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1 Analyzing Half-Lives for Pesticide Dissipation in Plants

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10

11

12 Abstract

13 Overall dissipation of pesticides from plants is frequently measured, but the contribution of
14 individual loss processes is largely unknown. We use a pesticide fate model for the quantification of
15 dissipation by processes other than degradation. The model was parameterized using field studies.
16 Scenarios were established for Copenhagen/Denmark and Shanghai/PR China and calibrated with
17 measured results. The simulated dissipation rates of 42 pesticides were then compared to measured
18 overall dissipation from field studies with tomato and wheat. The difference between measured
19 overall dissipation and calculated dissipation by non-degradative process should ideally be
20 contributable to degradation in plants. In 11% of the cases, calculated dissipation was above the
21 measured dissipation. For the remaining cases, the non-explained dissipation ranged from 30% to
22 83%, depending on crop type, plant part and scenario. Accordingly, degradation is the most relevant
23 dissipation process for these 42 pesticides, followed by growth dilution. Volatilization was less
24 relevant, which can be explained by the design of plant protection agents. Uptake of active
25 compound from soil into plants leads to a negative dissipation process (i.e. a gain) that is difficult to
26 quantify because it depends largely on interception, precipitation and plant stage. The process is in
27 particular relevant for soluble compounds.

28 Keywords: Plant protection; plant uptake; degradation; metabolism; transformation; herbicides;
29 insecticides; fungicides; modeling; simulation.

30 **Introduction**

31 Pesticides are used with the primary objective to control agricultural pests and to increase crop
32 yield. It is estimated that for example the economic return of the usage of pesticides from the past
33 60 years in the USA is around \$16 billion per year [1,2]. The grain production in India increased
34 nearly fourfold over a period of 50 years from 1948, and similar patterns are found in countries all
35 over the world [1,3]. With a projected increase in the world population from 6.1 billion in 2000 to
36 9.1 billion in 2050 the pressure on high crop yields will be even growing [4]. However, pesticides
37 have by definition toxic properties and can distribute within several media like air, soil and water,
38 followed by uptake into the tissues of living organisms including humans where they can be subject
39 to bioaccumulation and lead to negative effects [5-7]. The predominant exposure pathway for the
40 general public is thereby the intake of pesticides via residues in treated food crops [8,9]. In 2008, a
41 study investigating the presence of pesticides in food commodities throughout the 27 European
42 Union member states and Norway and Iceland with 11610 samples found residues of 365 different
43 pesticides in fruits and vegetables [10]. The percentage of samples with residues of two or more
44 pesticides present was 27%. Similar studies in 1997 and 2007 found the percentage of samples
45 containing residues of several pesticides to be 15% and 26%, respectively, underlining the presence
46 of pesticide residues in food commodities [10].

47 As controlled usage of agricultural pesticides is important, modeling of pesticide distribution in
48 crops is a key tool in limiting the overuse of pesticides and quantifying human exposure as relevant
49 component in human safety assessments. Several models estimating the uptake and translocation of
50 pesticides into food crops have been developed and an overview of such models is given elsewhere
51 [11-14].

52 All mechanistic plant uptake models critically rely on information describing different processes
53 contributing to dissipation from the treated crops and represent potential dissipation processes
54 typically in terms of process-specific rate coefficients or half-lives. Moreover, results of such
55 models (i.e. residual concentrations of pesticides in crop harvest) are highly sensitive to information
56 regarding specific dissipation processes, such as degradation. However, information for individual
57 dissipation processes in plants is often not available from experimental data. Instead, experimental
58 studies mostly report aggregated dissipation estimated from measuring the evolution of the overall
59 residual pesticide concentration in the plant over time. Fantke and Juraske [15] compiled a database
60 of such reported pesticide dissipation half-lives in plants based on the analysis of 811 studies

61 published between 1956 and 2012 with a total of 4513 experimental half-lives reported for 183
62 plant species. Despite the magnitude of this database, dissipation half-lives for many pesticide-crop
63 combinations are still not available, but need to be estimated instead. As a rule of thumb, the
64 disappearance half time from plants is four times faster than that from soil [16]. However, this easy
65 rule was disputed by use of other data sets, and a log-log regression for the relation between
66 disappearance in soil and plants was suggested instead [17]. A recent study showed that also plant
67 characteristics, temperature, and study conditions affect the overall dissipation of pesticides in
68 plants [18]. Process-specific information along with an insight of which processes are
69 predominantly contributing to overall dissipation in plants is still not available but required by most
70 mechanistic plant uptake models for estimating pesticide residues in harvested products. Such
71 information would furthermore be useful for interpreting the rather large variability of measured
72 data [15].

73 Collins et al. [19] reviewed key loss processes in modeling plant uptake of organic chemicals and
74 found metabolism, photolytic degradation on plant surfaces, volatilization to air and dilution due to
75 plant growth to be potentially significant processes. Of these, volatilization from plant surfaces to
76 air is a well-known loss process contributing to overall dissipation from plants. Van den Berg et al.
77 [20] report that the loss of pesticides to air after application as a function of pesticide, soil and crop
78 properties, application technique and environmental conditions ranges from a few percentages up to
79 60% of the total applied pesticide mass. Wolters et al. [21] identified volatilization as one of the
80 primary processes determining dispersion of pesticides throughout the general environment and
81 Riederer [22] described the equations for volatilization from leaves.

82 Growth is a dissipation process that does not reduce compounds' mass but leads to lower
83 concentrations by dilution. Hopkins et al. [23] found the loss through growth dilution alone could
84 account for 60% to 80% of initial pesticide deposit and Miles et al. [24] estimated that growth
85 dilution is of equal importance for dissipation as degradation and volatilization. Growth of annual
86 plants follows a logistic curve, and typical doubling times for plant volume during the exponential
87 phase range from 3 days for maize in May to 3 weeks for typical meadows in summer (own
88 observations, non-published). Growth can therefore be a very efficient dissipation process when
89 pesticides are applied during the exponential growth phase.

90 Degradation has been reported to be one of the predominant dissipation processes [25-27], but
91 measured values are rarely available. Komossa et al. [28] compiled values for the metabolism of

92 xenobiotics in cultures of suspended soybean and wheat cells. In these tests, there is often seen
93 rapid degradation within short time periods. For example, more than 90% of the herbicide 2,4-D
94 was degraded to mostly polar metabolites within 48 h by wheat cells [28]. These cell cultures are
95 quite different from intact plants, and parameters like substrate availability and temperature are
96 optimal for degradation, while endophytic microbes and photolysis do not contribute to degradation
97 in such experiments. The transferability of these results to field conditions is thus uncertain.
98 However, in vivo degradation by plants is difficult to track due to the complexity of processes.
99 Radiolabeled compounds have been used in several studies, e.g., Trapp et al. [29], but this method
100 is restricted to laboratory or controlled lysimeter studies. In those studies, the concentration of
101 transformation products is usually higher in plants than in soil. This indicates fast metabolism by
102 plant cells, but polar metabolites may concentrate in plants due to translocation from soil.

103 Even though individual dissipation processes are known and described, there is a lack of knowledge
104 on the contribution of these processes to the overall dissipation of pesticides from plants. Hence, an
105 accurate model able to describe the dissipation through both degradation and non-degradation
106 processes including volatilization and growth dilution is needed as resource-efficient element for
107 improving risk and comparative impact assessment models used by industry and regulating
108 authorities to reduce the unintentional impacts of pesticide usage. To address the need of applying
109 such a combined, process-specific model, the three main objectives of this study are (i) to
110 parameterize a dynamic soil-plant model for pesticides applied to plant and soil and to simulate the
111 non-degradation processes of pesticide dissipation, (ii) to compare simulated pesticide dissipation in
112 crops with measured overall dissipation data from published literature and (iii) to estimate the
113 contribution of degradation, growth dilution and volatilization to the overall loss of pesticides from
114 plants.

115

116 **Methods**

117 *Model description*

118 A coupled soil and plant uptake modeling framework was applied and extended that describes the
119 transport of water and solutes in soil and plants. The tipping buckets approach is applied for water
120 and solute transport in soil, and the dynamic plant uptake model (“Cascade model”) is used to
121 calculate the uptake, transport and fate of compounds in plants.

122 The tipping buckets model is based on the principals of water budgeting in discretized soil layers
123 [30-32]. The dynamic plant uptake model is well-described and consists of the four plant
124 compartments roots, stem, leaves and fruits [33-35]. The resulting differential equations are solved
125 analytically. The simulation time is divided into n periods, all having specific input data and
126 corresponding to the periods of the tipping buckets algorithm. This allows an easy coupling of soil
127 and plant modules and also the simulation of non-linear scenarios. For the current study the
128 simulated time was divided into 100 periods of one day lengths. Weekly precipitation events were
129 introduced to reflect the non-constant rain pattern in temperate climates. Spray application of
130 pesticides on leaves and soil surface was implemented as pulse source term. The combined soil and
131 plant uptake model is implemented in a Microsoft Excel spreadsheet and is taught in course 12906
132 at DTU. It was used and validated by Trapp and Eggen [36] for polar organic compounds and by
133 Højrup [37] for ionizing organic compounds. The model has previously been evaluated by Prosser
134 et al. [38], where it was concluded that the approach is able to predict the uptake of chemicals into
135 plants for real field studies.

136 ***Measured field dissipation data for model set-up***

137 For the establishment of the simulation scenario, the model was applied to literature data from three
138 field experiments where the dissipation of pesticides from plants was examined over time.

139 *Triazophos*. Li et al. [39] reported overall dissipation of triazophos in wheat. The field experiment
140 was conducted in 2003 on a site near Beijing, China. The triazophos residues in the sampled plant
141 components were measured two hours and 1, 3, 5, 7, 14, 21 and 30 days after application. For the
142 comparison with results from this study, our model was implemented with the soil degradation rate
143 reported by Liang et al. [40]. No measured degradation for triazophos in wheat plants was found in
144 the literature. Daily temperature and precipitation data for Beijing (see Supporting Information, SI)
145 during the reported growth season were used and the germination day was estimated based on
146 records of the local temperature and a minimum wheat germination temperature of 4 °C [41].

147 *Propiconazole*. Bai and Liu [42] reported overall dissipation of propiconazole in wheat. The field
148 experiment was conducted near Tianjin, China, between April and June 1984. During three
149 experiments, wheat fields were treated twice within 30 days with 125, 250 and 500 g/ha. Samples
150 were taken on the day of the application and 3, 10, 19, 29 and 34 days after the application. For the
151 comparison with results from this study, our model was implemented with the soil degradation rate

152 reported by Bromilow et al. [43] and the metabolic degradation rate for propiconazole in wheat
153 reported by Owen et al. [44]. Daily temperature and precipitation data for Beijing, China, were
154 used.

155 *Tralkoxydim*. Srivastava et al. [45] reported dissipation of tralkoxydim from wheat. The field
156 experiment was conducted in Pantnagar, India, from December 1991 to February 1992. Two
157 experimental fields were treated with 400 and 800 g/ha, respectively. Samples were taken 1 hour
158 and 1, 3, 7, 14, 28, 45 and 60 days after the application. The germination day was given in the
159 description of the experiments. An average degradation rate in soil was derived from the Footprint
160 database [46]. No degradation rate of tralkoxydim in wheat was found in the literature. Daily
161 temperature and precipitation data for New Delhi, India, were used.

162 ***Model scenarios for simulation of dissipation***

163 The model was applied to pesticides covering different target classes and a wide range of
164 physicochemical properties. Data of 42 pesticides were chosen from the pesticide dissipation
165 database provided by Fantke and Juraske [15] (Table S1). The data set includes herbicides,
166 fungicides, insecticides and plant growth regulators applied to tomato and wheat, with seven
167 pesticides simulated for both crop types. 56 different pesticide-plant combinations were simulated
168 in two scenarios with 25 pesticides simulated in tomato fruit, eight pesticides in tomato leaves and
169 23 in wheat leaves.

170 *Location*. Two locations, Copenhagen and Shanghai, were simulated as virtual agricultural fields
171 positioned near the two cities. Copenhagen (55.6761 °N, 12.568 °E) is located on the eastern coast
172 of the island Zealand in Denmark and has a temperate climate. Shanghai (31.2000 °N, 121.5000 °E)
173 is located on the Yangtze River delta on the eastern Chinese coastline near the Pacific Ocean and
174 has a subtropical climate. A description of the metrological data [47] can be found in the SI.

175 *Crops*. The two crop types selected for the simulations are wheat (*Triticum aestivum* L.) and tomato
176 (*Solanum lycopersicum*). In the most recent world production estimates of the Food and Agriculture
177 Organization of the United Nations, the global production of wheat for 2014 is 707 million tons
178 [48]. The combined worldwide production of tomato exceeded 160 million tons in 2012 [49]. Data
179 for the crop-specific parameters for wheat simulations were taken from [34], for tomatoes from
180 [14,50] and cell data from [51].

181 *Initial mass distribution.* The distribution of the applied active ingredient sprayed on plant and soil
182 is based on the crop interception factors suggested by the FOCUS group [52], where an interception
183 coefficient, depending on the growth stage, of 25% for wheat and 50% for tomato is suggested. A
184 similar interception coefficient for wheat was found by Bai and Liu [42]. All active ingredients
185 were uniformly distributed to the above-surface plant compartments, weighted with their specific
186 surface area at the time of application.

187 *Chemicals.* A list of the 42 selected pesticides with their chemical class and physical and chemical
188 properties can be found in the SI (Table S1). The chemical properties range from log K_{OW} -3.8
189 (chlormequat, growth regulator) to 6.6 (cypermethrin, insecticide) and molar mass M from 141.1
190 g/mol (methamidophos, insecticide) to 682.3 g/mol (flubendiamide, insecticide) and thus cover a
191 wide chemical space.

192 *Overall dissipation rate.* The simulated overall dissipation rates of each modeled compartment were
193 calculated as pseudo-first order loss rates from the peak concentrations of the compartments and the
194 concentrations at the 75th percent dissipation. If the simulation period expired before reaching the
195 75th percent dissipation, the concentration at the end of the simulation period was used. The
196 individual loss rates of the compartments were calculated from the average of the rates of a given
197 process over a seven day period, starting at the day of pesticide application. The calculated
198 dissipation rates were compared to experimental rates collected from literature [15] (SI Tables S2
199 and S3).

200 *Significance of loss processes*

201 To examine the significance of three key physical and chemical properties of the pesticides on the
202 distribution of the individual dissipation processes, nine chemicals with high/low values of the three
203 key properties K_{OW} , K_{AW} and molar mass M were simulated. These are phorate, penconazole,
204 chlorothalonil, propiconazole, azoxystrobin, cyfluthrin and methomyl plus one theoretical chemical
205 with mean values of the three parameters from the 42 chemicals simulated in the current study and
206 the fictive chemical fantene (low log K_{OW} = 1.5, high log K_{AW} = -5 and M = 450 g/mol).

207 **Results**

208 *Model performance*

209 Figure 1 shows the simulation results compared to the reported results from three field dissipation
210 studies. Figure 1a shows the residues of the insecticide triazophos after the application on wheat
211 [39]. The input of active ingredient (39.6 g/ha intercepted by leaves) was calculated from the
212 measured initial concentration of pesticide in the crop, to avoid false mass balances. The initial
213 concentration in the leaves was 19.4 mg/kg fresh weight (fw), and the mass of leaves at the time of
214 application (day 46 after plant growth started) was 0.204 kg. Subsequently, the calculated input for
215 the leaf compartment is 3.95 mg. The remainder of the applied pesticide was input into the soil.
216 Therefore, the peak of the modeled concentrations of the leaf compartments is identical with the
217 peak of the measured concentrations (Fig. 1a). The modeled dissipation of triazophos is lower than
218 the measurements. Assuming pseudo-first order loss, Li et al. [39] fitted a dissipation half-life of
219 5.59 days. The simulated half-life in leaf due to non-degradation loss processes alone is 9.59 days,
220 nearly twice as long as the fitted dissipation half-life from the measurement study that includes
221 degradation.

222 Figures 1b and 1c show the measured and the simulated leaf concentrations of the herbicide
223 tralkoxydim after a low and high dose application of 400 and 800 g/ha, respectively. The peaks of
224 the measured concentrations of 0.27 and 0.55 mg/kg for the two scenarios occur with the
225 application of the pesticide, whereas the peaks for the two simulated concentrations occur five days
226 later and are 0.34 and 0.68 mg/kg fw for the low and high dose application, respectively. This delay
227 is due to calculated uptake of active ingredient from soil to the leaf compartment after the
228 application. Due to uptake from soil after application, the simulated dissipations curves are delayed
229 compared to the measured data points. The input of the pesticide was adjusted as explained for
230 Figure 1a. The calculated curve could be fitted but the underlying problem seems to be a
231 disagreement of plant biomass. A mass balance with measured initial concentrations, applied mass
232 of tralkoxydim and with 25% interception by the plants [52] reveals that the biomass at the time of
233 the application (day 30) should have been 37 kg/m² (a value that is very unrealistic). In the model
234 scenario, the mass of the leaf compartment at the day of application is only 0.09 kg/m², a difference
235 of nearly a factor 400. The true plant size was not measured or not given, a common problem in the
236 simulation of measured field data. We decided to keep the top soil concentrations data of the
237 authors and the plant scenario and accept the deviation caused by uncertain input data for plant

238 biomass. According to Srivastava et al. [45], the dissipation of the low and high dose application
239 measurements occurred with half-lives of 5.5 and 4.25 days, respectively. The simulated dissipation
240 curves, without degradation and expressed as pseudo-first decay, gives for both simulations a half-
241 life of 9.86 days.

242 Figures 1d-f show the measured and simulated concentrations of propiconazole in wheat after
243 application of 125, 250 and 500 g/ha. In the field experiments the wheat crops were exposed to two
244 applications of equal dimensions with a 30-day interval. For the three scenarios the pesticide
245 interceptions given by Bai and Liu [42] (between 24.2% and 27.5% of the applied amount, in total
246 99.3 g/ha to wheat straw and 310 g/ha on top soil) were used instead of the FOCUS
247 recommendations (25% interception, [52]) but the difference is small. Different from the previous
248 comparisons, it was not necessary to adjusted to the measured initial concentrations because the
249 interception was given. The day the biomass of the model scenario reaches the biomass reported for
250 the experiment is six days apart. This leads to a small overestimation of the leaf concentrations
251 immediately after the application but the agreement later on is satisfying. The calculated peak
252 concentrations are on average 154% of the measured peak concentrations. The 125 and 500 g/ha
253 scenarios show 160% of the measured peak concentrations, while the 250 g/ha scenario shows
254 143% of the measured peak concentration. The experimental half-lives derived from the measured
255 concentrations are 3.7, 3.7 and 5.9 days for the 125, 250 and 500 g/ha applications, respectively.
256 The corresponding simulated half-life is 2.92 days for all three scenarios, and this includes the
257 measured degradation in plants [44].

258 *Dissipation rates*

259 In Figure 2, the simulated dissipation rates from wheat and tomatoes of the 42 different pesticides
260 (sorted by measured loss rates) are shown in comparison to experimental dissipation rates collected
261 from literature [15]. The error bars denote the range of literature data for each individual pesticide
262 (numbers to names see SI Table S1). The minimum, geometrical mean and maximum of literature
263 data together with the calculated loss rates, the contribution of individual processes, and the
264 difference between experimental and calculated loss rates is shown for each pesticide in the SI
265 (Tables S2 and S3).

266 Most of the calculated loss rates – sum of growth dilution and volatilization minus uptake from soil
267 – are in a narrow band between 0.05 and 0.1 d⁻¹, while the measured loss rates (that additionally

268 include degradation) vary in a much broader range. Ideally, all simulated dissipation rates should be
269 equal to or slower than the experimentally derived dissipation rates because degradation is not
270 included in the simulation, but adds to the loss processes.

271 Figure 2ab shows the simulated dissipation rates of 25 pesticides in tomato fruits near Copenhagen
272 and Shanghai, respectively. Only four of the simulated dissipation rates in the Copenhagen scenario
273 are higher than their corresponding experimental dissipation rates from literature (geometric mean),
274 that are the rates of cyproconazole (no. 3), penconazole (no. 2), triazophos (no. 4) and phorate (no.
275 1). These four compounds have the lowest measured dissipation rates. The simulated rates of
276 cyproconazole, triazophos and phorate also exceed the maximum dissipation rates given in
277 literature. For the Shanghai scenario, the simulated rates of cyproconazole, penconazole, phorate,
278 procymidone (no. 5) and triazophos exceed the geometrical mean of literature dissipation rates,
279 while only the simulated rates of cyproconazole, phorate, procymidone and triazophos exceed the
280 maximum literature dissipation rates. For both scenarios, most of the calculated dissipation is due to
281 growth dilution. Growth dilution does not depend on the chemical but only on the crop growth and
282 the time of application. Volatilization increases the loss only for a few compounds. Uptake of active
283 ingredients from soil into plants is an input process that counter-acts loss, i.e. it decreases the
284 simulated overall dissipation from leaves or fruits. For both scenarios the simulated dissipation rate
285 of mancozeb (no. 17) is much lower than the mean experimental rate, and also those by growth
286 dilution and volatilization alone. The reason for this outlier is a very high (calculated) uptake of
287 mancozeb from soil. Mancozeb is a polar weak acid, and the estimated distribution coefficient
288 between soil matrix and soil solution, K_d , as well as the root uptake are rather uncertain and pH
289 dependent [35,53,54]. If uptake from soil is neglected, then calculated results are closer to the
290 dissipation values of mancozeb from literature.

291 The dissipation rates of 25 pesticides in tomato fruits and of eight pesticides in tomato leaves from
292 literature versus calculated dissipation are shown in Figure 2c (Copenhagen) and 2d (Shanghai
293 scenario). Growth dilution is again the most relevant calculated dissipation process. For both
294 scenarios, three of the 23 simulated pesticide rates are higher than the corresponding literature rates
295 that are chlorothalonil (no. 31), diazinon (no. 36) and tebuconazole (no. 27). Two simulated rates of
296 chlorothalonil and diazinon are considerably higher than their literature values in both scenarios,
297 and high volatilization is the reason for the calculated rapid loss. The adsorption to leaves, which is
298 indirectly proportional to volatilization from leaves, depends in the model on the ratio of the

299 partition coefficients K_{OW} and K_{AW} , and together with phorate (no. 1), these two compounds have
300 the lowest value for this property of all (non-ionic) substances under consideration.

301 *Loss distribution*

302 Figure 3 illustrates the importance of the individual loss processes for the example of triazophos in
303 the field experiment [39]. Both volatilization and growth dilution are important in this case. The
304 effect of uptake from soil is a negative loss rate, i.e. input to the plant. Due to the non-steady
305 precipitation events (rain every 7 days) the line is not smooth.

306 The contribution of individual loss processes of nine example compounds is shown in Table 1. Each
307 compound in this list has a typical combination of the three key properties K_{OW} , K_{AW} and M : each
308 property was divided into a high and low category and eight pesticides were chosen to represent the
309 spectrum of all 42 pesticides under investigation. A ninth, theoretical compound represents the
310 average of the 42 compounds of the study. The scenario is tomato grown in Copenhagen.

311 The growth dilution for all nine chemicals in each of the four plant compartments is identical, 0.06,
312 0.06, 0.07 and 0.13 d^{-1} for the compartments root, stem, leaves and fruits, respectively. The %
313 contribution to the overall loss, however, varies widely and depends on the magnitude of additional
314 loss and transport processes. Growth dilution is most relevant for compound no. 8, cyfluthrin,
315 which is the most insoluble, non-polar compound in the list. For the remaining compounds, which
316 are all more soluble, the dominant loss process from roots and stems is translocation upwards.
317 Uptake from soil balances the loss by translocation to a varying degree, most for compound no. 4
318 (the theoretical compound with $\log K_{OW}$ 1.5) and no. 7 azoxystrobin, a non-volatile medium polar
319 fungicide. The translocation ends in fruits and leaves, and growth dilution gains importance. It
320 competes with volatilization to air, in particular for loss from leaves. For average compound no. 4,
321 phorate (no. 2) and chlorothalonil (no. 5) volatilization is the dominant loss process. All three have
322 a partition coefficient air-to-water $K_{AW} \geq 10^{-5}$ L/L, which is relatively high for pesticides. Overall,
323 volatilization plays a minor role, compared to growth dilution and translocation, because most
324 pesticides have by design a low K_{AW} (Table SI 1).

325 Table 1 also includes the calculated impact of transfer from soil into plants on the overall
326 dissipation from each plant compartment. Uptake from soil has, no surprise, the highest influence
327 on the root and stem compartments. The highest transfer rate from soil was calculated for chemical

328 no. 9, methomyl, which represents a pesticide with a low K_{OW} , low K_{AW} and low molar mass, with
329 a corresponding rapid uptake rate of -8.70 d^{-1} .

330 **Discussion**

331 *Simulations.* As seen in Figures 1a-c, all calculated concentrations are above the measured data
332 points. This was expected because the three simulations do not include internal plant degradation.
333 The simulation of penconazole (Figures 1d-f) fits best the measured data points even though it is the
334 only compound where the input was not adjusted. But this simulation of penconazole includes a
335 measured rate for internal plant degradation [44]. The dissipation of penconazole occurs slightly
336 faster in the simulation than in the field experiments (Figures 1d-f), indicating an overestimated
337 degradation rate. The plant variety used in the study by Owen et al. [44] is *Triticum aestivum* var.
338 “Heines Koga II” whereas the exact variety of the *Triticum aestivum* used in the field experiments
339 [42] is not given. The internal plant degradation rate found by Owen et al. [44] is higher than the
340 dissipation rate found by Bai and Liu [42] but no other degradation rate of penconazole in wheat is
341 reported in the literature.

342 *Location matters.* As can be seen in Figures 2a-f, the differences in measured dissipation rates (and
343 thus perhaps also of degradation rates) can be considerable. In the simulations, the dissipation rate
344 for Shanghai was in many cases less than that for Copenhagen, but only after uptake from soil was
345 added. Both temperatures and precipitation are higher in Shanghai, and subsequently also
346 transpiration and translocation from soil to plant are higher, leading to increased uptake of
347 compound from soil to plant. This uptake from soil depends very much on the chemical properties.
348 In Figure 1bc a strong effect of tralkoxydim uptake from soil leads to an increase and delay of the
349 peak. This is not the case for triazophos (Figure 1a). Triazophos has a $\log K_{OW}$ of 3.5 and sorbs
350 stronger to the soil organic carbon than tralkoxydim with a $\log K_{OW}$ of 2.1. Methomyl had the
351 highest change of loss rates due to uptake from soil in Table 1. In agricultural practice, the good
352 translocation of methomyl from soil to plants allows the application of this insecticide by drip
353 irrigation. A cascade plant uptake model like the one used in our study (but with only one soil
354 compartment) was well able to calculate this uptake from soil accurately [25], which shows both
355 that this process is of relevance for polar non-volatile compounds, and that the model is a valid tool
356 for the prediction of uptake from soil. Simulations show that the relevance of this process depends
357 on the interception (i.e., how much of the active ingredient reaches the soil at all) and thus on the
358 growth stage; on the availability of water to the roots in the various soil layers (and therefore also

359 on precipitation events before and after application); on the transpiration of the plants (and thus on
360 leaf area, light and temperature); and on the sorption, leaching and degradation of the substance in
361 soil. In summary, the underlying processes are complex, highly variable, site-specific and difficult
362 to predict.

363 Higher temperature is typically associated with higher degradation rates [18,25,55] but this did not
364 affect the simulations not explicitly considering degradation in plants. FOCUS distinguishes
365 between nine different scenarios that shall represent the span of agricultural practices in Europe
366 [52]. However, field studies on pesticide degradation in soils gave little differences in degradation
367 between Northern and Southern Europe and between North America and Europe [56,57]. The
368 reason could be humidity: microbial degradation of pesticides in soil works best at optimal, medium
369 water contents and is reduced in dry but also in very wet soil [58,59].

370 *Degradation rates.* Degradation can be directly measured by use of labeled compounds [58], but
371 this is nowadays not permitted for field conditions. Under the assumption that the model
372 appropriately describes the dissipation processes of chemicals other than degradation, the difference
373 between the empirical and the calculated loss rates represents degradation inside plants, either by
374 enzymatic transformation or by photolysis. Then, the difference between the predicted loss (without
375 degradation) and the experimentally determined loss (including degradation) gives the unknown
376 degradation. This difference between predicted dissipation and the geometric mean of
377 experimentally determined values from literature varies greatly between the 42 modeled compounds
378 (Figure 2 or SI Tables S2 and S3). For most compounds, measured loss rates are clearly higher,
379 which means that degradation is an important and often the dominant loss process. The average
380 distribution between the loss processes for all 25 chemicals simulated in the Copenhagen tomato
381 fruits scenario is 54.8% growth dilution, 1.6% volatilization and 43.6% (calculated) degradation in
382 plants, respectively. The average distribution between the three loss rates for tomato fruits in the
383 Shanghai scenario is similar with 56.4%, 1.2% and 42.3% for growth dilution, volatilization and
384 degradation, respectively. For tomato leaves the equivalent distributions are 13%, 2% and 85% and
385 15%, 2% and 83% for the Copenhagen and Shanghai scenarios, respectively. For the wheat scenario
386 the distribution between growth dilution, volatilization and degradation is 41%, 67% and -8% for
387 the Copenhagen scenario and 31%, 39% and 30% for the Shanghai scenario.

388 As reported, the simulated loss rates from tomato fruits of the four chemicals cyproconazole,
389 penconazole, phorate and triazophos exceed the geometrical mean of the literature rates, and this

390 leads to negative loss percentages for degradation and skews the average distribution. Without, the
391 numbers for dissipation from tomato fruits are 37.1%, 0.5% and 62.4% growth dilution,
392 volatilization and degradation for the Copenhagen scenario and 40%, 0% and 60% for the Shanghai
393 scenarios. The corrected values for wheat are 27%, 5% and 68% growth dilution, volatilization and
394 degradation for the Copenhagen scenario and 21%, 3% and 76% for the Shanghai scenario. These
395 numbers show that degradation of pesticides in plants will usually be the main dissipation process,
396 closely followed (and often exceeded) by growth dilution. Most pesticides have a rather low vapor
397 pressure, because this increases their residence time on plant surfaces, and thus volatilization is of
398 little relevance for this kind of compounds.

399 *Bound residues and metabolites.* Plants are well known to incorporate pesticides into bound and
400 non-extractable residues that are not accessible to standard analysis [60]. This is because plants
401 often use conjugation reactions for detoxification, and vacuolization or deposition in cell walls
402 replace excretion processes [28]. These bound residues may therefore still pose a risk to consumers
403 and deserve consideration in risk assessment [60]. Contrary, dissipation by growth dilution or
404 volatilization does not lead to bound residues. Risk assessments using a default, minimum
405 dissipation rate based on the latter processes are therefore conservative and safe, and we
406 recommend, in cases where no loss rate is known, to calculate the loss by these processes.

407 *Other findings.* Previous studies quantifying the effect of growth dilution found conflicting results.
408 Miles et al. [24] found that effect of growth dilution was of minor importance for the short-lived
409 residues of malathion ($\log K_{OW}$ 2.75) but relevant for the more persistent methoxychlor ($\log K_{OW}$
410 5.83) [55]. Hopkins et al. [23] gives an average reduction by growth dilution of 60-80% on alfalfa
411 within four to six weeks after application. Both Miles et al. [24] and Génard et al. [61] note the
412 importance of the time of application (i.e. the growth stage) for the relevance and amount of growth
413 dilution. This is confirmed by the model simulations, where growth of the crops is expressed by the
414 logistic growth function [34,50]. Growth dilution is highest during the initial, exponential growth
415 phase and slows down towards ripening.

416 Fantke et al. [18] developed a regression model for the estimation of pesticide dissipation half-lives
417 (including degradation) from substance properties, plant characteristics and environmental
418 conditions including temperature. 95% of the predicted half-lives were within a factor 4.5 of the
419 reported half-lives taken from Fantke and Juraske [15].

420 **Conclusions**

421 In this study we parameterized a coupled dynamic model for the simulation of neutral and ionizable
422 organic compounds in soil, soil water and crops for the application and residence of pesticides after
423 spray application on wheat and tomatoes in Copenhagen and Shanghai.

424 The comparison to measured residues in leaves and fruits showed reasonable dissipation results
425 which were – with few exceptions – slower than experimental loss rates from experimental field
426 studies. This can be explained by the metabolism and degradation of pesticides in plants which were
427 disregarded in the simulations. From the difference to measured dissipation of 42 pesticides, we
428 thus quantified the contribution of degradation, growth dilution and volatilization to the overall loss
429 of pesticides from plants.

430 The average distribution between the growth dilution and the volatilization rate for the calculated
431 dissipation rates from tomato fruits showed the growth dilution to be far more significant than
432 volatilization, while this latter process was of higher relevance for leaves. The average reduction in
433 residual concentrations in tomato fruits by growth dilution was found to be 37% of the overall
434 dissipation. For tomato leaves the average reduction of pesticide concentration by growth dilution
435 was 13%, and in wheat 21%. Volatilization contributed in all simulation scenarios with up to 5%
436 only. Growth dilution is thus the next most important dissipation process, after degradation, for the
437 reduction of the pesticide residues and the crops studied. Uptake of active compound from soil to
438 plant leads to a negative dissipation process (i.e. a gain) that is difficult to quantify because it
439 depends largely on interception, precipitation and plant stage. The process is in particular relevant
440 for soluble compounds. For the root and stem compartments, translocation of residues by the
441 transpiration stream in and out is of very high importance, depending on the adsorption of the
442 studied compounds. The process increases with decreasing K_{ow} .

443 It finally became obvious that the number of studies published with sufficient data for a comparison
444 to simulations is small. In particular plant properties often lack but are of importance [62]. This
445 hampers the development and validation of predictive relationships and models.

446 **Acknowledgements**

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449

450 **References**

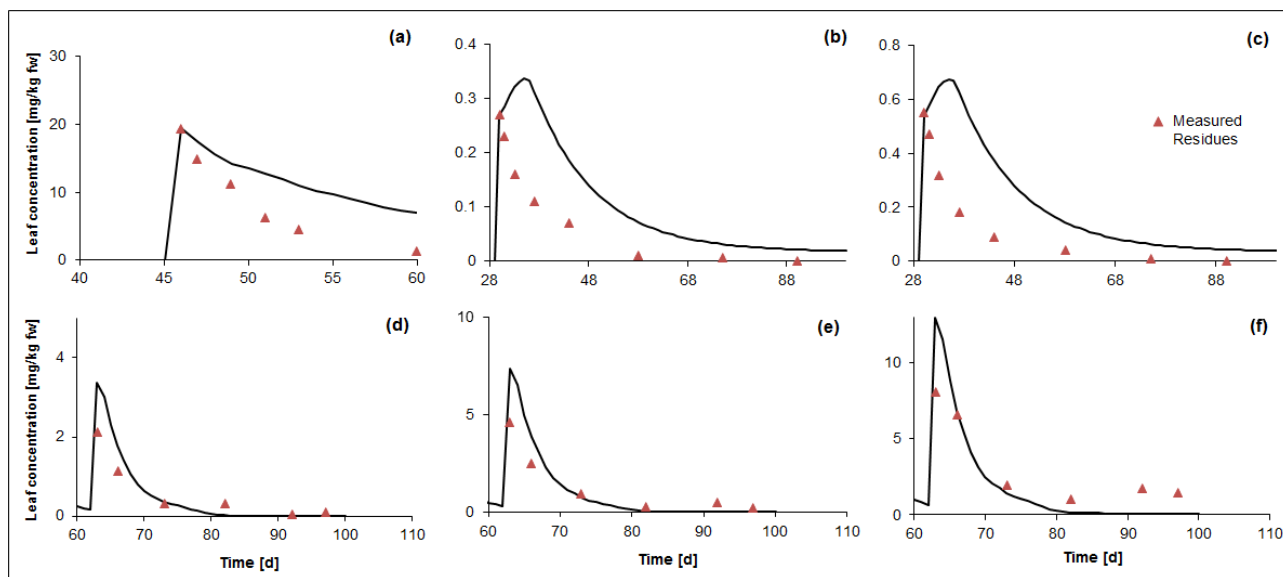
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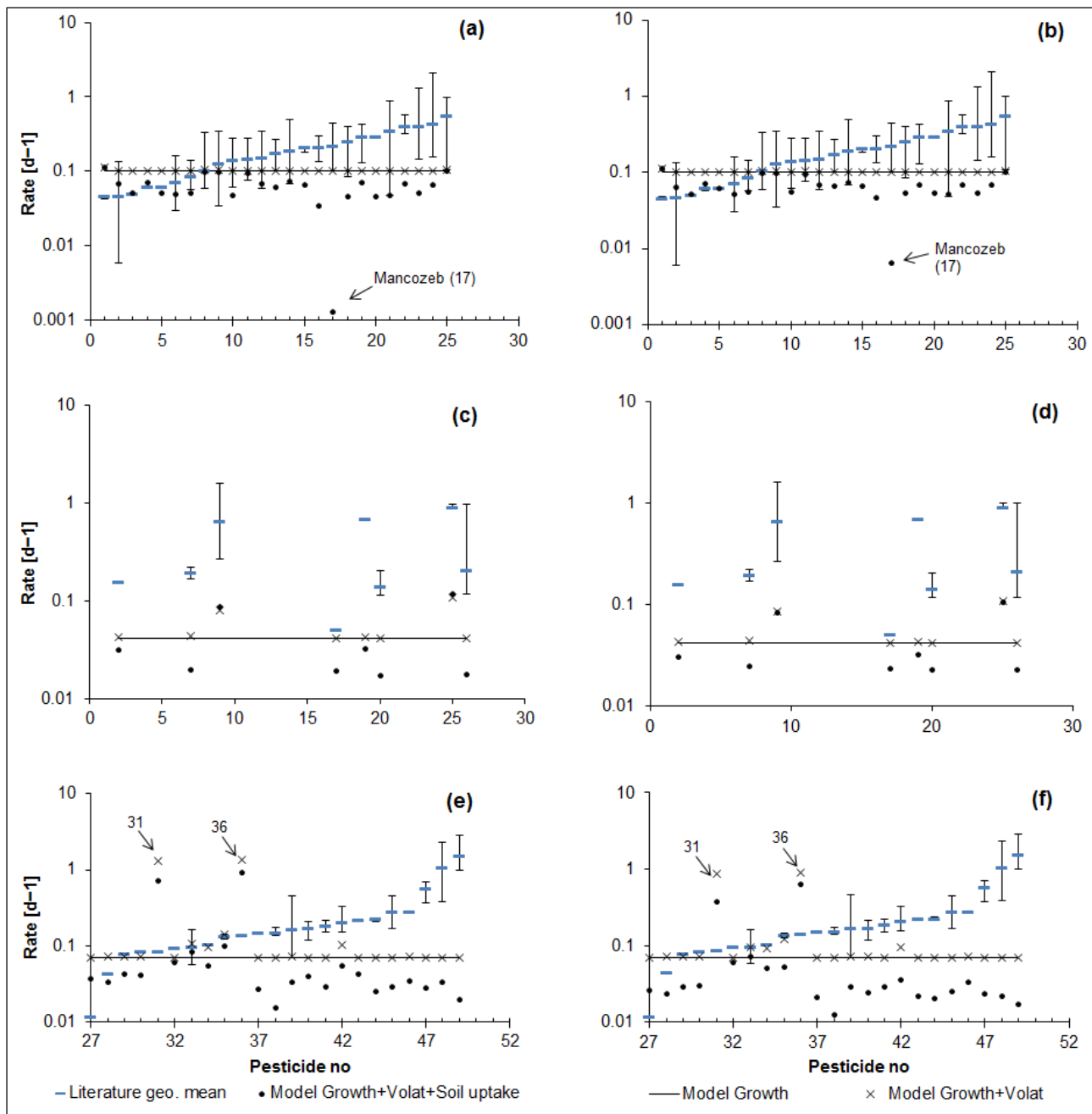
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- 611



613

614 **Figure 1.** Measured (symbols) and simulated (solid line) concentration in leaves (mg pesticide per
 615 kg sampled plant fresh weight) versus time (days after germination); a) triazophos [39], b) and c)
 616 tralkoxydim [45], d), e) and f) penconazole [42].

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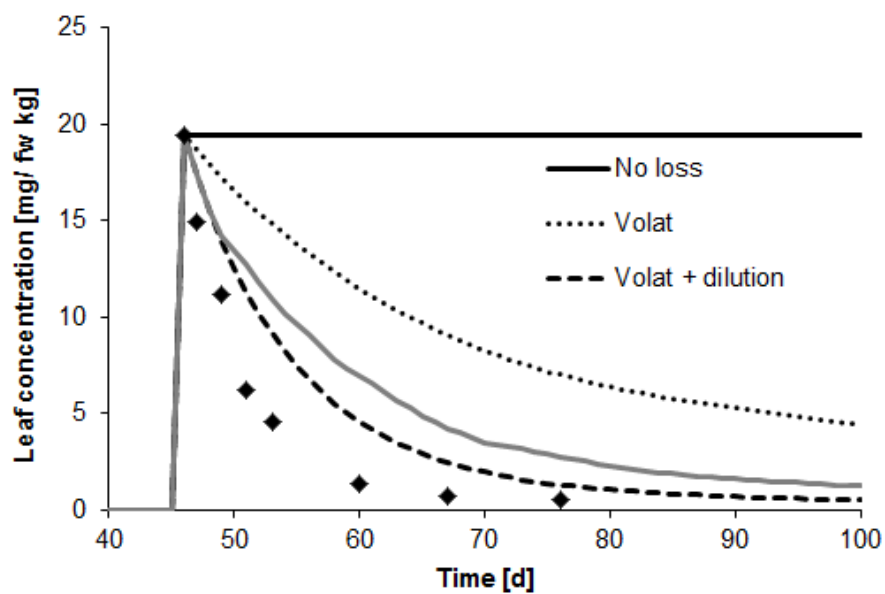


618

619 **Figure 2.** Geometric mean of experimentally derived dissipation rates [15, SI Tables S2 and S3]
 620 compared with simulated dissipation rates for growth dilution, volatilization and overall dissipation
 621 including uptake from soil. Error bars denote minimum and maximum of reported experimental
 622 data. Scenarios: a) tomato fruit in Copenhagen b) tomato fruit in Shanghai c) tomato leaf in
 623 Copenhagen d) tomato leaf in Shanghai e) wheat leaf in Copenhagen f) wheat leaf in Shanghai.
 624 Arrows in a) and b) denote mancozeb (17) with high uptake from soil, in e) and f) chlorothalonil
 625 (31) and diazinon (36), with high volatilization from leaves, see text.

626

627



628

629 **Figure 3.** Simulated loss, step-by-step addition of processes for triazophos compared to measured
630 residues in wheat straw [31].

631

Table 1. Process rates and percentage loss from each plant compartment (tomato, Copenhagen scenario) for nine chemicals illustrating the influence of the chemical properties (SI Table S4) on dissipation. Negative loss rates and percentages indicate input into the plant.

		Root			Stem				Leaf			Fruit		
		Growth dilution	Transfer to Stem	Uptake from soil to root	Growth dilution	Vola-tilization to air	Transfer to Leaf and fruit	Uptake from soil to stem	Growth dilution	Vola-tilization to air	Uptake from soil to leaf	Growth dilution	Vola-tilization to air	Uptake from soil to fruit
C#1 ^a	Rate %	0.06 2%	2.33 98%	-1.31 -55%	0.06 2%	1.63×10 ⁻³ 0%	3.04 98%	-1.28 -41%	0.07 88%	0.01 12%	-0.03 -44%	0.13 98%	2.14×10 ⁻³ 2%	-0.01 -5%
C#2 ^b	Rate %	0.06 14%	0.35 86%	-0.07 -17%	0.06 18%	4.80×10 ⁻³ 1%	0.26 80%	-0.04 -12%	0.07 3%	2.18 97%	-0.04 -2%	0.13 15%	0.74 85%	-0.03 -3%
C#3 ^c	Rate %	0.06 10%	0.50 90%	-0.14 -26%	0.06 13%	1.86×10 ⁻³ 0%	0.40 87%	-0.08 -17%	0.07 86%	0.01 14%	-0.01 -16%	0.13 97%	3.82×10 ⁻³ 3%	-4.14×10 ⁻⁰³ -3%
C#4 ^d	Rate %	0.06 1%	8.72 99%	-5.75 -66%	0.06 0%	0.01 0%	23.09 100%	-5.75 -25%	0.07 1%	9.76 99%	-5.72 -58%	0.13 15%	0.73 85%	-0.22 -26%
C#5 ^e	Rate %	0.06 3%	1.78 97%	-0.94 -51%	0.06 3%	0.01 0%	2.10 97%	-0.88 -41%	0.07 5%	1.21 95%	-0.48 -38%	0.13 29%	0.32 71%	-0.05 -12%
C#6 ^f	Rate %	0.06 10%	0.50 90%	-0.14 -26%	0.06 13%	3.40×10 ⁻⁴ 0%	0.40 87%	-0.08 -17%	0.07 98%	1.76×10 ⁻³ 2%	-0.01 -8%	0.13 100%	0.00 0%	0.00 -3%
C#7 ^g	Rate %	0.06 2%	3.34 98%	-2.00 -59%	0.06 1%	3.43×10 ⁻⁷ 0%	5.08 99%	-1.99 -39%	0.07 100%	1.73×10 ⁻⁶ 0%	-0.01 -9%	0.13 100%	3.37×10 ⁻⁷ 0%	-0.03 -22%
C#8 ^h	Rate %	0.06 86%	0.01 14%	-1.04×10 ⁻⁰³ -2%	0.06 95%	6.58×10 ⁻⁴ 1%	2.74×10 ⁻³ 4%	-5.16×10 ⁻⁵ 0%	0.07 94%	4.45×10 ⁻³ 6%	0.00 0%	0.13 99%	1.58×10 ⁻³ 1%	-4.06×10 ⁻⁰⁸ 0%
C#9 ⁱ	Rate %	0.06 0%	12.48 100%	-8.40 -67%	0.06 0%	6.84×10 ⁻⁴ 0%	40.31 100%	-8.40 -21%	0.07 94%	4.59×10 ⁻³ 6%	-0.02 -26%	0.13 100%	2.16×10 ⁻⁴ 0%	-0.04 -33%

^aTheoretical compound with K_{OW} , K_{AW} and MW as mean of the 42 modeled compound of the current study, ^bphorate, ^cpenconazole, ^dtheoretical compound with $\log K_{OW}=1.5$, $K_{AW}=10^{-5}$ L/L and $M=450$ g/mol, ^echlorothalonil, ^fpropiconazole, ^gazoxystrobin, ^hcyfluthrin, ⁱmethomyl