194 transferred into a test tube and evaporated to dryness under a gentle stream of nitrogen on a  
195 sample concentrator at room temperature. The residue was re-dissolved in 1 mL of hexane  
196 prior to analysis by GC-MS.

197 Leachate from columns treated with azoxystrobin was concentrated using solid-phase  
198 extraction (SPE), based on a method adapted from Montagner et al. (2014). Oasis HLB

199 cartridges ( $6\text{ cm}^3$ ) packed with 200 mg of  $30\ \mu\text{m}$  sorbent material were conditioned with 5  
200 mL each of methanol followed by acetonitrile followed by water using a 12-port SPE vacuum  
201 manifold (Supelco, UK). Leachate samples were passed through cartridges at  $1\ \text{mL min}^{-1}$ .  
202 After sample loading, cartridges were dried under vacuum for 20 mins and eluted with 4 mL  
203 methanol followed by 4 mL acetonitrile. Samples were evaporated to dryness under nitrogen  
204 and re-dissolved into 2 mL ethyl acetate. A further fourfold dilution step in ethyl acetate was  
205 undertaken prior to analysis by GC-MS.

206 Leachate samples containing triadimenol and cyproconazole were also concentrated  
207 using SPE. Oasis HLB cartridges ( $6\text{ cm}^3$ ) were pre-conditioned with 2 x 5 mL acetonitrile  
208 followed by 2 x 5 mL water. After loading samples, cartridges were dried under vacuum for  
209 20 mins and pesticides eluted with 5 mL acetonitrile. Samples were evaporated to dryness  
210 under nitrogen and then re-dissolved into 1 mL methanol. Subsequent dilutions in methanol  
211 (eight- to 28-fold) were required to deliver all samples for analysis within the range of the  
212 calibration standards.

213

#### 214 *2.4. Pesticide analysis*

215 Propyzamide and azoxystrobin were analysed by GC-MS. A PerkinElmer  
216 (Cambridge, UK) Clarus 680 gas chromatograph equipped with a Clarus 600 mass  
217 spectrometer and automatic split-splitless injector was operated in electron impact ionization  
218 mode with an ionizing energy of 70eV, scanning from  $m/z$  50-500 at 0.2 s per scan. The ion  
219 source temperature was  $180^\circ\text{C}$ . The electron multiplier voltage was maintained at 323 V, and  
220 a solvent delay of 3 min was employed. An Elite-5MS fused silica capillary column ( $30\ \text{m} \times$   
221  $0.25\ \mu\text{m}$  i.d. and  $0.25\ \mu\text{m}$  film thickness) supplied by PerkinElmer was used. The oven  
222 temperature was maintained at  $90^\circ\text{C}$  for 1 min, followed by a ramp to  $270^\circ\text{C}$  at a rate of  $20^\circ\text{C}$   
223  $\text{min}^{-1}$  for propyzamide, while for azoxystrobin, the oven temperature was programmed as

224 45°C for 1 minute, followed by a ramp to 295°C at 25°C min<sup>-1</sup> and held for 5 minutes.  
225 Helium was used as carrier gas with a flow rate of 20 mL min<sup>-1</sup> for both chemicals. Sample (1  
226 µL) was injected in splitless mode and the injector temperature was maintained at 250°C.  
227 There were six pre- and post-injection needle washes were programmed at six respectively.  
228 Analysis was performed with selected ion monitoring (SIM) mode using primary mass ions  
229 of m/z 173 and 344 for quantification of propyzamide and azoxystrobin, respectively. The  
230 target and qualifier abundances were determined by injection of propyzamide and  
231 azoxystrobin standards under the same chromatographic conditions using full scan with the  
232 mass/charge ratio ranging from m/z 50-500. Compounds were confirmed by their retention  
233 times and the identification of target and qualifier ion. Retention times had to be within 0.2  
234 min of the expected time, and qualifier-to-target ratios had to be within a 10% range for  
235 positive confirmation. The limit of detection (LoD) and limit of quantification (LoQ) for  
236 propyzamide were 0.02 and 0.05 µg mL<sup>-1</sup>, respectively whilst those for azoxystrobin were 0.1  
237 and 0.4 µg mL<sup>-1</sup>, respectively.

238 Triadimenol and cyproconazole were analysed on a PerkinElmer Flexar Chromera  
239 HPLC system with UV-vis detector and a Supelco 516 C-18-DB column (15 cm x 4.6 mm x  
240 5 µm). The mobile phase was an isocratic mixture of methanol and water (70:30 v/v) at a  
241 flow rate of 1.0 mL min<sup>-1</sup>. The injection volume was 20 µL and the oven temperature was  
242 maintained at 30°C. All analytes were determined at 221 nm. The retention time for  
243 triadimenol was 5.4 minutes whilst those for diastereomers A & B of cyproconazole were 4.7  
244 and 5.3 min, respectively. The LoD and LoQ for triadimenol were 0.3 and 0.7 µg mL<sup>-1</sup>,  
245 respectively, whilst those for cyproconazole were 0.4 and 0.9 µg mL<sup>-1</sup>, respectively.

246

247 *2.5. Data analysis*

248 Leaching behaviour was assessed based on the total mass of pesticide lost in leachate from  
249 individual soil columns. In addition, the relative difference in leaching from columns treated  
250 with formulated and technical pesticide was calculated by dividing the mean mass of  
251 pesticide in leachate from the former by that from the latter. Datasets were tested for  
252 normality using the Shapiro-Wilk test. Two-sided t-tests were used to investigate differences  
253 in losses from columns treated with technical grade and commercial formulations of  
254 individual pesticides. Two-way and multi-way ANOVA were carried out to test the  
255 significance of formulation and interval between application and irrigation on the leaching  
256 behaviour of pesticides. Tukey post-hoc tests were undertaken to test for differences between  
257 individual treatments over time; this is a pairwise comparison, similar to a t-test, but designed  
258 to compensate for the increased likelihood of a significant result occurring due to chance as  
259 the number of comparisons increases. All statistical analyses were undertaken in SPSS (IBM  
260 Analytics).

261

262 **3. Results**

263 *3.1 Influence of formulation on leaching behaviour*

264 The total volume of leachate collected from individual columns ranged between 53.28  
265 and 55.76 mL (96.5 and 101.0% of irrigation volume). There were no significant differences  
266 between treatments or between leaching time intervals (2-sided t-test).

267 Fig. 1 presents mass recovery for pesticides in leachate. Diastereomer A and B of  
268 cyproconazole were quantified separately, but are combined within Fig. 1 for simplicity.  
269 Statistical analyses reported below were undertaken both for each individual diastereomer  
270 and for the combination of the two. Leaching of the technical material was similar for  
271 azoxystrobin, cyproconazole and propyzamide (e.g. 6.0-7.8% of applied for irrigation 1 day

272 after treatment) despite a range in representative Koc of 364-840 mL g<sup>-1</sup>. Triadimenol leached  
273 to a much greater extent despite having a representative Koc value of 750 mL g<sup>-1</sup> (Table 1);  
274 this anomaly in behaviour was not investigated further. For reference, the average penetration  
275 depth (e.g. Leonard & Knisel, 1987) through the columns under the experimental conditions  
276 can be calculated at 2.2 cm assuming piston flow for a pesticide with Koc of 500 mL g<sup>-1</sup>. This  
277 value is consistent with the relatively small masses leached from the technical grade  
278 treatments (with the notable exception of triadimenol).

279         The mass of pesticide lost from treatments with commercial formulations of pesticide  
280 was consistently larger than that from treatments with technical pesticide (Fig. 1). This result  
281 applied for all compounds studied and for both leaching intervals and was highly statistically  
282 significant in every instance (two-sided t-tests, p<0.001). Two different formulations were  
283 investigated and compared with the technical treatment for azoxystrobin. Mass of pesticide  
284 leached from the three treatments (Fig. 1) were statistically different at both leaching  
285 intervals (two-sided t-tests) and increased in the order technical pesticide (6.0% of applied  
286 pesticide) < Priori Xtra® soluble concentrate (SC) formulation (8.5-9.1% of applied  
287 pesticide) < Headway™ emulsifiable concentrate (EC) formulation (15.8-21.0% of applied  
288 pesticide).

289         Absolute differences in pesticide leaching after 1 and 7 days were relatively small  
290 within any single treatment (maximum decrease in leached loss at 7 days relative to 1 day  
291 was 21% for propyzamide formulated material). Two-way ANOVA was used to test the  
292 effects of formulation and interval between application and irrigation on the leaching of  
293 individual pesticides (Table 3). The effect of formulation was highly statistically significant  
294 with p-values of <0.001 for all pesticides. The effect of interval to irrigation was statistically  
295 significant for azoxystrobin EC formulation and cyproconazole (p-values <0.001 and 0.002,  
296 respectively), but not azoxystrobin SC formulation, propyzamide or triadimenol. Interaction

297 between formulation and interval to irrigation was statistically significant for azoxystrobin  
298 EC formulation and cyproconazole (p-values <0.001 and 0.021, respectively), but not for the  
299 other chemicals. A multi-way ANOVA across the whole dataset showed highly statistically  
300 significant effects of pesticide type, formulation and an interaction between these two factors  
301 (all  $p < 0.001$ ). There was no effect of interval to irrigation on leaching ( $p = 0.096$ ), and no  
302 interaction between formulation and interval to irrigation on leaching ( $p = 0.584$ ). However,  
303 the interaction of formulation and pesticides was highly statistically significant ( $p < 0.001$ ).

304

### 305 *3.2 Influence of formulation as a function of pesticide solubility*

306 The ratio of the mass leached from the formulated treatment to that from the technical  
307 treatment was calculated (section 2.5) and is plotted in Fig. 2. All values were larger than one  
308 because leaching was greater from commercial formulations than from their equivalent  
309 treatments with technical pesticides in all cases. Values for the ratio of mass leached from  
310 formulated and technical treatments ranged between 1.4 for the SC formulation of  
311 azoxystrobin and 4.3 for the SC formulation of triadimenol. For our set of chemicals  
312 (solubility range  $6.7 - 93 \text{ mg L}^{-1}$ ), there was a clear trend of larger relative differences in  
313 leaching for more soluble compounds. In contrast, there was no consistent pattern in the  
314 relative effect of formulation on leaching for the two leaching intervals. Sometimes the ratio  
315 of mass leached from formulated and technical treatments was greater at day 1 and  
316 sometimes at day 7.

317

### 318 *3.3 Leaching of triadimenol through to full breakthrough*

319 Separate soil columns treated with triadimenol were leached with 18 pore volumes of  
320  $0.01\text{M CaCl}_2$  to investigate whether the effect of formulation on leaching was solely to retard  
321 leaching or also to influence the total amount of pesticide leached through soil. Breakthrough

322 curves (Fig. 3) showed more rapid leaching for columns treated with formulated material than  
323 for those treated with technical pesticide; breakthrough occurred in the 20-30 mL fraction for  
324 formulated material and in the 30-40 mL fraction for technical pesticide, whilst maximum  
325 leached mass was in the 30-40 and 40-50 mL fractions for formulated and technical  
326 materials, respectively. There was also a large difference in the mass of triadimenol leached  
327 across the experiment. Total leached loss from columns treated with formulated material was  
328  $79 \pm 1.2\%$  of applied, whilst that from columns treated with technical material was  $61 \pm 3.1\%$   
329 of applied. The maximum concentration of triadimenol in any fraction of leachate was  $2.6 \pm$   
330  $0.13$  and  $1.2 \pm 0.13 \mu\text{g mL}^{-1}$  for columns treated with formulated and technical materials,  
331 respectively. Total leaching of triadimenol from both treatments in the full breakthrough  
332 experiment (ca. 18 pore volumes; Fig. 3) was less than that from the main experiment (6 pore  
333 volumes; Fig 1). This suggests some variability in the hydraulic properties of the soil  
334 columns in the two experiments, but does not detract from the main findings of the study  
335 which always rely on comparison between treatments within a single experiment.

336

#### 337 **4. Discussion**

338 The most important finding from this research is that we observed enhanced leaching  
339 of all four pesticides from their commercial formulations relative to the technical materials.  
340 Relative differences in leached masses ranged between factors of 1.4 and 4.3, and all  
341 differences were highly statistically significant and were observed for leaching both 1 and 7  
342 days after treatment (Fig. 1 and Table 3). Examples of similar studies in the literature are  
343 rare. Our results are in accordance with those of Wybieralski (1992) who reported faster  
344 washout from soil columns by leaching of propoxur for emulsifiable and suspension  
345 formulations than for the technical material. The extended leaching experiment reported here  
346 for triadimenol adds to this early study by demonstrating that not only was breakthrough of

347 the pesticide observed earlier for the formulated treatment, but also both peak concentration  
348 and total mass of pesticide lost via leaching were larger for the commercial formulation than  
349 for the technical material. Co-formulants in the emulsifiable concentrate product of  
350 triadimenol influenced the initial availability of the active substance for leaching, resulting in  
351 earlier breakthrough; centrifugation experiments have shown a similar effect of a suspension  
352 concentrate formulation on availability of propyzamide in pore water (Khan and Brown, this  
353 issue). The full breakthrough experiment with triadimenol also indicates that the effect of co-  
354 formulants extends beyond influencing initial availability; less of the active substance  
355 became available for leaching for the technical treatment over the course of column elution  
356 with 18 pore volumes, implying a substantive change to sorption for at least a part of the  
357 active substance applied to soil.

358 Rank order for leaching losses of azoxystrobin reported here (Fig. 1) match the  
359 observations of Wybieralski (1992), with leaching increasing in the order technical material <  
360 suspension concentrate (Priori Xtra®) < emulsifiable concentrate (Headway™). Emulsifiable  
361 concentrate (EC) formulations comprise a solution of pesticide with emulsifying agents in a  
362 water insoluble organic solvent which is designed to form an oil-in-water emulsion upon  
363 dilution (Mulqueen, 2003; Knowles, 2008). The presence of oily water-insoluble organic  
364 solvents in EC formulations may affect the behaviour of pesticide active substances in two  
365 ways. First, it may restrict the pesticide molecule from dissolving in water and secondly, the  
366 oily organic solvents surrounding the pesticide molecule may retard processes controlling  
367 sorption to soil. Suspension concentrate (SC) formulations, also called flowables, usually  
368 comprise particles covering a wide size range (0.1-10 µm) dispersed in a liquid medium,  
369 generally water, at high solid volume fractions (up to 60%) and usually contain suspension  
370 agents, wetting agents and thickeners (Luckham, 1989).

371 Environmental fate of pesticides in soil is known to be influenced by solubility of the  
372 active substance in water (Delle Site, 2001; Fernández-Pérez et al., 2011; Langeron et al.,  
373 2014). Hydrophobicity of non-ionic pesticides can be a significant driver for partitioning of  
374 pesticides out of soil solution (Kah and Brown, 2006). It was plausible to hypothesise that  
375 any effect of co-formulants that increased the availability of the active substance in soil  
376 solution would be greater for pesticides with smaller solubility in water. In fact, the  
377 experiments demonstrated the opposite effect, with the difference in leaching between  
378 formulated and technical treatments being largest for pesticides with larger solubility (Fig. 2).  
379 We selected pesticides with low to moderate solubility (6.7 to 93 mg L<sup>-1</sup>) on the basis that  
380 solubility could be a limiting factor for availability in soil pore water soon after application.  
381 The mechanisms responsible for our findings are unclear, though it should be noted that we  
382 did not control for formulation ingredients so there may have been some systematic change in  
383 either the nature or concentration of co-formulants for the four active substances along our  
384 gradient of solubility.

385 As noted by Khan and Brown (this issue), the leaching experiments controlled for  
386 most aspects of study design but not for the means of initial addition of test materials to soil.  
387 All commercial formulations were added to columns in 0.5 mL 0.01M CaCl<sub>2</sub> solution,  
388 whereas technical materials were added in 0.1 mL acetone which was allowed to evaporate  
389 prior to adding pesticide-free CaCl<sub>2</sub> solution to match that added in the formulated  
390 treatments. Dosing in acetone is a possible source for experimental artefacts if, for example,  
391 the solvent resulted in enhanced transfer of pesticide into soil aggregates or precipitation of  
392 propyzamide on soil surfaces. A further possible confounder in the current experiments is that  
393 several of the commercial formulations contained a second active substance (Table 2). If  
394 there was competition for sorption then this could have exacerbated leaching from  
395 commercial formulations. This is considered plausible but unlikely on the basis of the

396 literature to date; there are occasional studies that investigate competition for sorption, but  
397 results are conflicting. Turin and Bowman (1997) investigated competition effects between  
398 herbicides by saturating other herbicides to 50% of their maximum sorbed amount; under  
399 these highly unrealistic conditions, they reported weaker sorption of bromacil and  
400 napropamide but not prometryn in the presence of the other herbicides. An opposite  
401 behaviour was shown by Tan and Singh (1995), with weaker leaching of norflurazon and  
402 either no effect or weaker leaching of bromacil when applied in combination with diuron,  
403 metolachlor, oxadiazon, simazine, terbacil or trifluralin. Ebato and Yonebayashi (2005)  
404 developed a method specifically to investigate competition effects, but reported that there  
405 was no competition for sorption between atrazine and linuron. Thus, evidence for direct  
406 competition for sorption between actives substances is sparse; any such competition between  
407 active substances in a single product could itself be considered a consequence of formulation  
408 into a commercial product that is not assessed routinely within risk assessment procedures.  
409 The strongest evidence that results were not due to experimental artefacts comes from the  
410 comparison of two formulations and technical material for azoxystrobin. Not only were there  
411 differences between formulated and technical material, but there were also large and  
412 consistent differences in behaviour of the two formulation types, confirming a genuine  
413 impact of co-formulants on leaching of the active substance.

414

## 415 **5. Conclusion**

416 Experiments have demonstrated a highly significant and consistent effect of  
417 commercial formulation on the leaching behaviour of four pesticides relative to the pure  
418 technical active substances in systems comprising small soil columns with intense irrigation  
419 applied 1 or 7 days after pesticide treatment. Relative differences in leaching between  
420 formulated products and technical materials ranged between factors of 1.4 and 4.3, and

421 differences were larger for active substances with greater solubility in water. Leaching to full  
422 breakthrough with triadimenol indicated that co-formulants influence both the initial and the  
423 total availability of pesticide for leaching; thus breakthrough from the formulated treatment  
424 occurred earlier and leached a greater total mass of the compound relative to the technical  
425 treatment. Experiments with two contrasting formulations of azoxystrobin showed  
426 differentiated influence on leaching for emulsifiable concentrate and suspension concentrate  
427 formulations. Results are reported for small, controlled systems with intense irrigation and  
428 these need to be scaled up to investigate behaviour under conditions closer to the field.  
429 Potentially, there are important implications for the assessment of environmental fate of  
430 pesticides which has been based to date on the assumption that sprayable formulations do not  
431 influence behaviour of the active substance in soil.

432

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**Table 1***Key physicochemical properties of the pesticides studied (Source: University of Hertfordshire, 2016)*

Properties	Azoxystrobin	Propyzamide	Triadimenol	Cyproconazole
CAS number and name	[131860-33-8] methyl ( $\alpha$ E)-2-[[[6-(2-cyanophenoxy)-4-pyrimidinyl]oxy]- $\alpha$ -(methoxymethylene) benzeneacetate	[23950-58-5] 3,5-dichloro-N-(1,1-dimethyl-2-propynyl)benzamide	[55219-65-3] $\beta$ -(4-chlorophenoxy)- $\alpha$ -(1,1-dimethylethyl)-1H-1,2,4-triazole-1-ethanol	[94361-06-5] $\alpha$ -(4-chlorophenyl)- $\alpha$ -(1-cyclopropylethyl)-1H-1,2,4-triazole-1-ethanol
Pesticide type and substance group	Fungicide, strobilurin	Herbicide, benzamide	Fungicide, triazole	Fungicide, triazole
Molecular mass (g mol <sup>-1</sup> )	403.4	256.1	295.8	291.8
Solubility in water (mg L <sup>-1</sup> ) at 20°C	6.7	9.0	72.0	93.0
Log octanol-water partition coefficient (Log P at pH 7, 20°C)	2.5	3.3	3.2	3.1
Soil organic carbon sorption coefficient (K <sub>oc</sub> , mL g <sup>-1</sup> )	589	840	750	364
Degradation half-life in aerobic soil at 20°C (days)	85 [persistent]	47 [moderately persistent]	137 [persistent]	142 [persistent]
Stability to aqueous hydrolysis	Stable	Stable	Stable	Stable
Half-life for photolysis in water (days)	9 [moderately fast]	41 [stable]	9 [moderately fast]	40[stable]

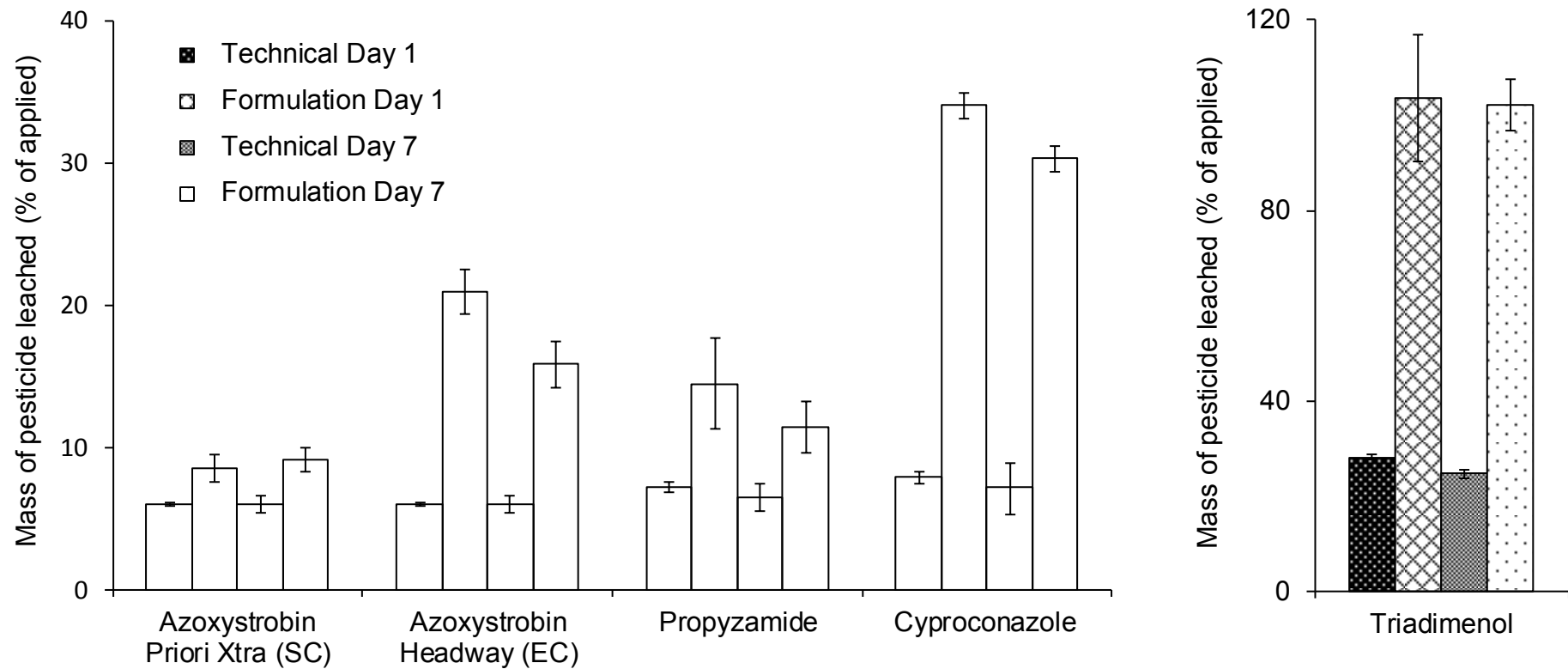
**Table 2***Information on formulation types and declared co-formulants for the commercial products used in experiments*

Active substance	Formulation	Additional active substance	Declared co-formulants	CAS of co-formulant	Principal role of co-formulant
Azoxystrobin	Headway™ Emulsifiable concentrate	Propiconazole (104 g L <sup>-1</sup> )	Tetrahydrofurfuryl alcohol (0.5 ppm)	97-99-4	Solvent
Azoxystrobin (200 g L <sup>-1</sup> )	Priori Xtra® Suspension concentrate	Cyproconazole (80 g L <sup>-1</sup> )	C16-18 alcohols, ethoxylated (10-20% w/w) Propane-1,2-diol (1-6% w/w) Naphthalene sulfonic acid,, dimethyl-polymer with formaldehyde and methyl- naphthalenesulfonic acid, sodium salt (1-5% w/w)	68439-49-6 57-55-6 9008-63-3	Nonionic surfactant Solvent Dispersant
Cyproconazole (80 g L <sup>-1</sup> )	Priori Xtra® Suspension concentrate	Azoxystrobin (200 g L <sup>-1</sup> )	See above	See above	See above
Propyzamide (400 g L <sup>-1</sup> )	Kerb® Flo Suspension concentrate	None	Propylene glycol (<5%)	57-55-6	Solvent
Triadimenol (75 g L <sup>-1</sup> )	Veto® F Emulsifiable concentrate	Tebuconazole (225 g L <sup>-1</sup> )	2-ethylhexanol propylene ethyleneglycol ether (1-25%) N,N-dimethylcapramide and N,N-dimethylcaprylamide (>1 - <25%)	64366-70-7 14433-76-2 & 1118-92-9	Nonionic surfactant Solvent

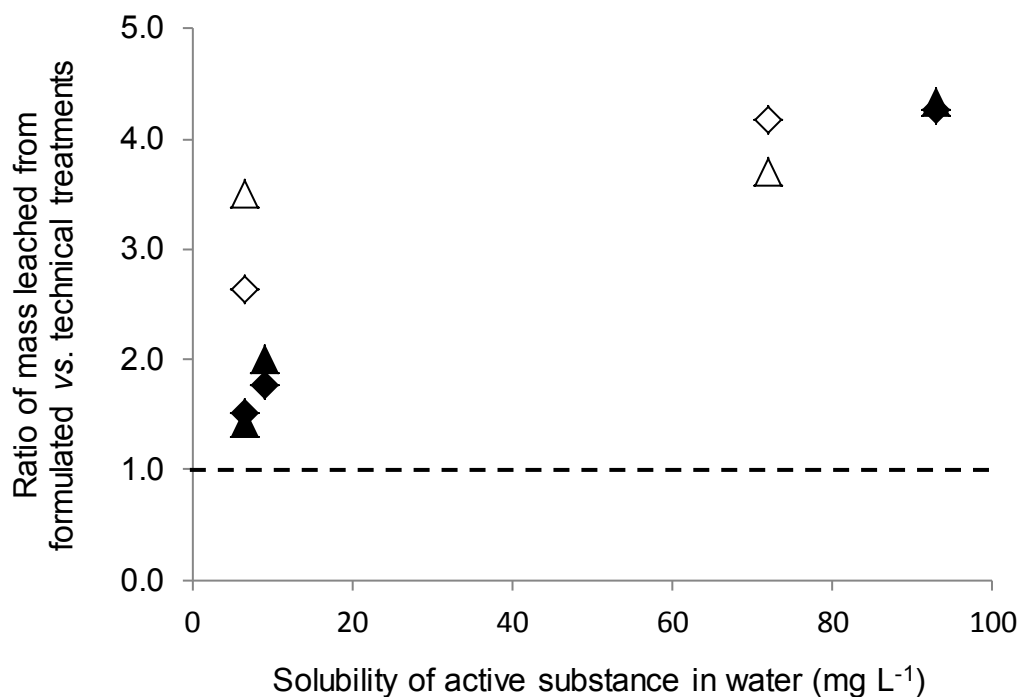
**Table 3**

*P-values from two-way ANOVA for the effects of formulation, interval between application and irrigation and interaction between formulation and interval on the leaching behaviour for the studied pesticides.*

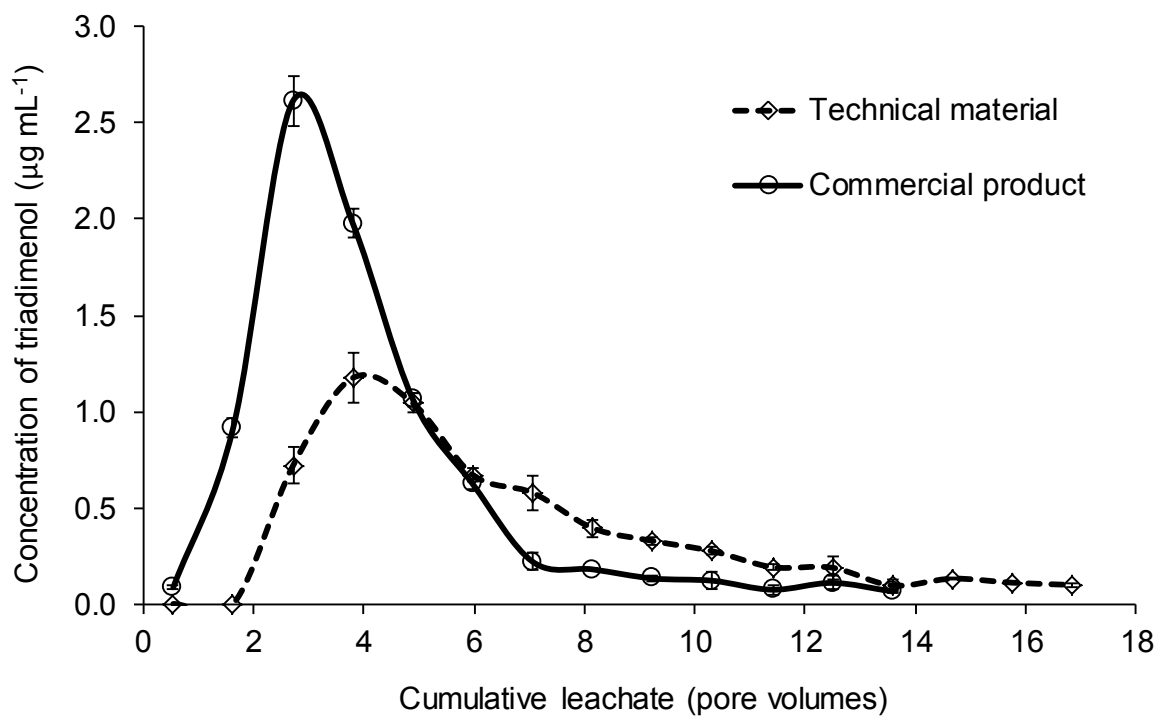
Pesticides	Formulation	Interval to irrigation	Formulation x Interval to irrigation
Azoxystrobin SC	<0.001	0.400	0.438
Azoxystrobin EC	<0.001	<0.001	<0.001
Propyzamide	0.001	0.221	0.526
Triadimenol	<0.001	0.515	0.771
Cyproconazole	<0.001	0.002	0.021
- Diastereomer A	<0.001	0.001	0.028
- Diastereomer B	<0.001	0.018	0.031



**Fig. 1.** Mass of pesticides leached through sandy loam soil treated with technical grade and commercial formulations of different pesticides. Error bars are  $\pm 1$  standard deviation for four replicates.



**Fig. 2.** Comparison of the relative difference in mass of pesticide leached between commercial formulations and technical material grade as a function of solubility in water of the active substance. Closed and open symbols are for suspension concentrate and emulsifiable concentrate formulations, respectively. Triangles and diamonds are for leaching 1 and 7 days after treatment, respectively. All values are above 1.0, indicating greater leaching from the commercial formulation than from the technical material.



**Fig.3.** Breakthrough curves of triadimenol following application of technical grade or commercial formulation to soil columns. Error bars are  $\pm 1$  standard deviation of four replicates.