

1 **SCIENTIFIC OPINION**

2

3 **DRAFT Guidance for evaluating and using results of field persistence and**
4 **soil accumulation experiments for exposure assessment of soil organisms to**
5 **substances in soil**

6 1

7 **EFSA Panel on Plant Protection Products and their Residues (PPR)^{2,3}**

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9 **ABSTRACT**

10 The European Commission asked the Panel to revise the Guidance Document on persistence in soil
11 (SANCO/9188VI/1997 of 12 July 2000). Therefore the Panel started the development of a revised methodology
12 for the assessment of exposure of soil organisms. This opinion provides guidance on how to derive the half-life
13 for degradation in the top 30 cm of soil at reference temperature and moisture conditions (ie 20°C and field
14 capacity) from the results of field and laboratory experiments. This half-life is an important input parameter in
15 model simulations of the exposure of organisms in soil and therefore this guidance is an important part of this
16 revised methodology. The Panel recommends evaluating field persistence experiments with models assuming a
17 biphasic decline and taking only the slow phase of this decline, taken to represent degradation in the soil matrix
18 rather than loss processes from the soil surface, into account for estimating this half-life. The Panel proposes
19 basing the relevant population of half-lives for a certain soil exposure scenario on the assumption that a half-life
20 measured for any non-volcanic agricultural soil from temperate regions can be used to predict the half-life for any
21 such soil within the EU. The aim is to estimate the geomean half-life of this relevant population. The Panel
22 considers it necessary to include the uncertainty resulting from the sample size of the population in the estimation
23 of this geomean. If the relevant population of half-lives for a certain exposure scenario consists of a mixture of
24 values obtained in the laboratory and in the field, the Panel recommends rejecting the laboratory values only if
25 the null hypothesis that laboratory and field half-lives are equal is rejected. The Panel considers this guidance
26 proposal also useful for assessment half-lives to be used in scenario calculations on leaching to groundwater and
27 surface water. For future field persistence studies, the Panel recommends incorporating the plant protection
28 product to a depth of about 10 cm in soil immediately after application.

1 On request [from [requesting party] [OR] of EFSA], Question No EFSA-Q-YYYY-NNNNN, adopted on DD Month YYYY.

2 Panel members [OR] Scientific Committee members: name surname, name surname and name surname. [In case of minority opinion(s), please add:] [Part of this/This] Opinion is not shared by the following members of the Panel: name surname, name surname and name surname. [names of Panel member(s) with minority opinion] [In case of identified conflict(s) of interest, please add:] x [number written in words, e.g. Three] members of the Panel did not participate in [part of] the discussion on the subject referred to above because of potential conflicts of interest identified in accordance with the EFSA policy on declarations of interests. Correspondence: unit-acronym@efsa.europa.eu

3 [If applicable] Acknowledgement: EFSA wishes to thank the members of the Working Group / Network on [name of the WG / Network] for the preparation of this opinion: name surname, name surname and name surname [names of members of WG and external experts] and EFSA's staff member(s) XXX for the support provided to this EFSA scientific output.

29 **KEY WORDS**

30 field persistence, degradation, half-life, accumulation, exposure, soil organisms

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32 SUMMARY

33

34 The Scientific Panel on Plant Protection Products and their Residues (PPR Panel) of EFSA was asked
35 in November 2007 by EFSA to prepare a revision of the Guidance Document on persistence in soil
36 (SANCO/9188VI/1997 of 12 July 2000). This revision will consist of a tiered exposure assessment
37 for organisms in soil based on scenarios for analytical and numerical models (EFSA, 2010). In this
38 exposure assessment, degradation parameters derived from field persistence and soil accumulation
39 experiments are important input parameters for the numerical models. Therefore this opinion aims to
40 provide guidance on best practice for using the results of field experiments and soil accumulation
41 studies in the exposure assessment of organisms in soil.

42

43 The half-life for degradation in the top 30 cm of soil at 20°C and $pF = 2$ is an important input
44 parameter for numerical models that simulate exposure of organisms in soil. For soil under
45 conventional or reduced tillage, the main use of this half-life is to simulate the degradation rate for
46 soil depths between 1 and 30 cm. When deriving such a half-life from field persistence and soil
47 accumulation experiments, appropriate measures have to be taken to ensure that the value obtained is
48 not influenced strongly by processes in the top millimetres of soil.

49 Based on current knowledge and data commonly available in dossiers of plant protection products, it
50 is impossible to estimate with enough certainty photodegradation rates of plant protection products in
51 the top millimetres in soil. Studies with sieved soils in the laboratory demonstrate that
52 photodegradation is limited to the top 2 mm of soil. Furthermore there are uncertainties assessing
53 volatilisation for surface-applied compounds.

54 Current numerical models used for simulating behaviour of plant protection products in soil in the
55 context of the EU regulatory exposure assessment are unable to describe satisfactorily the daily
56 fluctuations of the soil temperature and of the volume fraction of water in the top millimetres of soil.

57 The parameters describing the relationship between on the one hand the degradation rate coefficient
58 in soil and on the other hand soil temperature (ie the Arrhenius activation energy) or volume fraction
59 of water in soil (ie the exponent B) show a considerable variation between soils and plant protection
60 products. This uncertainty results in a considerable uncertainty in the degradation half-life within the
61 top 30 cm of soil obtained from field experiments by inverse modelling assuming default values of the
62 Arrhenius activation energy and the exponent B .

63 Assessment of degradation half-lives in the top 30 cm of soil derived from field persistence
64 experiments can be based on inverse modelling using the approach of normalised decline curves
65 proposed by FOCUS (2006). The normalised decline curves can be either described with the DFOP
66 (double first-order kinetics in parallel) or Hockey-Stick models.

67 The Panel considers soil accumulation experiments with only two or three soil samplings per year not
68 suitable for estimating the degradation half-life in the top 30 cm of soil because the fraction of the
69 dosage that penetrates to soil depths deeper than a few millimetres cannot be estimated with sufficient
70 accuracy.

71 Once appropriate degradation half-lives from laboratory and field experiments are available, the
72 estimation of the half-life to be used as input for the required exposure scenario consists of two more
73 steps: (i) assess the relevant population of half-life values for the required exposure scenario, and (ii)
74 estimate reliably the required statistical attribute (certain percentile or some mean value) based on this
75 population. The Panel proposes to base the relevant population of half-lives on the assumption that a
76 half-life measured for any non-volcanic agricultural soil from temperate regions can be used to predict
77 the half-life for any such soil within the EU. This assumption is a working hypothesis that has to be
78 underpinned further. The type of attribute has to be consistent with the scenario-selection procedure

79 which was based on taking the geomean half-life assuming a log-normal distribution. So the Panel
80 recommends taking the geomean half-life. The estimation of the geomean half-life of the population
81 has to consider the uncertainty resulting from the limited number of samples in the sample population.

82 If the relevant population of half-lives for a certain exposure scenario consists of a mixture of values
83 obtained in the laboratory and in the field, the Panel recommends excluding the laboratory values only
84 if the null hypothesis that laboratory and field values are equal is rejected. If the relevant population
85 of half-lives for a certain exposure scenario consists of less than four values based on field
86 experiments, the Panel recommends using both laboratory and field values for estimating the
87 geomean.

88 The Panel considers the guidance proposals for estimating half-lives also useful for assessment of
89 leaching to groundwater and surface water because the main use of the half-lives in these groundwater
90 and surface water scenarios is the same as for the soil exposure assessment considered in this opinion
91 (ie simulating the degradation rate for soil depths between 1 and 30 cm).

92 The Panel recommends compiling a database of all relevant and reliable half-lives of agricultural top
93 soils within the temperate regions at 20°C and pF = 2 to test the assumption that this half-life does not
94 vary systematically between geographical zones in the temperate regions for non-volcanic soils.

95 In case the notifier wants to use results of field persistence studies for estimating the half-life in the
96 top 30 cm of soil as an input parameter for exposure models, the Panel recommends incorporating the
97 plant protection product to a depth of about 10 cm into the soil immediately after application.

98 The Panel recommends improving the validation status of mechanistic models for simulating loss
99 processes at the soil surface (especially for photodegradation and volatilisation).

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141 **BACKGROUND AS PROVIDED BY EFSA**

142 During the review process of the substances of the second list, several concerns were raised regarding
143 the Guidance Document on persistence in soil. A number of Member States have expressed interest in
144 a revision of the current Guidance Document on persistence in soil during the general consultation of
145 Member States on Guidance Documents in answer to the request by the Director of Sciences of EFSA
146 in a letter dated 3 July 2006 sent *via* the Standing Committee on the Food Chain and Animal Health.
147 Furthermore, the EFSA PRAPeR Unit has noted that the Guidance Document needs to be brought in
148 line with the FOCUS degradation kinetics report (SANCO/100058/2005, version 2.0, June 2006).

149
150 FOCUS (1997) developed the first guidance at EU level for exposure assessment in soil. This
151 included a simple approach for estimating PEC_{SOIL} but FOCUS (1997) did not develop first-tier
152 scenarios (in contrast to subsequent FOCUS workgroups that developed such scenarios for surface
153 water and groundwater as development of soil scenarios was a lower priority at that time). FOCUS
154 (2006) developed detailed guidance on estimating degradation rate parameters from laboratory and
155 field studies, but did not develop exposure scenarios. Nevertheless there is a need for such scenarios
156 in view of ongoing discussions in PRAPeR experts' groups regarding PEC_{SOIL} as current approaches
157 at EU level only represent the range of climatic conditions covered by available field dissipation
158 and/or accumulation studies, and Member States would like tools to be able to extrapolate to a wider
159 range of climates present in the EU.

160
161 The existing Guidance Document on Persistence in Soil (9188/VI/97 rev 8) published in 2000 did not
162 include scenarios. The intention with the new guidance document is to update the existing Guidance
163 Document on Persistence in Soil to include European exposure scenarios for soil and to provide
164 guidance on best practice for using the results of field experiments and soil accumulation studies in
165 the exposure assessment.

166
167 The revision will not include guidance that is in the existing guidance document but has been replaced
168 by newer guidance e.g. in FOCUS (2006). Some parts of the current guidance will not be considered
169 in the revision, e.g. for soil-bound residues, as these sections are better dealt with separately. The
170 revision will also exclude risk-management guidance and hazard cut-offs e.g. PBT classification as
171 this is not within the mandate given to EFSA.

172
173 Member States and stakeholders have been and will be consulted through web-conferences and
174 stakeholder workshops to collect comments during the revision of the Guidance Document.

175

176 **TERMS OF REFERENCE AS PROVIDED BY EFSA**

177 The Scientific Panel on Plant Protection Products and their Residues (PPR Panel) of EFSA was asked
178 in November 2007 by EFSA to prepare a revision of the Guidance Document on persistence in soil
179 (SANCO/9188VI/1997 of 12 July 2000).

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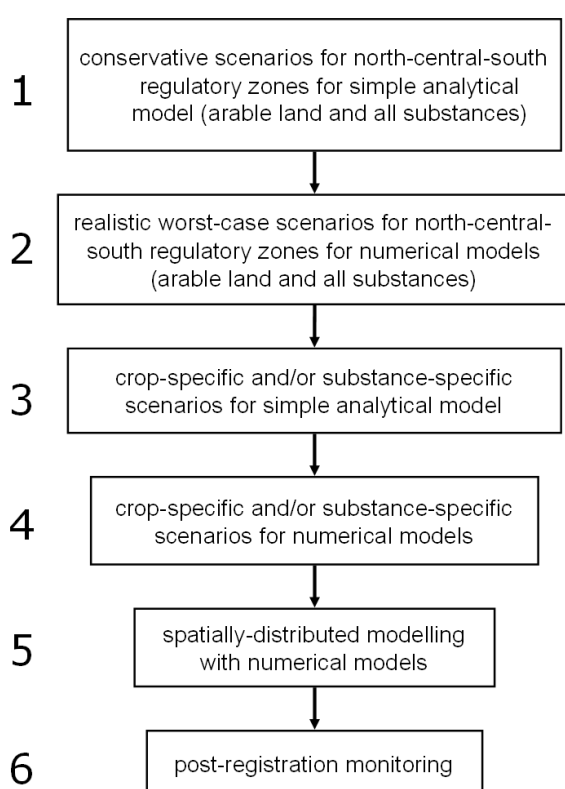
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183 **1. Introduction**

184 **1.1. Role of field persistence and soil accumulation experiments in the tiered exposure**
 185 **assessment**

186 EFSA (2010a) proposed a tiered approach for the assessment of exposure of organisms to plant
 187 protection products⁴ in soil after spray applications in annual crops under conventional and reduced
 188 tillage. Its purpose is to assess the all-time high (either peak or TWA values) of the spatial 90th
 189 percentile concentration resulting from the use of the plant protection product and considering the
 190 population of agricultural fields (in one of the three regulatory zones North-Centre-South) where the
 191 crop is grown in which this plant protection product is applied (assuming a fraction of the target crop
 192 treated of 100%). The tiered approach consists of six tiers, of which five are based on calculations
 193 with simple or numerical models (Figure 1; see EFSA, 2010a, for further details of the tiers).



194

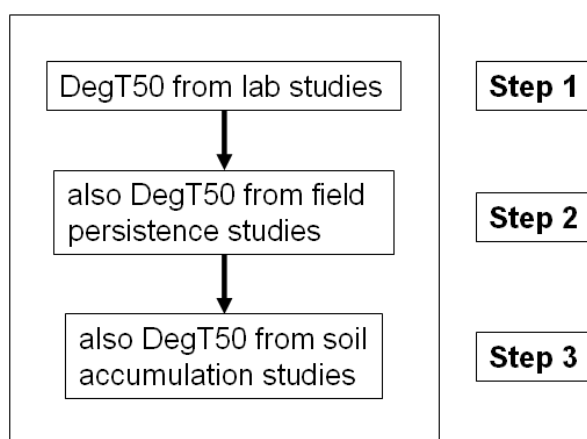
195 **Figure 1:** Tiered scheme for the exposure assessment of soil organisms in annual crops with
 196 conventional or reduced tillage after spray applications (taken from EFSA, 2010a).

197 For the exposure assessment in soil, the degradation⁵ half-life (*DegT50*) in top soil at 20°C and field
 198 capacity (pF = 2) is an important input parameter of the simple and numerical models used in Tiers 1
 199 to 5 (Figure 1). In a dossier there will be usually four laboratory studies on the degradation rate.
 200 Annex II to Council Directive 91/414/EC requires four field persistence studies if the degradation
 201 half-life (*DegT50*) in top soil at 20°C at pF = 2-2.5 exceeds 60 days. As a consequence, for many plant

⁴ In the context of this opinion, the term ‘plant protection products’ is used for both the applied formulation and the active substances themselves.

⁵ The Panel uses in this opinion the definition of ‘degradation’ (which includes transformation) as suggested by FOCUS (2006).

202 protection products there are additionally four field persistence studies. For persistent compounds
 203 (time needed for 90% dissipation in the field longer than 1 year) there may be additionally one or two
 204 soil accumulation studies. In principle all these studies may generate *DegT50* values. EFSA (2010a)
 205 proposed basing the estimation of the *DegT50* on a stepped approach (Figure 2) for all relevant tiers:
 206 (i) considering only values from laboratory studies, (ii) including also values from field persistence
 207 studies and (iii) including additionally values from soil accumulation studies. This is done because
 208 field persistence studies and soil accumulation studies may provide more realistic estimates of this
 209 half-life than the laboratory studies.



210

211 **Figure 2:** Schematic representation of stepped approach for estimating the *DegT50* in the soil to be
 212 used in the tiered exposure assessment (EFSA, 2010a).

213

214 It has long been known (Anderson, 1987) that the viability of soil microbial populations decreases
 215 with time in laboratory studies. Therefore OECD (2002b) recommended restricting the duration of
 216 laboratory studies to 120 days. So field studies may be better suited to measure the degradation rate of
 217 persistent substances. A substantial proportion of the parent molecules and metabolites of plant
 218 protection products registered at EU level may be so persistent that study duration of 120 days is too
 219 short for a good measurement of the degradation rate. As will be explained in detail below, the
 220 procedure for estimating the *DegT50* of top soil at 20°C and pF = 2 from field studies is more
 221 complicated and has more uncertainties than that from laboratory studies. The Panel proposes to
 222 handle these uncertainties by developing procedures based on scientifically conservative
 223 methodologies. Conservative is defined in the context of this opinion defined as ‘on the safe side with
 224 respect to the risk assessment’. For the tiered exposure assessment of Figure 1, the safe side means
 225 higher concentrations. In general, a longer *DegT50* leads to higher exposure concentrations, so a
 226 conservative methodology is defined in this opinion as a methodology that generates a *DegT50* that is
 227 longer than the true value in case of uncertainties. However, a longer *DegT50* of a parent substance
 228 may lead to lower concentrations of soil metabolites. Therefore the proposed guidance in this opinion
 229 is restricted to the exposure assessment of parent compounds. For the exposure assessment of soil
 230 metabolites, the Panel recommends a case-by-case approach.

231 Considering a certain exposure scenario in Figure 1, the first step is to select the relevant population
 232 of experiments to be included in the estimation of the *DegT50* value for the required exposure
 233 scenario. For example, a *DegT50* value at 20°C and pF = 2 derived from a field experiment on a heavy
 234 clay soil with 10% of organic matter in Finland may perhaps not be considered relevant for estimating
 235 the *DegT50* value at 20°C and pF = 2 for a sandy soil with 1% of organic matter in Spain. Once the
 236 relevant population of *DegT50* values has been defined, the question is how to derive the *DegT50*

237 value to be used in the exposure assessment from this population. EFSA (2010a) indicated that the
238 *DegT50* should be part of the scenario-selection procedure. EFSA (2010b) developed this scenario
239 selection procedure and they selected scenarios assuming that the median *DegT50* will be used as the
240 input to the scenario calculations. FOCUS (2006; p. 234) recommended using the geometric mean of
241 the *DegT50* values based mainly on the argument that taking the geomean of a number of rate
242 coefficients will give the same result as taking the geomean of the corresponding half-lives. The Panel
243 proposes to use the geomean of the relevant *DegT50* values and considers this to be in line with both
244 EFSA (2010b) and FOCUS (2006) because the median is considered to be a good estimator for the
245 geomean for lognormal distributions (such a distribution is commonly assumed the best guess for
246 quantities that cannot be negative such as the *DegT50*).

247 As described by EFSA (2010a), there is a complication with respect to the estimation of the individual
248 *DegT50* values from field persistence studies. These *DegT50* values will be used to simulate long-
249 term accumulation of plant protection products with ploughing up to 20 cm depth every year. So they
250 have to reflect the degradation rate within the soil matrix. Field dissipation studies regularly show a
251 fast initial decline (Walker et al., 1983). Immediately after application, the plant protection product is
252 concentrated in the top millimetres of the soil. For example, an application of 1 kg active substance in
253 250-500 L water per hectare gives a content of 500-1000 mg/kg of this substance in the top 0.1-0.2
254 mm of soil. In the top millimetres of soil, loss processes other than degradation within the soil matrix
255 may play a significant role (volatilisation, photochemical degradation, runoff etc.). So it has to be
256 ensured that the estimated *DegT50* is not influenced by these loss processes. Additionally, it is not
257 clear whether the degradation rate within the soil matrix in these top millimetres can be safely
258 extrapolated to estimate the degradation rate at depths between 1 and 30 cm (see Chapter 2).
259 Therefore a procedure is needed that ensures that the *DegT50* derived from field persistence studies
260 reflects the degradation rate within the soil matrix between 1 and 30 cm depth with sufficient
261 accuracy. This *DegT50* within the soil matrix in the 1-30 cm layer of soil will be further called
262 *DegT50_{matrix}*. Thus the measured decline has to be split into two parts, one reflecting the behaviour in
263 the top millimetres and the other reflecting the behaviour in deeper soil.

264 This interpretation problem with respect to the decline in the top millimetres applies also to soil
265 accumulation studies. However, for these studies there is an additional complication. They may
266 contain only two to three samplings per year and the plant protection product may have been sprayed
267 on a full-grown crop. In such a situation it may be difficult to estimate the fraction of the dose that
268 eventually penetrated the soil. This may complicate an accurate estimation of the *DegT50_{matrix}* from
269 soil accumulation studies. So also here a procedure is needed to ensure that the *DegT50* derived from
270 soil accumulation studies reflects the degradation rate within the soil matrix between 1 and 30 cm
271 depth.

272 This interpretation problem is relevant for soil exposure assessments in which the concentration
273 endpoint has to be based on multi-year simulations and in which a significant fraction of the dosage
274 penetrates to below 1 cm depth (either by leaching or by soil tillage). This is the case for the soil
275 exposure assessment under conventional and reduced tillage and by definition for the leaching
276 assessment. The relevance of this problem for the soil exposure assessment for no-tillage systems and
277 for permanent crops is not yet clear. This can only be clarified after tiered exposure approaches for
278 no-tillage systems and for permanent crops (similar to the one in Figure 1) have been defined.

279 This interpretation problem is of no importance if the plant protection product is incorporated into the
280 top 10 cm of soil immediately after application. However, this is not common practice in the field
281 persistence studies available in the dossiers. It is not clear whether incorporation is a solution also for
282 the no-tillage systems because the tiered approach for the no-tillage systems has not yet been defined.

283 At this moment the only guidance to address this interpretation problem is the bullet list on p. 177 of
284 FOCUS (2006). This list describes only in very general terms how to handle initial loss processes.

285 This leads in current EU regulatory practice to rejection of a substantial proportion of the field
286 persistence studies.

287 **1.2. Aims of this guidance proposal**

288 In view of the foregoing, the aims of this guidance proposal are:

289 (i) to develop procedures for estimating $DegT50_{matrix}$ values reliably from results of individual field
290 persistence and soil accumulation experiments

291 (ii) to develop procedures for assessing the relevant population of $DegT50_{matrix}$ values for the required
292 exposure scenario

293 (iii) to develop procedures for estimating reliably the geomean of the relevant population of
294 $DegT50_{matrix}$ values for the required exposure scenario.

295 As described in Section 1.1, procedures will have to be developed for splitting the measured decline
296 found in field persistence studies into the two parts. These procedures will generate as spin-off
297 information on losses from the top millimetres of soil under field conditions (eg due to
298 photodegradation or volatilisation). It may be relevant to take this information into account in the
299 exposure assessment. Therefore the Panel aims at additionally developing procedures for using this
300 information in the exposure assessment. This aim can be split up (in analogy with the guidance for the
301 $DegT50_{matrix}$) into:

302 (i) to develop procedures for estimating top-soil decline parameters reliably from results of individual
303 field persistence and soil accumulation experiments

304 (ii) to develop procedures for assessing the relevant population of top-soil decline parameters values
305 for the required exposure scenario

306 (iii) to develop procedures for estimating reliably the endpoint of the top-soil decline parameters for
307 the required exposure scenario from the relevant population of values.

308 The processes underlying these top-soil declines were not included in the scenario-selection
309 procedure by EFSA (2010b). Therefore the Panel considers it not justifiable to use, for example,
310 geomean or median values of the top-soil decline parameters. Instead this endpoint of the top-soil
311 decline parameters should be a kind of worst case.

312 **1.3. Bird's eye view of opinion**

313 Chapter 2 describes the background of the problems of using measured declines in the top millimetres
314 of soil for estimating the $DegT50_{matrix}$ and provides a proposal for the solution of these problems. This
315 proposal is the basis for the guidance for evaluating results from field persistence studies described in
316 Chapter 3. The Panel made an attempt to develop guidance for soil accumulation studies but this
317 proved not to be feasible (Chapter 4). The next step is to use the available and relevant information
318 from all laboratory and field studies for the exposure assessment in the required scenario (Chapter 5).
319 Finally, the Panel considers the possible usefulness of the developed proposals for another purpose, ie
320 the assessment of leaching to groundwater at EU level (Chapter 6).

321

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324

325 **2. Background of the problems of estimating the $DegT50_{matrix}$ from measured declines**
 326 **after spraying onto bare soil in field persistence studies and a proposed solution**

327 **2.1. Introduction to the problem**

328 FOCUS (2006) proposed a procedure to derive $DegT50_{matrix}$ values at 20°C and pF = 2 from field
 329 persistence studies via inverse modelling procedures. This procedure is the current guidance for
 330 extracting this $DegT50_{matrix}$ value from field persistence studies which has been applied widely in the
 331 EU exposure assessments. However, the Panel has serious reservations with respect to this procedure.
 332 These reservations are explained below.

333 Let us first explain the principles of this inverse modelling procedure. It is generally recognised that
 334 the degradation rate in soil is a function of soil moisture, soil temperature and soil depth (FOCUS,
 335 2000a). So any $DegT50_{matrix}$ is a function of these three soil properties. The relationship between
 336 $DegT50_{matrix}$ and soil moisture content is commonly described by an empirical equation (Walker,
 337 1974):

$$338 \quad DegT50_{matrix} = DegT50_{matrix,FC} \left(\frac{\theta}{\theta_{FC}} \right)^{-B} \quad (1)$$

339 where

340 ‘FC’ = at field capacity, i.e. matric suction of 100 hPa or pF = 2

341 θ = volume fraction of water in soil (m^3/m^3)

342 B = moisture-dependency parameter (-).

343 The relationship between $DegT50_{matrix}$ and soil temperature is commonly described with the Arrhenius
 344 equation (eg EFSA, 2008) and thus characterised by an Arrhenius activation energy:

$$345 \quad DegT50_{matrix} = DegT50_{matrix,20Celsius} \exp \left(\frac{E_a}{R} \left[\frac{1}{T} - \frac{1}{T_{ref}} \right] \right) \quad (2)$$

346 where

347 E_a = Arrhenius activation energy (kJ/mol)

348 R = gas constant ($0.008314 \text{ kJ K}^{-1} \text{ mol}^{-1}$)

349 T = soil temperature (K)

350 T_{ref} = reference soil temperature ($20^\circ\text{C} = 293.15 \text{ K}$)

351 The relationship between $DegT50_{matrix}$ and soil depth is described by:

$$352 \quad DegT50_{matrix} = \frac{DegT50_{matrix,topsoil}}{f_z} \quad (3)$$

353 where

354 $DegT50_{matrix,topsoil} = DegT50_{matrix}$ of the top 30 cm of soil

355 f_z = depth parameter (-).

356 FOCUS (2000a) recommended using $f_z = 1$ for the layer 0-30 cm, $f_z = 0.5$ for the layer 30-60 cm, and
 357 $f_z = 0.3$ for the layer 60-100 cm.

358 It is commonly assumed that the effects of these three soil properties act independently of each other
 359 which results in:

$$360 \quad DegT50_{matrix} = DegT50_{matrix, 20Celsius, FC, topsoil} \left(\frac{\left(\frac{\theta}{\theta_{FC}} \right)^{-B}}{f_z} \exp \left(\frac{E_a}{R} \left[\frac{1}{T} - \frac{1}{T_{ref}} \right] \right) \right) \quad (4)$$

361 When analysing results of field persistence experiments, the inverse of Eqn 3 is more relevant:

$$362 \quad DegT50_{matrix, 20Celsius, FC, topsoil} = DegT50_{matrix} f_z \left(\frac{\theta}{\theta_{FC}} \right)^B \exp \left(\frac{E_a}{R} \left[\frac{1}{T_{ref}} - \frac{1}{T} \right] \right) \quad (5)$$

363 For scenario calculations with numerical models, the agreed convention is to specify this $DegT50_{matrix}$
 364 of the top 30 cm of soil at a reference temperature of 20°C and a matric potential of pF = 2 (ie a
 365 matric suction of 100 hPa) and to simulate the substance behaviour in soil based on default values for
 366 the relationships between on the one hand the $DegT50_{matrix}$ and on the other hand soil moisture, soil
 367 temperature and soil depth. Usually most of the plant protection product and of its soil metabolites
 368 will remain in the top 30 cm during the field persistence experiment so the depth-dependency of the
 369 degradation rate is not considered to have an appreciable role. The moisture content and the
 370 temperature of the soil vary of course with time in field persistence experiments. Thus the
 371 $DegT50_{matrix}$ has to be calculated back via some inverse modelling procedure to the reference
 372 conditions 20°C and pF = 2. Only after this back calculation can the $DegT50_{matrix}$ be compared with
 373 $DegT50_{matrix}$ values from the laboratory studies at the same reference conditions. So the $DegT50_{matrix}$
 374 derived from the field experiments is not a direct measurement but may be ‘contaminated’ by a
 375 number of problems resulting from the inverse modelling procedure. The Panel identified several
 376 problems that undermine the soundness of this inverse modelling procedure:

377 (1) it is difficult to exclude loss due to photodegradation from the top millimetres with enough
 378 certainty based on current knowledge;

379 (2) the inverse modelling usually is based on default values for the parameter B and the E_a which may
 380 lead to large errors in estimated values of the $DegT50_{matrix}$ at 20°C and pF = 2;

381 (3) the numerical models commonly used in the inverse modelling procedure (eg PELMO and
 382 PEARL) have not been designed to simulate accurately temperature, moisture content and degradation
 383 rate in the top millimetres.

384 These problems are described in more detail in the following sections.

385

386

387 **2.2. Difficulties with quantifying photodegradation and volatilisation losses at the soil**
388 **surface**

389

390 **Photodegradation losses**

391 The Panel considers current knowledge is insufficient to quantify photodegradation rates in the top
392 millimetres of soil under the range of field conditions to be expected in the EU. OECD (2002a)
393 developed a guideline for measuring soil photolysis in the laboratory. This study has become a
394 standard data requirement for plant protection products. However, the Panel is not aware of studies in
395 which photolysis rates measured under field conditions have been tested for a range of plant
396 protection products and soils against predictions of numerical models based on measurements from
397 this OECD guideline. This OECD study is commonly considered to be a ‘route study’ rather than a
398 ‘rate study’, ie it is considered suitable for identifying photometabolites that are formed at the soil
399 surface but it has not been designed to generate photodegradation rates that can be used to predict
400 such rates under field conditions. The Panel recommends improving the validation status of
401 mechanistic models for simulating photodegradation rates at the soil surface.

402 Light is efficiently absorbed by soil in a wavelength dependent manner (Tester & Morris, 1987).
403 Sometimes it is argued in dossiers that absence of absorption of light from wavelengths from 295 to
404 800 nm due to shielding by the soil (derived from the or due to the lacking overlap of the sunlight
405 emission spectrum with the absorption spectrum of the substance molecule) indicates that the
406 substance will not be photodegraded on soil surfaces in the field. It is obvious that the absence of
407 absorption of light indicates that direct photolysis of a substance does not occur. However, in surface
408 water there is ample evidence for indirect photolysis. For instance, dissolved humic substances are
409 efficient photosensitizers in surface waters (Miller & Chin, 2002) and may also act as photocatalysts
410 in top soil both in the solid and the liquid phase (i.e. in soil pore water). The Panel considers therefore
411 that indirect photolysis may also occur in the top millimetres of soil because also soil may contain
412 molecules that can act as a catalyst for the photodegradation process. So absence of light absorption
413 cannot be used to exclude photodegradation.

414

415 As there is always sunlight in field experiments, these considerations imply that losses from the top
416 millimetres can never be simply attributed to degradation within the soil matrix.

417 Ciani et al. (2005) found that light penetrated no deeper than 0.2 mm into pellets consisting of a
418 mixture of soils and barium sulphate. Soil photolysis studies with sieved soils indicated that direct and
419 indirect photolysis is usually limited to the top 2 mm of soil (Hebert & Miller, 1990; Frank et al.,
420 2002). These studies were done with soil surfaces that are prepared in the laboratory with sieved soil
421 (mesh of 0.5 mm) as flat as possible (like a plane sheet). In field persistence studies, the soil is usually
422 rolled before application of the plant protection product (B. Gottesbüren, personal communication,
423 2010). Zhixiong et al. (2005) measured the surface roughness of a rolled Dutch loamy soil and found
424 an average standard deviation of the surface height of 6 mm (the range was between 4 and 8 mm using
425 measurements over lengths varying from 0.5 to 5 m and using different angles of measurement).
426 Zobeck & Onstad (1987) reviewed rainfall and tillage effects on the so-called random roughness of
427 the soil surface. This random roughness is defined as the standard error of individual soil elevations
428 after oriented roughness has been removed. The lowest value of the random roughness in their review
429 is about 5 mm (for a no-tillage system). A rolled soil surface is expected to give a low value of the
430 surface roughness. So this minimum value is consistent with the measurement by Zhixiong et al.
431 (2005). In view of this surface roughness of rolled soil it is not clear whether the photolysis will be
432 limited to the top 2 mm of a rolled field soil and it will be difficult to define the level of the soil
433 surface accurately at a millimetre scale.

434

435 **Volatilisation losses**

436 It would be helpful for the interpretation of field persistence experiments if volatilisation losses could
 437 be excluded on the basis of the properties of the substance. FOCUS (2008) proposed a trigger value of
 438 the vapour pressure of $> 10^{-4}$ Pa (20°C) to check whether a substance has the potential to reach the air.
 439 However, Smit et al. (1997) collected volatilisation measurements from literature and they showed
 440 that measured volatilisation losses from soil are not well correlated to the saturated vapour pressure.
 441 Instead, these are better correlated to the fraction of the pesticide calculated to be present in the gas
 442 phase. For the evaluation of field persistence experiments, it is sufficient that the volatilisation loss is
 443 less than about 5%. Data from Smit et al. (1997) indicate that this requirement is met if the fraction in
 444 the gas phase is less than about 10^{-8} . The criteria from FOCUS (2008) and Smit et al. (1997) are based
 445 on different properties of the soil-substance system. So for part of the substance-soil systems the
 446 vapour pressure may be below 10^{-4} Pa (20°C) whereas the fraction in the gas phase is higher than 10^{-8} .
 447 Simulations with numerical models cannot solve this problem as they are at the moment insufficiently
 448 accurate for low volatile substances (Ferrari et al., 2003). The Panel recommends improving the
 449 validation status of mechanistic models for simulating volatilisation of spray applications at the soil
 450 surface.

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453 **2.3. Uncertainties resulting from the use of default values of B and E_a**

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455 The inverse modelling procedure uses default values of B for the moisture dependency relationship
 456 and of E_a for the temperature relationship. Let us first consider B . FOCUS (2000a) recommends using
 457 a default B value of 0.7 based on Gottesbüren (1991). However, Gottesbüren (1991) reported 94 B
 458 values and these show considerable variability (minimum of 0.03 and maximum of 2.9); ten of these
 459 94 are above 1.5. Figure 3 shows that a B value of 1.5 in air-dry soil (θ/θ_{FC} of about 0.1) will lead to a
 460 $DegT50_{matrix}$ that is ten times longer than the default B value of 0.7. So when an inversely modelled
 461 $DegT50_{matrix}$ would have been mainly based on the decline in dry soil for a system with a true B value
 462 of 1.5, this would lead to a $DegT50_{matrix,FC}$ that is much too long as follows from the following
 463 example calculation:

464 (i) observed $DegT50_{matrix} = 50$ d in field

465 (ii) actual θ / θ_{FC} in field of 0.1

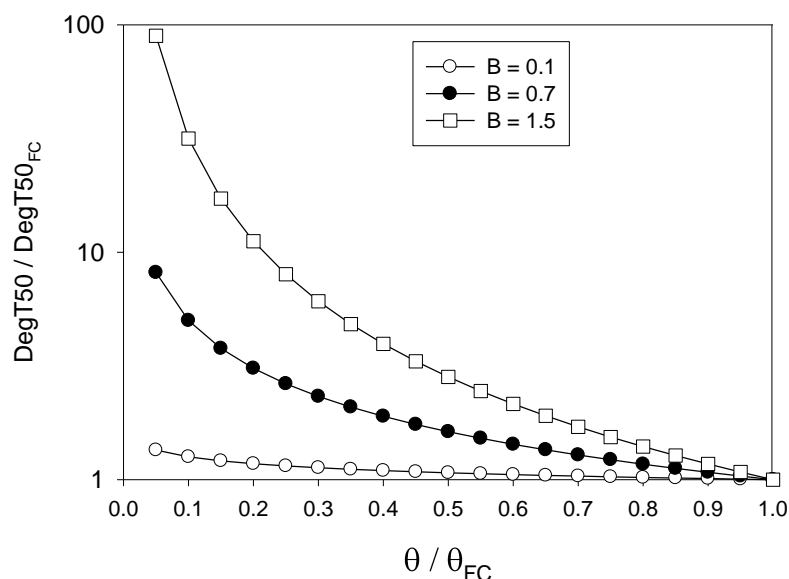
466 (iii) inversely modelled $DegT50_{matrix,FC} = 2$ d, based on true B of 1.5 using Eqn 5

467 (iv) inversely modelled $DegT50_{matrix,FC} = 10$ d, based on assumed B of 0.7 using Eqn 5.

468 The opposite (ie an inversely modelled $DegT50_{matrix,FC}$ that is too short) may of course also occur.
 469 This happens if the true B value is close to zero (see line for $B = 0.1$ in Figure 3). It may also happen
 470 if the $DegT50_{matrix}$ does not decrease continuously with decreasing moisture content as in most studies
 471 (see Smelt et al., 1979, for an exceptional example with a $DegT50_{matrix}$ of oxamyl in air-dry soil that
 472 was even shorter than the $DegT50_{matrix}$ at a moisture content of 0.2 kg/kg).

473 A conservative approach is not to simulate θ but to assume that it is continuously at field capacity
 474 (this approach is regularly used in regulatory exposure assessments). Then the value of B does not
 475 matter (see Eqn 1). However, it should be kept in mind that such an approach may generate an upper
 476 limit of the $DegT50_{matrix,FC}$ when using the resulting $DegT50_{matrix,FC}$ further in the exposure assessment
 477 (see Section 5.2).

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488 **Figure 3:** The ratio $DegT50_{matrix} / DegT50_{matrix,FC}$ as a function of the ratio θ / θ_{FC} for different B
489 values as calculated with Eqn 1.

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EFSA (2008) showed that the E_a value of 99 individual substance-soil combinations varied considerably: 95% of the values were in the range from about 35 to about 115 kJ/mol. So use of the default E_a of 65 kJ/mol may lead to a considerable uncertainty in the inversely modelled $DegT50_{matrix}$ at 20°C. Let us consider as an example a field study with an average soil temperature of 14°C that resulted in a $DegT50_{matrix}$ of 100 days. Eqn 5 gives then an inversely modelled $DegT50_{matrix,20Celsius}$ of 68 d for $E_a = 65$ kJ/mol but for $E_a = 35$ kJ/mol the inversely modelled value is 81 d and for $E_a = 115$ kJ/mol it is 51 d. So for true E_a values that are higher than the 65-kJ/mol default value, the inverse modelling procedure using the default value will give a $DegT50_{matrix,20Celsius}$ value that is too long and for true E_a values that are lower than the 65-kJ/mol the inversely modelled $DegT50_{matrix,20Celsius}$ will be too short.

501 It could be argued that this problem of uncertainty in B and E_a does not matter because the same
502 default values are used in the exposure calculations for the required exposure scenario. For example,
503 if a field persistence study is carried out at an average soil temperature of 10°C, about the same half-
504 life will be calculated in the required exposure scenario at 10°C irrespective of the value of the E_a
505 because the errors cancel out. The Panel agrees that this cancelling out is indeed expected to occur for
506 large numbers of experiments and scenarios. However, a dossier of a plant protection product will
507 usually contain no more than four field persistence studies. Let us assume that a field persistence
508 experiment in northern Germany at an average soil temperature of 10°C results in a $DegT50_{matrix}$ of 50
509 days. Let us further assume that the true E_a for this soil is 40 kJ/mol. The default E_a of 65 kJ/mol
510 gives a $DegT50_{matrix}$ at 20°C of 19 days with Eqn 5 whereas the true value based on 40 kJ/mol should
511 be 28 days. Next this value of 19 days may be used (admittedly after averaging with a few values from
512 other field persistence experiments) for a scenario in Spain at an average temperature close to 20°C
513 while the true value was 28 days. Thus the Panel considers this argument of cancelling errors not
514 convincing because it is not consistent with the approach of a scientifically conservative methodology
515 at the level of an individual plant protection product (which is the case to be considered).

516 **2.4. Weaknesses of the numerical models for describing moisture and temperature**
 517 **fluctuations and degradation rates in the top millimetres of soil**

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519 Numerical models such as PELMO and PEARL assume a potential evaporation rate that is constant
 520 over a day. However, measurements by Jackson (1973) showed that there may be a strong daily
 521 course in the moisture content of the top millimetres resulting from the daily variation in this
 522 evaporation rate (Figure 3). Thus modelling soil moisture dynamics in the top few millimetres is a
 523 daunting task. Diurnal surface soil moisture dynamics depends on processes like evaporation,
 524 condensation (dew), liquid flow in capillary pores and films and vapour diffusion in air-filled pores.
 525 Despite the fact that not all of these processes are included in currently used soil water flow models
 526 that are used for pesticide fate modelling in soils, these processes also depend strongly on soil
 527 properties and soil structures which change dynamically over time (due to compaction by rain,
 528 loosening by wetting-drying cycles, thawing-freezing cycles).

529 The numerical models usually use numerical compartment thicknesses in the top soil of about 2.5 cm
 530 (FOCUS, 2000a). This is another reason for inaccurate simulation of soil moisture contents in the top
 531 millimetres: eg measurements by Jackson (1973) showed considerable differences in measured
 532 moisture contents between the 0-5 mm and 5-10 mm layers during the drying process. The Panel
 533 expects that the numerical models in general will overestimate the soil moisture content of the top
 534 millimetres during a drying cycle in the field because of the constant potential evaporation rate and
 535 the 2.5-cm thick compartments. Such an overestimation will lead to inversely modelled values of the
 536 $DegT50_{matrix}$ at 20°C and pF = 2 that are too long. This is illustrated with the following example in
 537 which it is assumed that the total areic⁶ mass of plant protection product is present in the top 5 mm of
 538 soil at a constant volume fraction of water:

539 (i) observed $DegT50 = 50$ d in field

540 (ii) actual $\theta = 0.05$, simulated $\theta = 0.10$, $\theta_{FC} = 0.2$

541 (iii) inversely modelled $DegT50 = 19$ d based on actual θ using Eqn 5 with $B = 0.7$

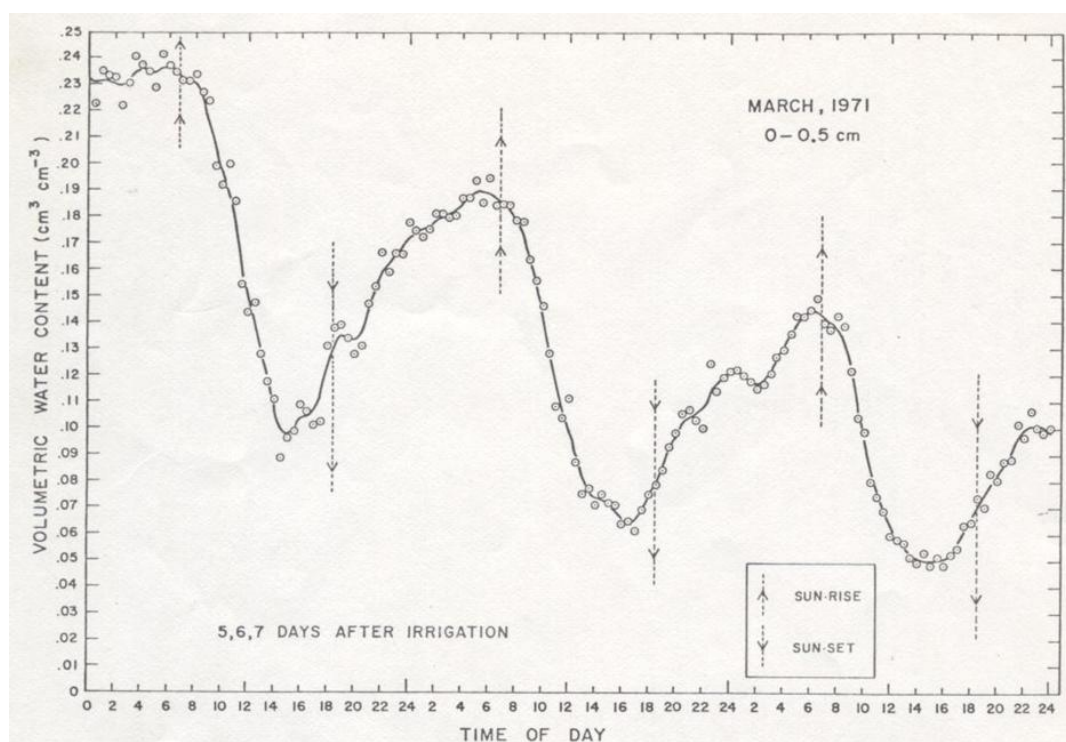
542 (iv) inversely modelled $DegT50 = 31$ d based on simulated θ using Eqn 5 with $B = 0.7$.

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⁶ ‘Areic mass’ means mass per area (Rigg et al., 1985).

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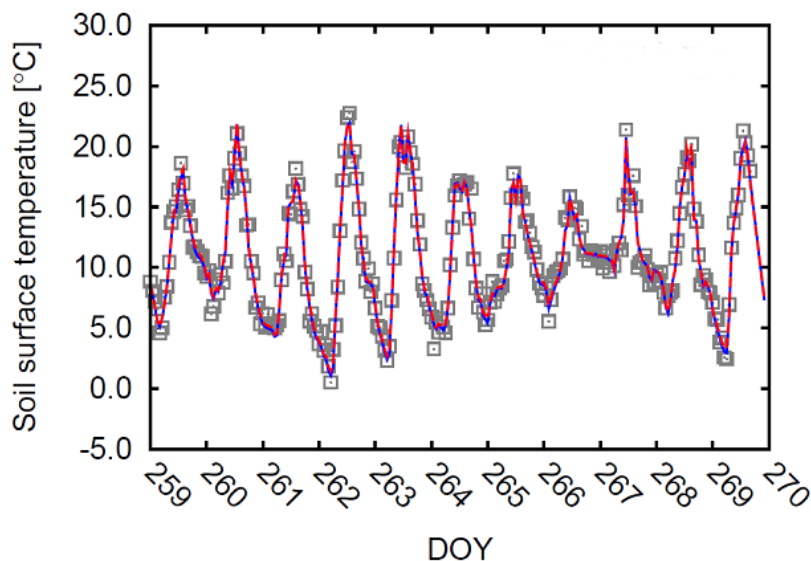
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547 **Figure 4:** Measured soil water content in the top 5 mm of bare Adelanto loam soil as a function of
 548 time on 7-9 March 1971 in Phoenix (Arizona) after 100 mm of irrigation on 2 March (taken from
 549 Jackson, 1973). Daily maximum air temperatures ranged from 17 to 24°C and daily minimum air
 550 temperatures from -2 to 5°C.

551

552 The numerical models use daily average air temperature as input and the effect of solar radiation on
 553 the soil temperature is ignored (FOCUS, 2000a). This has been shown to work well for simulation of
 554 daily averages of soil temperatures at 5 cm depth (eg Scorza Junior & Boesten, 2005). However it is
 555 unlikely that this works well for daily fluctuations in the top millimetres because solar radiation will
 556 have a considerable effect in these top millimetres and because also air temperatures may fluctuate
 557 considerably during the course of the day. The inadequacy of the numerical models to describe the
 558 moisture content in the top millimetres combined with ignoring solar radiation and using daily
 559 average air temperatures will therefore predictably lead to poor description of the daily course of soil
 560 temperature in the top millimetres. This can be illustrated by measurements by Steenpass et al. (2010)
 561 shown in Figure 5. These show daily fluctuations of the soil surface temperature of about 15 to 22 °C
 562 in September in Jülich (Germany) which is at about 51° Northern Latitude. One may expect that daily
 563 fluctuations of soil surface temperatures at more southern European latitudes in spring and summer
 564 are considerably higher than those measured in Jülich. This was confirmed by Braud et al (1993), who
 565 measured daily fluctuations of temperature at 1 cm depth of a bare silt loam soil from 20 June to 1
 566 July 1991 in Spain. They found that this temperature fluctuated typically between 17 and 50°C and on
 567 one day even from 15 to 55°C. So these are daily fluctuations of 33 to 40°C at 1 cm depth.

568 Steenpass et al. (2010) measured also soil temperatures at 3 and 6 cm depth in this soil and found
 569 daily fluctuations of about 14 °C at 3 cm and 11 °C at 6 cm (as compared fluctuations of 15-22°C at
 570 the soil surface). These data show that the daily fluctuations in soil temperature decrease only
 571 moderately with depth in the top centimetres.



572

573 **Figure 5:** Soil-surface temperature measured from 15 to 26 September 2008 at an experimental field
 574 close to Jülich (Germany). The soil was bare and its texture was silt loam. The points are the
 575 measurements and the line is a calculated with a simulation model (taken from Steenpass et al., 2010).

576

577 Let us assume that the Arrhenius equation gives a reliable description of the relationship between the
 578 $DegT50_{matrix}$ and soil temperature in the top millimetres. Let us furthermore consider the following
 579 example: (i) a substance with a $DegT50_{matrix}$ of 60 days at 20°C and an Arrhenius activation energy of
 580 65 kJ/mol, (ii) soil temperature fluctuates on a daily basis sinusoidally around an average temperature
 581 of 20°C. Figure 6 shows that introducing a fluctuating temperature in this example calculation speeds
 582 up the simulated decline. The simulated time points were fitted to a first-order decline and this
 583 resulted in half-lives of 60 days for constant temperature, 50 days for an amplitude of 10 °C and 32
 584 days for an amplitude of 20°C. So an amplitude of 20°C speeds up the degradation rate by about a
 585 factor of two. One might argue that this effect of the daily temperature fluctuations is consistently
 586 included in the exposure assessment: the fluctuations are both ignored in the inverse modelling
 587 procedure and in the scenario calculations with the numerical models. However, the effect of these
 588 fluctuations is expected to be considerably larger in Southern Europe than in Northern Europe. Thus it
 589 may be questioned whether $DegT50_{matrix}$ values derived from field experiments in Southern Europe
 590 can be used for exposure assessments in Northern Europe.

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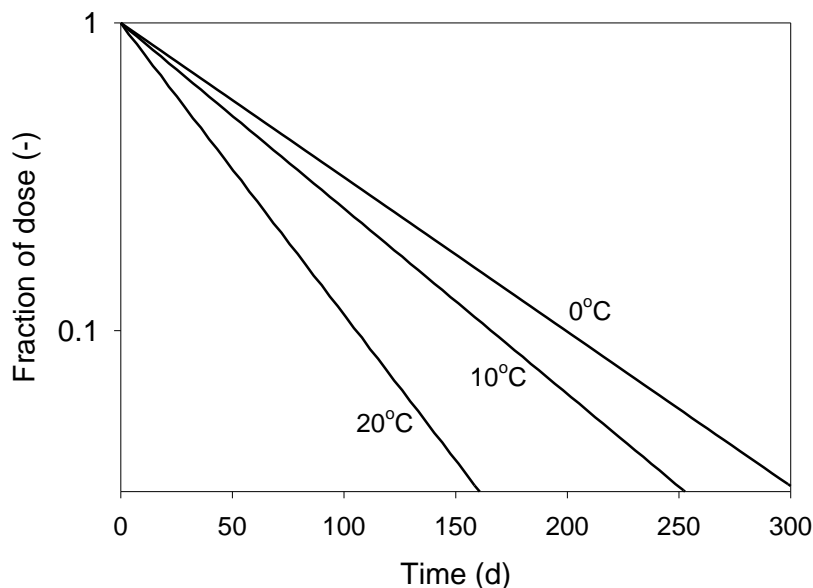
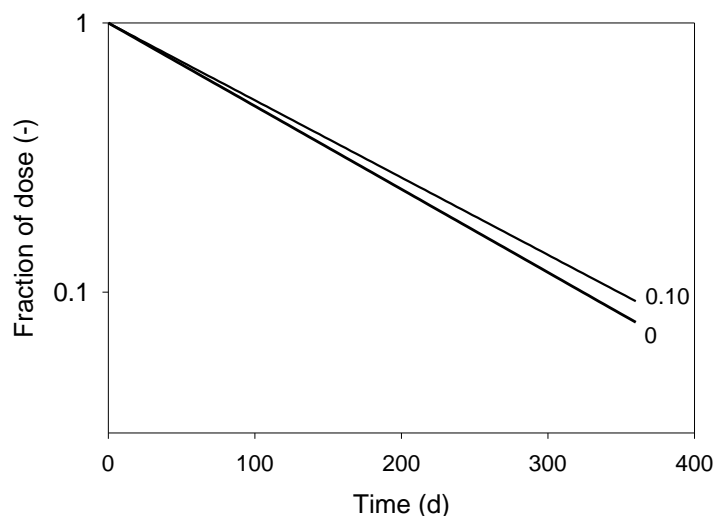


Figure 6: Effect of the daily amplitude of soil temperature on calculated decline of substance in a closed laboratory soil system assuming first-order degradation kinetics and using the Arrhenius equation to describe the effect of temperature on the degradation rate coefficient. The $DegT50$ at 20°C was 60 d and the Arrhenius activation energy was 65 kJ/mol. Calculations were made for an average soil temperature of 20°C and a daily sinusoidally fluctuating soil temperature with amplitudes of 0, 10 and 20°C as indicated in the graph.

So if we assume that the Arrhenius equation is correct at a time scale of hours, the current procedure will lead to an inversely modelled $DegT50_{matrix}$ value that is too short. Additionally, there is the problem that we have no evidence that the Arrhenius equation adequately describes the effect of the temperature on the degradation rate for temperatures that fluctuate at a time scale of hours. So even if the numerical models would be able to describe adequately the soil temperature in the top millimetres at a time scale of hours, the problem remains whether it is appropriate to use the Arrhenius equation at this time scale.

Similarly there is no evidence that the relationship between $DegT50_{matrix}$ and the soil moisture content of Eqn 1 works well at a time scale of hours for changing courses of moisture content with time as shown in Figure 4. Let us assume that Eqn 1 gives a reliable description of the relationship between the $DegT50_{matrix}$ and the volume fraction of water, θ , in the top millimetres. Let us furthermore consider the following example: (i) a substance with a $DegT50_{matrix}$ of 60 days at a θ of 0.2 (field capacity) 20°C and a B value of 0.7, (ii) θ fluctuates on a daily basis sinusoidally around an average θ of 0.1. Figure 7 shows that introducing a fluctuating θ in this example calculation slowed down the degradation rate slightly. However, this problem may be overcome by ignoring the effect of soil moisture in the inverse modelling procedure which leads to a conservative $DegT50_{matrix}$.

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647 **Figure 7:** Effect of the daily amplitude of volume fraction of water in soil on calculated decline of
 648 substance in a closed laboratory soil system assuming first-order degradation kinetics and using Eqn 1
 649 to describe the effect of the volume fraction of water on the degradation rate coefficient. The $DegT50$
 650 at $\theta = 0.2$ was 60 d and the exponent B was 0.7. Calculations were made for a daily sinusoidally
 651 fluctuating volume fraction of water with amplitudes of 0 and 0.10 (as indicated in the graph) around
 652 an average volume fraction of water of 0.10.

653

654 **2.5. Concluding remarks on the problem and proposed solution**

655

656 The problems described in the preceding sections fall into two categories:

657 A. the impossibility of excluding a competing loss process from the top millimetres

658 B. the impossibility of obtaining a reliable $DegT50_{matrix}$ at 20°C and pF = 2 from measured declines in
 659 the top millimetres via the described inverse modelling procedure.

660 These two problem categories are independent of each other. Both problem categories are difficult to
 661 solve and will require considerable research efforts. If problem A is ignored, this will lead to a too
 662 short $DegT50_{matrix}$. The direction of the error in the $DegT50_{matrix}$ resulting from problem B is variable:
 663 the $DegT50_{matrix}$ may be either too short or too long. It is in general undesirable that a higher-tier
 664 estimation of a model input parameter such as the $DegT50_{matrix}$ is not very reliable. However, this lack
 665 of reliability has to be balanced against the advantage that field persistence experiments are closer to
 666 the reality to be assessed than are laboratory incubations. For persistent compounds especially, the
 667 laboratory incubations may generate too long $DegT50_{matrix}$ values.

668 The Panel proposes to base this guidance proposal on the assumption that an inversely modelled
 669 $DegT50_{matrix}$ at 20°C and pF = 2 needs to be based on a measured decline that took place below the top
 670 millimetres of the soil. So the experimental period of a field persistence experiment has to be split
 671 into two parts: in the first part the bulk of the substance is still in the top millimetres and in the second
 672 part this bulk has moved to lower depths.

673 The Panel proposes to split the field persistence experiment into two parts based on the following
674 procedure: (i) fit the normalised decline curve to a biphasic decline model, and (ii) accept the rate
675 coefficient of the slow phase of this biphasic decline only if at the transition between the two phases
676 at least 10 mm of rain has fallen since application of the plant protection product. This rainfall
677 criterion is added to ensure that the slow phase of the biphasic decline does not represent a second
678 initial loss process (eg first very quick photodegradation followed by volatilisation without any rain
679 falling onto the field).

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683 3. Proposed guidance for analysing results of field persistence experiments

684 3.1. Introduction

685 Field persistence experiments are commonly carried out by spraying a plant protection product onto
686 bare soil in spring, with usually a crop then being grown. The decline of the soil residues with time is
687 measured by regular soil samplings often up to 50 or 100 cm depth. However, the guidance proposal
688 in this chapter is restricted to experiments with spraying onto bare soil; experiments with spraying
689 onto a crop are discussed in Chapter 4.

690 This guidance proposal is restricted to experiments in which plant uptake did not contribute
691 significantly to the dissipation of the plant protection product. This implies that experiments with
692 weakly sorbing substances in cropped soil are excluded.

693 This guidance proposal is intended to be used for experiments in which most of the remaining areic
694 mass is present in the top 30 cm depth. The background is that the Panel considers experiments with
695 significant leaching below 30 cm depth not suitable for estimating a $DegT50_{matrix}$ for the top layer in
696 view of the additional uncertainty in the inverse modelling procedure resulting from uncertainty in the
697 depth factor f_z (Eqn 5).

698 The aims of the guidance proposal in this chapter are the following subset of the general aims
699 described in Section 1.2:

700 (i) to develop procedures for estimating $DegT50_{matrix}$ values reliably from results of individual field
701 persistence studies

702 (ii) to develop procedures for estimating top-soil decline parameters reliably from results of individual
703 field persistence experiments.

704 3.2. Estimation of model input parameters using normalised decline curves

705 Introduction

706 In the past five years, the time-step normalisation procedure as described by FOCUS (2006; p. 179)
707 has become popular in the EU registration. This procedure assumes that the decline in the field can be
708 described well by numerical models that assume first-order degradation kinetics such as PELMO,
709 PRZM and PEARL (see Appendix 8 of FOCUS, 2006, for details). The procedure implies that the
710 decline curve after normalisation can be used directly to estimate the $DegT50_{matrix}$ of the top soil at
711 20°C and $pF = 2$. As described before, the Panel considers such an estimate only acceptable if
712 measures are taken to ensure that the $DegT50_{matrix}$ is based on the decline in soil below 5 mm depth.
713 Therefore the Panel describes here a proposal to use these normalised decline curves for estimating
714 the $DegT50_{matrix}$ plus a parameter describing the fraction of the initial decline in the soil surface layer.

715 The proposal is structured as follows. First an overview is given of the available candidate models
716 that might be used to describe the decline curve and the most suitable models are selected. Next
717 stepped approaches are proposed for these models to derive the appropriate endpoints from each field
718 persistence experiment.

719

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721 Selection of models for describing bi-phasic kinetics

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723 As described earlier, the dissipation rate in field persistence experiments is expected to be faster in
724 the initial stage of the experiment than subsequently. Such dissipation patterns cannot be described

725 adequately with first-order kinetics. Instead models describing biphasic kinetics are to be preferred.
 726 FOCUS (2006) recommended three models for describing bi-phasic kinetics: the bi-exponential
 727 model, the Gustafsen-Holden model and the hockey-stick model.

728
 729 The bi-exponential model (hereafter called the DFOP-model from ‘Double First-Order in Parallel’) is
 730 based on the assumption that a mass of plant protection product is present in two non-interacting
 731 compartments in the system which each degrade the product at their own rate assuming first-order
 732 kinetics. This results in the following expression of the time course of the mass m in the system:

$$733 \quad m = m_{ini,fast} \exp(-k_{fast} t) + m_{ini,slow} \exp(-k_{slow} t) \quad (6)$$

735 where

- 737 $m_{ini,fast}$ = mass in system in the fast-degrading compartment at the start (kg)
- 738 $m_{ini,slow}$ = mass in system in the slow-degrading compartment at the start (kg)
- 739 k_{fast} = rate coefficient in the fast-degrading compartment (d^{-1})
- 740 k_{slow} = rate coefficient in the slow-degrading compartment (d^{-1})
- 741 t = time (d).

742
 743 The qualifications ‘slow’ and ‘fast’ have no absolute meaning in this context: the highest rate
 744 coefficient of the two is by definition the fast one and the other is thus the slow one.

745
 746 Eqn 6 can be rewritten as:

$$747 \quad m = m_{ini} \left[g \exp(-k_{fast} t) + (1-g) \exp(-k_{slow} t) \right] \quad (7)$$

749 where

- 751 m_{ini} = total mass in the system at the start (kg)
- 752 g = fraction of total mass in the system applied to the fast-degrading compartment (-)

753
 754 The Gustafsen-Holden model (hereafter called the FOMC-model from ‘First-Order Multi-
 755 Compartment’) is based on the assumptions that there are an infinite number of non-interacting
 756 compartments which each degrade at their own rate (assuming first-order kinetics) and that the
 757 frequency distribution of the rate coefficients of these compartments can be described by a gamma
 758 function. This gives the following equation for the FOMC model:

$$759 \quad m = \frac{m_{ini}}{\left(\frac{t}{\beta} + 1 \right)^\alpha} \quad (8)$$

761 where

- 762 α = so-called shape parameter (-)
- 763 β = so-called location parameter (d)

764
 765
 766 The Hockey-Stick model (hereafter called the HS model) is based on the assumption that the mass in
 767 the system declines according to first-order kinetics but at a certain point in time (‘the breakpoint’)
 768 the rate coefficient changes:

$$769 \quad \begin{aligned} 770 \quad t \leq t_b \quad m &= m_{ini} \exp(-k_1 t) \\ 771 \quad t > t_b \quad m &= m_{ini} \exp(-k_1 t_b) \exp(-k_2 (t - t_b)) \end{aligned} \quad (9)$$

772 where

773 t_b = breakpoint time (d)

774 k_1 = rate coefficient until t_b (d^{-1})

775 k_2 = rate coefficient after t_b (d^{-1})

776

777 Our aim is to describe a normalised decline of the areic mass of a plant protection product in soil of a
778 field persistence experiment. This decline is expected to show a rapid initial phase in the period that
779 surface loss processes play an important role followed by a slower phase that is dominated by the
780 degradation rate within the soil matrix. It is also possible that the normalised decline shows a slow
781 initial phase followed by a faster decline later. The purpose of this proposal is to use the decline in the
782 second phase to derive a normalised $DegT50_{matrix}$ as input to models such as PRZM, PELMO and
783 PEARL. These models are based on first-order kinetics and also the time-step normalisation
784 procedure is based on the assumption of first-order kinetics. Thus the Panel considers the FOMC model
785 not suitable because it does not describe a first-order decline in the second phase.

786

787 So the remaining options are the DFOP and HS models. The Panel recommends considering both
788 models for deriving a normalised $DegT50_{matrix}$. The DFOP model has the advantage that it describes a
789 gradual transition between the two phases but the disadvantage that it can only describe a decline that
790 is faster at the start than at the end. The HS model has the advantage that it can describe both a
791 decline that is faster at the start than at the end and a decline that is slower at the start than at the end.
792 However it has the disadvantage that there is an abrupt transition between the two phases.

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798 **Stepped approach for evaluating normalised decline curves with the DFOP or Hockey-Stick**
 799 **models**

800
 801 The Panel proposes to use the DFOP model for evaluating normalised decline curves unless a visual
 802 inspection of the measured decline curve shows no slowing down or unless a visual inspection of this
 803 curve shows even a speeding up at later times.

804
 805 The proposal for evaluating results of field persistence experiments with the DFOP model consists of
 806 the following steps:

- 807 i. transform the measured time series of remaining amounts into a normalised time series using the
- 808 time-step normalisation approach described by FOCUS (2006; p. 179)
- 809 ii. fit the normalised time series to the DFOP model as described by FOCUS (2006)
- 810 iii. estimate a breakpoint time t_b from the DFOP fit
- 811 iv. use the flow chart in Figure 8 to decide on usefulness of the rate coefficient k_{slow}
- 812 v. if this results in a useful k_{slow} then calculate the resulting $DegT50_{matrix}$ as $\ln 2 / k_{slow}$ and calculate the
- 813 rapidly dissipating fraction F_{field} on the basis of the difference between the initial areic mass and the
- 814 areic mass at the breakpoint time t_b .

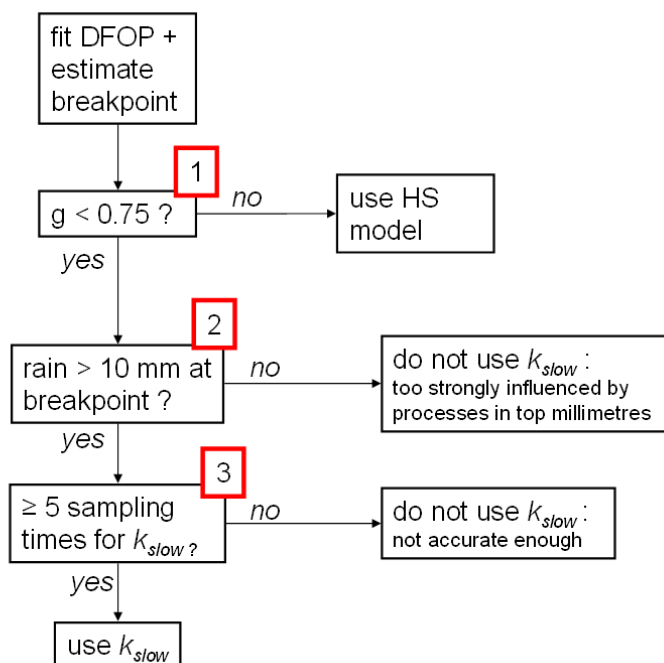
815
 816 The determination of the breakpoint time (step iii) is not straightforward because the slope of the
 817 DFOP decreases gradually. The Panel proposes to define the breakpoint time as:

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$$t_b = \frac{3 \ln 2}{k_{fast}} \quad (10)$$

820
 821 This implies that the breakpoint time corresponds with a time equal to three half-lives of the fast-
 822 degrading compartment, so $g \exp(-k_{fast} t_b) = 0.125 g$. This implies that, at this breakpoint time, 87.5%
 823 of the decline of the fast-degrading compartment has taken place. Therefore it is likely that after this
 824 breakpoint time, the slow-degrading compartment dominates the overall decline. Only for high g
 825 values may this not be the case. For example, if $g = 0.9$ then $0.125 g = 0.11$ whereas $(1 - g)$ may still
 826 be close to 0.1. In such a case the breakpoint time estimated with Eqn 10 may be too short.

827
 828 The rationale behind the flow chart in Figure 8 is as follows. Decision box 1 tests whether g is below
 829 0.75. If no, the Panel recommends using the HS model instead of the DFOP model because the
 830 estimate of the breakpoint time with Eqn 10 is not reliable enough. Decision box 2 tests whether
 831 cumulative rain is at least 10 mm at the breakpoint. If this is not the case, k_{slow} has to be rejected
 832 because it is too strongly influenced by processes in top millimetres. If cumulative rain was at least 10
 833 mm at the breakpoint, box 3 is reached. The problem here is that k_{slow} may be based on only a few data
 834 points and thus may be not reliable enough. EFSA (2008, p. 9) required five data points for an
 835 accurate $DegT50$ calculation for laboratory studies. The scatter in field data may be expected to be
 836 larger than in laboratory data. Therefore the Panel considers five data points to be a minimum quality
 837 requirement in decision box 3. The decision on the five data points is to be based on the number of
 838 data points at times later than the breakpoint time.

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Figure 8. Flow chart for assessment of results of field persistence experiments after analysis with the DFOP model. The numbers 1 to 3 act as references to the corresponding decision boxes in the main text.

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The proposal for evaluating results of field persistence experiments with the HS model consists of the following steps:

- i. transform the measured time series of remaining amounts into a normalised time series using the time-step normalisation approach described by FOCUS (2006; p. 179)
- ii. fit the normalised time series to the HS model as described by FOCUS (2006)
- iii. use the flow chart in Figure 9 to decide on usefulness of the rate coefficient k_2
- iv. if this results in a useful k_2 then calculate the resulting $DegT50_{matrix}$ as $\ln 2 / k_2$.

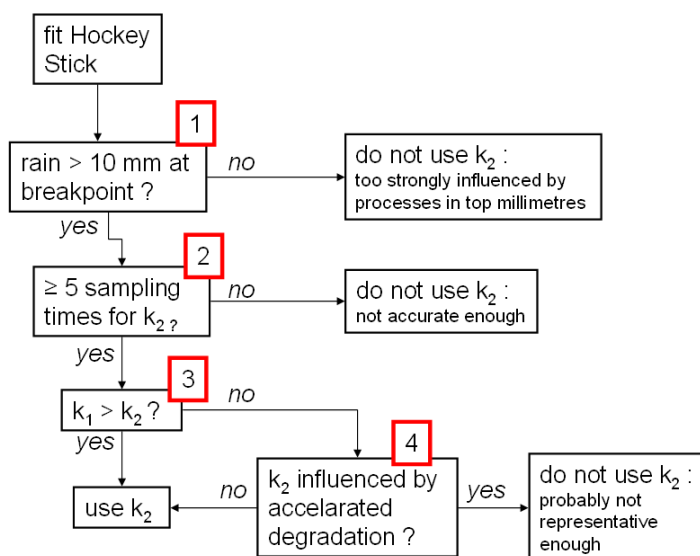
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For the flow chart in Figure 9, the rationale for the boxes 1 and 2 is the same as for the flow chart of Figure 8. Decision box 3 tests whether $k_1 > k_2$. If this is indeed the case, k_2 can be accepted. If this is not the case, there is the possibility that after some time accelerated degradation occurred in the field experiment which may happen in some soils but not in others. This requires a case-by-case analysis.

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It is only meaningful to calculate the rapidly dissipating fraction F_{field} if $k_1 > k_2$. If this is the case, F_{field} can be calculated on the basis of the difference between the initial areic mass and the areic mass at the breakpoint time t_b .

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Figure 9. Flow chart for assessment of results of field persistence experiments after analysis with the Hockey-Stick ('HS') model. The numbers 1 to 4 act as references to the corresponding decision boxes in the main text.

The flow charts of Figures 8 and 9 do not consider explicitly cases where k_{slow} is close to k_{fast} or where k_1 is close to k_2 . Then the uncertainty in the breakpoint time t_b is considerable. In such a case, the notifier could first assess the time when cumulative rainfall has reached 10 mm, fix the breakpoint to this time and follow the flow charts of Figures 8 and 9.

The findings from this kinetic modelling (DFOP or HS model) should be interpreted with consideration of existing information in the dossier on potential volatilisation and potential photodegradation (Section 2.2.) and the degradation rates from the laboratory soil tests. Once a $DegT50_{matrix}$ value is obtained with either the DFOP or HS model, the Panel recommends checking whether this value is significantly longer (t-test at 5% level) than the laboratory $DegT50$ values. In general $DegT50_{matrix}$ values from field studies are expected to be shorter than $DegT50$ values from laboratory studies but the opposite may happen in a small proportion of the cases (Beulke et al., 2000). The Panel considers it very unlikely that a laboratory study with a certain soil shows systematically and consistently a faster degradation rate than a field study with the same soil at the same temperature and moisture content. The Panel considers it far more likely that a field $DegT50_{matrix}$ that is significantly longer than the geomean laboratory $DegT50$ is caused by systematic errors in the inverse modelling procedure (eg B or E_a values of this substance-soil combination that differ strongly from the assumed default values or poor simulation of soil temperature or soil moisture in the soil layer below 5 mm depth). It can of course also happen by coincidence because the number of measured laboratory $DegT50$ values is usually limited to four values in a dossier. Therefore the Panel recommends assessing in such a case the magnitude of the effects of conservative assumptions in the inverse modelling procedure; if this effect is so large that it may explain the difference with the laboratory $DegT50$ values, then it is considered justifiable to discard the $DegT50_{matrix}$ value of this field experiment.

908 **4. Proposed guidance for analysing results of soil accumulation experiments**

909 In the context of Tiers 1 to 4 of Figure 1, the possible endpoints from soil accumulations experiments
910 are a $DegT50_{matrix}$ (of top soil at 20°C and pF = 2) plus the F_{field} parameter describing a fast initial
911 decline at the soil surface..

912 Soil accumulation experiments can broadly be divided into two categories:

913 A. experiments with only two to three samplings per year: one just before the yearly application, one
914 just after the yearly application and one mid-year

915 B. experiments in which each year a number of samplings has taken place.

916 The remainder of this section applies to type-A soil accumulation experiments. If type-B experiments
917 contain enough samplings and if crop interception of the plant protection product was insignificant,
918 the guidance for the field persistence experiments might be applicable.

919 Based on the experimental design of soil accumulation experiments (two-three samplings per year),
920 the Panel expects that it is impossible to estimate the fraction that penetrates into the soil separately
921 from the $DegT50_{matrix}$.

922 The Panel considered the option to obtain the $DegT50_{matrix}$ by inverse modelling using a fixed,
923 prescribed fraction that penetrates into the soil. This fixed fraction could be based on the calculations
924 for the exposure scenario (eg using the crop interception tables proposed by FOCUS, 2000a). Thus at
925 least consistency would be assured: the $DegT50_{matrix}$ would be estimated on the basis of inverse
926 modelling using the same fraction that penetrates into the soil as would be used later in the scenario
927 calculations for the exposure assessment.

928 However, the Panel rejected this option for two reasons:

929 - the soil accumulation experiment may have been carried out under conditions that differ
930 significantly from the required exposure scenario and thus it may be inappropriate to use the same
931 fraction for strongly different situations (e.g. in the soil accumulation experiment application to full
932 grown wheat crop and in required exposure scenario application to bare soil);

933 - this procedure prescribes the fraction that penetrates into the soil to the inverse modelling procedure;
934 the true fraction in the soil accumulation experiment will differ from this prescribed fraction;
935 therefore the inverse modelling procedure will return a $DegT50_{matrix}$ value with an unknown
936 systematic error; such a $DegT50_{matrix}$ value cannot be simply compared in statistical tests to
937 $DegT50_{matrix}$ values obtained from other sources (laboratory studies or field persistence studies); so
938 this makes it impossible to give such a $DegT50_{matrix}$ value an appropriate place in the stepped
939 approach of Figure 2.

940 As a next option the Panel considered the possibility of estimating conservative $DegT50_{matrix}$ values
941 (of top soil at 20°C and pF = 2) from soil accumulation experiments (i.e. upper limits). An upper limit
942 of the $DegT50_{matrix}$ is obtained by assuming a lower limit of the fraction of the dose that penetrates
943 into the soil. This can be illustrated with the following example:

944 - on 1 June 2008 a dose of 1 kg/ha was sprayed onto a winter wheat crop; one year later 0.25 kg/ha
945 was recovered from the soil

946 - if it is assumed that the whole dosage penetrated into the soil, the half-life under these field
947 conditions is 0.5 year

948 - if it is assumed that only half of the dosage penetrated into the soil, the half-life under these field
949 conditions is 1.0 year.

950 A lower limit of the fraction of the dose that penetrates into the soil implies an upper limit of the crop
951 interception (and ignoring wash-off). The Panel is currently setting up a database of all available crop
952 interception measurements which will be followed by an analysis of these data. The Panel hopes to be
953 able to estimate reliable upper limits of the fraction intercepted by the crop (lower than the trivial 1.0)
954 from this analysis at a later stage. The procedure might work in exceptional cases where the true
955 $DegT50_{matrix}$ in soil accumulation experiments is much shorter than in field persistence experiments.

956 If soil accumulation experiments are carried out with spray applications to bare soil, another
957 complication occurs: it will usually be impossible to derive from the experiment which fraction of the
958 dose dissipated while most of the areic mass of the plant protection product was still in the top
959 millimetres. If loss processes other than degradation in the soil in this top layer are ignored in the
960 analysis, the $DegT50_{matrix}$ is overestimated which is not defensible.

961 The consequence from the above reasoning is that processes above and at the soil surface may have a
962 large effect on the build-up of soil residues in soil accumulation experiments, which makes it difficult
963 to extrapolate results of soil accumulation experiments to a range of conditions within the EU.

964 In view of the above complications, the Panel recommends not using type-A soil accumulation
965 experiments for deriving $DegT50_{matrix}$ values.

966

967 **5. Proposed guidance for estimating model input parameters for the required exposure**
 968 **scenarios**

969 **5.1. Introduction**

970 The guidance in Chapter 3 implies that each laboratory degradation rate experiment and each field
 971 persistence experiment will lead to an estimated $DegT50^7$ at 20°C and pF = 2 for the topsoil layer.
 972 This guidance further implies that each field persistence experiment will lead to an estimate of F_{field} .

973 So the next step is to provide guidance on how these data should be used to generate model input data
 974 for the required exposure scenario.

975 The guidance for estimation of model input parameters for the required exposure scenario will not
 976 include guidance for parameters derived from soil accumulation experiments in view of the
 977 complications described in Chapter 4. This guidance will also not include estimation of model input
 978 parameters for Tiers 3 and 4 if these tiers are based on a relationship between the $DegT50$ and soil
 979 properties such as the pH or clay content. So the guidance below is restricted to substances whose
 980 $DegT50$ (at 20°C and pF = 2) is not a function of such soil properties.

981 **5.2. Estimation of the geomean $DegT50$ for the required exposure scenario from**
 982 **laboratory and field experiments**

983 Once $DegT50$ values (top soils at 20°C and pF = 2) from laboratory and field experiments are
 984 available, the estimation of the $DegT50$ to be used as input for the required exposure scenario consists
 985 of two more steps (see Section 1.1):

986 (i) developing procedures for assessing the relevant population of $DegT50$ values for the required
 987 exposure scenario

988 (ii) developing procedures for estimating reliably the geomean of the relevant population of $DegT50$
 989 values for the required exposure scenario.

990 So the first problem is to find the relevant population of $DegT50$ values for the required exposure
 991 scenario. This problem has been addressed in the current EU leaching assessment. FOCUS (2000a)
 992 developed nine EU groundwater scenarios. The $DegT50$ is a very important input parameter for the
 993 scenario calculations. The current procedure is to calculate a geomean $DegT50$ from either laboratory
 994 or field studies excluding only measurements with volcanic soils; soils from temperate regions outside
 995 the EU are considered also acceptable provided their pH, organic matter and clay contents are within
 996 the range of values to be expected for top soils in the EU. For field persistence experiments, it is
 997 additionally checked whether temperature and precipitation for the trial site are comparable to those
 998 in the EU where the assessed crop is grown. The geomean thus obtained is used for all nine
 999 groundwater scenarios. So it is implicitly assumed that a $DegT50$ measured for any non-volcanic
 1000 agricultural soil from temperate regions can be used to predict the $DegT50$ for any non-volcanic
 1001 agricultural soil within the EU. This assumption may be questioned of course: eg for a given
 1002 substance it cannot be excluded that there are systematic differences in $DegT50$ values of top soils (at
 1003 20°C and pF = 2) between the EU regulatory zones north and south or between the US and the EU
 1004 resulting eg from systematic differences in agricultural practices. The current Annex II data

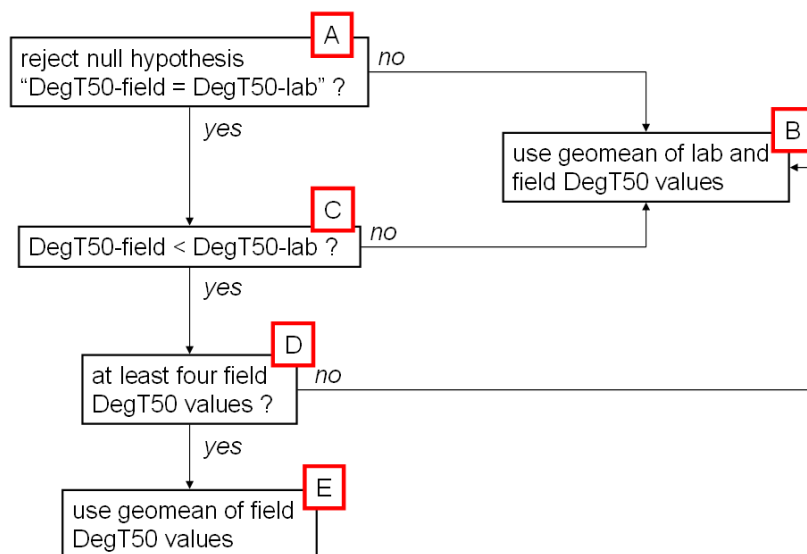
⁷ This chapter deals with $DegT50$ values obtained both in field and laboratory experiments. These will both be represented in this chapter by the acronym $DegT50$ so without the ‘matrix’ suffix because it is not meaningful to use this suffix for laboratory studies and because it is assumed in this chapter that the values derived from the field studies are appropriate.

1005 requirements for laboratory measurements of the *DegT50* state that studies with one soil are needed
 1006 for the degradation route plus three for the degradation rate which sums up to four. With respect to
 1007 the properties of the soils to be used, the current Annex II refers to SETAC (1995). This guideline
 1008 specifies ranges of 2-5% organic matter, pH 5.5-7.5 and clay 10-25% for the degradation route.
 1009 However, for the degradation rate studies, SETAC (1995) only states ‘The additional soils ... should
 1010 cover a range of pH, organic matter and clay content typical of the regions where the pesticide will be
 1011 used’. The draft version of the revised Annex II refers to OECD (2002a). This guideline prescribes
 1012 only that ‘the types of soils tested should be representative of the environmental conditions where use
 1013 or release will occur’. So the geographical origin of the soil is not considered at all.

1014 The Panel doubts whether such a crude approach for defining the relevant population of *DegT50*
 1015 values for the required exposure scenario is defensible (eg NAFTA, 2006, and US-EPA, 2008,
 1016 prescribe a more subtle approach: ie to base the soil-selection procedure for field persistence
 1017 experiment on GIS-based decision support models or on other GIS-based vulnerability assessment
 1018 tools that account for the critical factors affecting pesticide dissipation). To underpin this crude
 1019 approach, statistical analyses of existing *DegT50* data of a number of representative plant protection
 1020 products are needed. On the other hand, the Panel is not aware of information that indicates that this
 1021 crude approach is not defensible. Therefore the Panel proposes to accept this approach as a working
 1022 hypothesis and to initiate in parallel activities to test this working hypothesis by careful analysis of
 1023 relevant literature data.

1024 Let us now assume that a relevant population of *DegT50* values (all at 20°C and pF = 2) is available
 1025 and that it contains values from both laboratory studies and field persistence studies. The problem is
 1026 how to get to a geomean *DegT50*. Let us look back at the aim of the estimation of the *DegT50*: use of
 1027 field persistence studies (Step 2 in Figure 2) is only needed if Step 1 (ie using only laboratory *DegT50*
 1028 values) does not result in negligible risk to soil organisms. So within this Step 2 the notifier has to
 1029 demonstrate that a possible risk does not exist. In the context of a tiered approach as in Figure 2, the
 1030 information from higher steps should indicate a clear need to change the *DegT50* from Step 1. It
 1031 means also that rejecting laboratory data from Step 1 in favour of field data from Step 2 is only
 1032 defensible if there are convincing arguments to do so.

1033 Therefore the Panel proposes the flow chart shown in Figure 10. We consider the laboratory *DegT50*
 1034 as a first conservative and simple step and the field *DegT50* values as a more realistic and more
 1035 sophisticated second step. Let us consider e.g. the case where we have four laboratory *DegT50* values
 1036 of 120, 140, 160 and 180 days (geomean of 148 days) and one field *DegT50* value of 115 days. In
 1037 such a case, the Panel does not consider it defensible to reject immediately all the laboratory *DegT50*
 1038 and to switch to a *DegT50* of 115 days for the further exposure assessment. It may just be coincidence
 1039 that this one value is lower than the other four. Therefore the Panel proposes to test statistically the
 1040 null hypothesis that the geomean *DegT50* value from the laboratory studies is equal to that of the field
 1041 studies (box A in Figure 10). If this null hypothesis is not rejected, the Panel recommends pooling all
 1042 the laboratory and field *DegT50* values and calculating the geomean (box B). If the null hypothesis is
 1043 rejected, then the next test is whether the geomean *DegT50* of the field studies is shorter than that of
 1044 the laboratory studies (box C). If yes, then we discard the laboratory studies and move to box D. In
 1045 this box it is tested whether at least four field *DegT50* values are available. The four values are based
 1046 on the data requirement for laboratory *DegT50* values in Annex II to Council Directive 91/414/EC. If
 1047 this is indeed the case then the geomean field *DegT50* is calculated as the endpoint of this flow chart
 1048 (box E). If less than four values are available, the uncertainty of the estimated geomean of the field
 1049 *DegT50* values will be too high and the Panel proposes to pool all the laboratory and field *DegT50*
 1050 values (so back to box B).



1051

1052 **Figure 10:** Flow chart for assessment of *DegT50* values from laboratory and field persistence
 1053 experiments. The letters A to E act as references to the corresponding boxes in the main text.

1054

1055 The calculation procedure for the geomean to be used in the exposure assessment is not
 1056 straightforward because the geomean of the statistical population is needed and this may differ from
 1057 the geomean of the sample population. In general, the uncertainty of the estimated geomean decreases
 1058 with increasing sample size. The Panel intends to produce an estimate of the uncertainty of the
 1059 geomean as a function of this sample size (which implicitly requires a random set of experimental
 1060 fields) which can be taken into consideration in the further exposure assessments.

1061 **5.3. Estimation of model input parameters describing the decline at the soil surface for the**
 1062 **required exposure scenarios**

1063 As described above, the dissipation at the soil surface can be described with the parameter F_{field} . The
 1064 estimation of this input parameter for the required scenario can be subdivided into:

- 1065 A) does the observed fast decline also occur in the required exposure scenario?
- 1066 B) which value of the input parameter is to be used?

1067 For Step A, the Panel proposes that the fast surface decline is switched off ($F_{field} = 0$) unless the
 1068 notifier provides plausible arguments to support the position that a fast initial decline is expected to
 1069 occur in the required exposure scenario. Let us consider two examples: a case YES where this is
 1070 indeed expected and a case NO where this is not expected. In case YES, the field persistence
 1071 experiment was in Germany and it showed a fast initial decline of 70% of the dose as a result of
 1072 photodegradation. The required exposure scenario for this case was spraying onto bare soil in
 1073 southern Europe in spring. In case NO, we have the same field experiment but now the required
 1074 exposure scenario is spraying onto a crop with 80% deposition on the crop and 20% on the soil with
 1075 most of the soil usually in the shadow of the plants.

1076 For Step B, the Panel proposes to use the worst-case value of four accepted values. For example, four
 1077 field persistence experiments show F_{field} values of 30, 40, 60 and 80% for experiments in France, UK,
 1078 Germany and Spain under normal agricultural use conditions. If less than four such values are

1079 available, the Panel proposes to use an estimate of the 12.5th percentile which is equivalent to the
1080 worst case of four values.

1081 The argument for using a worst case of four values (as described before) is that the uncertainty
1082 resulting from this surface processes was ignored in the scenario selection, so the uncertainty has to
1083 be explicitly accounted for in the scenario parameterisation phase. The basis for the worst case of four
1084 is that, in EU regulatory practice, field persistence studies with four soils are usually required.

1085

1086 **5.4. Proposal for using the revised $DegT50$ and F_{field} in the exposure assessments in the**
 1087 **different tiers**

1088 Based on the previous sections, final values of $DegT50$ and F_{field} are assumed to be available. The next
 1089 step is to use these values in the exposure assessment for spray applications to annual crops under
 1090 conventional and reduced tillage proposed by EFSA (2010a).

1091 These values are relevant for Tiers 1 to 4 of Figure 1. The Panel proposes that a revised $DegT50$ can
 1092 be used for all these tiers. The Panel proposes to include the fast surface decline only in Tiers 2 or 4.
 1093 Tiers 1 and 3 are based on simple analytical models (Figure 1) with no crop interception in Tier 1 and
 1094 probably also no interception in Tier 3. It seems not in balance for Tiers 1 and 3 to exclude crop
 1095 interception while including a fast surface decline (in contrast to Tiers 2 and 4).

1096 The procedure for the parameterisation of the fast surface decline is given by the following four steps.

1097 Step-1- F_{field} : run the model for the required simulation period (26 years for annual applications, 46
 1098 years for application every two years or 66 years for application every three years; see EFSA, 2010a)
 1099 using a corrected dosage A_{cor} (kg/ha) given by

$$1100 \quad A_{cor} = A (1 - F_{field}) \quad (11)$$

1101

1102 where A is the recommended dosage.

1103 Step-2- F_{field} : calculate from this run (excluding the six ‘warming-up’ years; EFSA, 2010a) the average
 1104 fraction of the dosage lost due to simulated volatilisation (F_{vola}) and runoff (F_{runoff}).

1105 Step-3- F_{field} : extract from this run the application at which the all-time high concentration occurs.

1106 Step-4- F_{field} : run the model a second time but now with a dosage given by

$$1107 \quad A_{cor} = A (1 - F_{field} + F_{vola} + F_{runoff}) \quad (12)$$

1108 for all applications except the application in the year where the all-time high concentration occurs; for
 1109 this application use A as the dose.

1110 The background to this procedure is as follows. Firstly there is the problem of ‘double counting’ of
 1111 loss processes: the measured F_{field} may include runoff and volatilisation and so using F_{field} in
 1112 combination with a model that already simulates volatilisation and runoff will lead to systematic
 1113 underestimation of exposure concentrations. This is prevented by Eqn 12. Secondly there is the
 1114 problem that the all-time high concentration would be systematically underestimated if Eqn 12 were
 1115 always to be used because in reality the full dosage is sprayed.

1116 If the application is onto a crop, part of the plant protection product will be intercepted by the crop
 1117 and part will be deposited onto the soil. The areic mass intercepted by the crop will partly be washed
 1118 off to the soil in the simulations (EFSA, 2010a). So also if there is crop interception, the Panel
 1119 recommends using Eqn 12 (F_{field}) with A_{cor} being the sum of the areic masses sprayed onto crop and
 1120 soil.

1121

1122 **6. Usefulness of the proposed guidance for assessment of leaching to groundwater and**
1123 **surface water**

1124 The degradation rate of plant protection products in soil plays also an important role in the assessment
1125 of their leaching to groundwater and surface water. The problems associated with the use of field
1126 persistence studies for estimating *DegT50* values described in Chapter 2 apply also to the leaching
1127 assessment. In the EU groundwater leaching simulations, the *DegT50* values are even extrapolated to
1128 the 30-100 cm layer by assuming a single and unique f_z relationship (see Eqn 3) for all plant
1129 protection products and all their metabolites in all soils in EU agriculture (FOCUS, 2000a). So also
1130 for the leaching it is very important that the assessment of the *DegT50* is not ‘contaminated’ by loss
1131 processes occurring in the top millimetres of soil.

1132 The Panel considers the guidance proposals for estimating the *DegT50_{matrix}* as described in Chapter 3
1133 and Sections 5.2 also useful for assessment of leaching to groundwater and surface water because
1134 these proposals are not specific for the soil exposure assessment. Also the guidance for the estimation
1135 of the model input parameters describing the decline at the soil surface in Section 5.3 is not specific
1136 for soil exposure and can therefore be used for the leaching assessments.

1137 However, the guidance for the initial-decline parameters to be used in the soil exposure scenario
1138 calculations in Section 5.4 contains elements that are specific to the soil exposure assessment and
1139 needs therefore to be modified as follows for leaching assessments:

1140 1. if the leaching calculations are based on the convection-dispersion equation, then the proposed
1141 procedure of Step-1- F_{field} to Step-4- F_{field} should be followed with the modification that Eqn 12 can be
1142 used for all application years (so it is not necessary to make calculations with a full dose in one of the
1143 years); this is justifiable because leaching in such model calculations is a multi-year process;

1144 2. if the leaching calculations include preferential flow, then the calculations have to be carried out
1145 assuming $F_{field} = 0$ because preferential flow events may take place shortly after application when the
1146 almost the full dosage is still present.

1147

1148 CONCLUSIONS AND RECOMMENDATIONS

1149 CONCLUSIONS

1150

1151 1. The half-life for degradation in the top 30 cm of soil at 20°C and pF = 2 is an important input
1152 parameter for numerical models that simulate exposure of organisms in soil. For soil under
1153 conventional or reduced tillage, the main use of this half-life is to simulate the degradation rate for
1154 soil depths between 1 and 30 cm. When deriving such a half-life from field persistence and soil
1155 accumulation experiments, appropriate measures have to be taken to ensure that the value obtained is
1156 not influenced strongly by processes in the top millimetres of soil.

1157 2. Based on current knowledge and data commonly available in dossiers of plant protection products,
1158 it is impossible to estimate with enough certainty photodegradation rates of plant protection products
1159 in the top millimetres in soil. Studies with sieved soils in the laboratory demonstrate that
1160 photodegradation is limited to the top 2 mm of soil. Furthermore there are uncertainties assessing
1161 volatilisation for surface-applied compounds.

1162 3. Current numerical models used for simulating behaviour of plant protection products in soil in the
1163 context of the EU regulatory exposure assessment are unable to describe satisfactorily the daily
1164 fluctuations of the soil temperature and of the volume fraction of water in the top millimetres of soil.

1165 4. The parameters describing the relationship between on the one hand the degradation rate
1166 coefficient in soil and on the other hand soil temperature (ie the Arrhenius activation energy) or
1167 volume fraction of water in soil (ie the exponent *B*) show considerable variation between soils and
1168 plant protection products. This uncertainty results in a considerable uncertainty in *DegT50_{matrix}*
1169 values obtained from field experiments by inverse modelling assuming default values of the Arrhenius
1170 activation energy and the exponent *B*.

1171 5. Assessment of *DegT50_{matrix}* values based on field persistence experiments can be based on inverse
1172 modelling using the approach of normalised decline curves proposed by FOCUS (2006). The
1173 normalised decline curves can be either described with the DFOP (double first-order kinetics) or
1174 Hockey-Stick models.

1175 6. The Panel considers soil accumulation experiments with only two to three soil samplings per year
1176 not suitable for estimating the *DegT50_{matrix}* because the fraction of the dosage that penetrates to soil
1177 depths deeper than a few millimetres cannot be estimated with sufficient accuracy from the results of
1178 such experiments.

1179 7. Once appropriate *DegT50* values from laboratory and field experiments are available, the
1180 estimation of the *DegT50* to be used as input for the required exposure scenario consists of two more
1181 steps: (i) assess the relevant population of *DegT50* values for the required exposure scenario, and (ii)
1182 estimate reliably the required statistical attribute (certain percentile or some mean value) based on this
1183 population. The Panel proposes basing the relevant population of *DegT50* values on the assumption
1184 that a *DegT50* measured for any non-volcanic agricultural soil from temperate regions can be used to
1185 predict the *DegT50* for any such soil within the EU. This assumption is a working hypothesis that has
1186 to be underpinned further. The type of attribute has to be consistent with the scenario-selection
1187 procedure which was based on taking the geomean *DegT50* value assuming a log-normal distribution.
1188 So the Panel recommends taking the geomean *DegT50* value. The estimation of the geomean *DegT50*
1189 of the population has to consider the uncertainty resulting from the limited number of samples in the
1190 sample population.

1191 8. If the relevant population of *DegT50* values for a certain exposure scenario consists of a mixture of
1192 values obtained in the laboratory and in the field, the Panel recommends excluding the laboratory
1193 values only if the null hypothesis that laboratory and field values are equal is rejected. If the relevant
1194 population of *DegT50* values for a certain exposure scenario consists of less than four values based on
1195 field experiments, the Panel recommends using both laboratory and field values for estimating the
1196 geomean.

1197 9. The Panel considers the guidance proposals for estimating *DegT50* values also useful for
1198 assessment of leaching to groundwater and surface water because the main use of the *DegT50* values
1199 in these groundwater and surface water scenarios is the same as for the soil exposure assessment
1200 considered in this opinion (ie simulate the degradation rate for soil depths between 1 and 30 cm).

1201 RECOMMENDATIONS

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1203 1. The Panel recommends compiling a database of all relevant and reliable *DegT50* values of
1204 agricultural top soils within the temperate regions at 20°C and pH = 2 to test the assumption that this
1205 *DegT50* does not vary systematically between geographical zones in the temperate regions for non-
1206 volcanic soils.

1207 2. In case the notifier wants to use results of field persistence studies for estimating the *DegT50_{matrix}* as
1208 an input parameter for exposure models, the Panel recommends incorporating the plant protection
1209 product to a depth of about 10 cm into the soil immediately after application.

1210 3. The Panel recommends improving the validation status of mechanistic models for simulating loss
1211 processes at the soil surface (especially for photodegradation and volatilisation).

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1314 **ABBREVIATIONS**

<i>DegT50</i>	Half-life resulting from transformation of substance in the soil matrix
FOCUS	<u>F</u> orum for <u>C</u> o-ordination of pesticide fate models and their USe
PBT	<u>P</u> ersistence <u>B</u> ioaccumulation <u>T</u> oxicity
PEC	<u>P</u> redicted <u>E</u> nvironmental <u>C</u> oncentration
PEC _{SOIL}	<u>P</u> redicted <u>E</u> nvironmental <u>C</u> oncentration in soil
PPP	<u>P</u> lant <u>P</u> rotection <u>P</u> roduct
PPR Panel	Scientific Panel on Plant Protection Products and their Residues
TWA	<u>T</u> ime- <u>W</u> eighted <u>A</u> verage

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