Draft being consulted prepared by the German Environment Agency (Umweltbundesamt, UBA),

Guidance for consideration and parameterisation of photo transformation compounds in groundwater simulations in the exposure assessment of plant protection products

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1 Abstract

This paper gives recommendations how to consider transformation products from photolysis ('photo transformation compounds') in simulations for the predicted environmental concentrations in ground water (PECgw). It describes possible parameterisations of the input parameters for the photolytic pathway (i.e. the photolytic half-life and the corresponding reference irradiation) in a tiered approach. The FOCUS-PELMO software has the option to simulate the photolytic pathway in PECgw simulations of photo transformation compounds. Furthermore, the recommendations of the EFSA guidance (2014) describe how to derive separate half-lives for the surface processes ($DT50_{fast}$) and the biodegradation in the soil matrix ($DT50_{slow}$) from field dissipation studies by using biphasic models (DFOP, HS). From field dissipation studies evaluated with biphasic kinetics, the k_{fast} value can be representative for the photolytic degradation on soil surface for non-volatile substances. This value should be determined after a time-step normalisation according to irradiance data for the location and period of the field trial, to a reference irradiance of 100 W m^{-2}. In case, irradiance values are not available in the study, these values can be derived from databases such as AGRI4CAST or NASA, freely available in the internet.

2 Introduction

European Commission (2014) guidance covers the groundwater exposure assessment of plant protection products and their degradation products in the EU as well as in the national assessment for authorisation procedure. The report is based on the requirements and criteria of the Directive 91/414/EWG and subsequent regulation EC (No) 1107/2009. Advanced simulation models were introduced and evaluated, which can calculate predicted environmental concentrations (PEC) of active substances and their transformation products in groundwater. In addition, a tiered approach was developed to consider extended modelling options in the groundwater exposure assessment.

The refinement procedure of ground water exposure assessment for active substances is not in the focus of this paper and will only be mentioned in the margin (chapter 8). The main intention of the provided recommendations is to consider the photo transformation compounds formed by soil photolysis as a standard requirement in the ground water exposure assessment using the best available models and parameters in accordance with the current guidelines and scientific opinions. Since May 2013, the FOCUS-PELMO 5.5.3 software has been provided on the FOCUS website. This software makes it possible to consider the soil photolysis pathway together with the biodegradation pathway as a higher tier option in the leaching assessment of active substances on the one hand, and the consideration of photo transformation compounds in the leaching simulation as an essential lower tier approach on the other hand.

With the FOCUS-PELMO 5.5.3 version and subsequent versions there is no need to simulate a fixed apportionment of the total application rate into two virtual pathways as it was performed in the past. With the model representation of 'tipping buckets' (Michael Klein, 2012), FOCUS-PELMO 5.5.3 and more recent versions keeps track of the increasing depth of the modelled molecules. The soil photolysis process is simulated until the active substance has been completely transported from the soil surface (1 mm) into deeper soil matrix by rainfall or irrigation. Only for the portion of active substance located in the upper 1 mm of the soil photolysis takes place, concomitantly with biodegradation.

The climate files used for the FOCUS groundwater models include among others also the daily irradiation values for each FOCUS scenario. In FOCUS-PELMO 5.5.3 and subsequent versions the photolytic half-life at the corresponding reference irradiance is recalculated for every day based on the light conditions in the different climate scenarios. Thus, the influence of the photolysis process can be very different in the different FOCUS scenarios.

At least two validated models are available for regulatory purposes in EU (FOCUS-PELMO and FOCUS-PEARL). For PEARL it is possible to deal with the Tier 1 of photolysis scheme. Some further development of the PEARL software package in respect to the use of complete soil photolysis approach would be welcomed. For the time being, users of PEARL are advised to switch to PELMO, in case the higher Tiers 2A or 2B are necessary.

3 Decision tree for consideration of photo transformation compounds in PECgw-simulations

First, it needs to be checked, whether photo transformation compounds have to be considered in the further PECgw exposure assessment. The decision scheme for consideration of photo transformation compounds in PECgw simulations is provided in Figure 1.

If the photolytic degradation pathway is relevant for an active substance according to the results of a soil photolysis study, this pathway <u>can be considered</u> in the groundwater simulation additionally to the biodegradation pathway as higher tier option and would lead to lower PECgw values of the active substance. This option is out of the current scope of this document and a proposal for this approach is only noted in the margin in chapter 8.

If photo transformation compounds are observed in a soil photolysis study in relevant amounts according to SANCO/221/2000 rev.10-final and with a relevant difference in comparison to the dark control, these transformation products have to be considered in the lower tier approach of the groundwater exposure assessment (Box 1 in Figure 1) following the decision tree provided in Figure 1. The design of a soil photolysis study leads to extreme test conditions concerning temperature and soil dryness and minimises the biodegradation pathway extensively. The consequence is a higher formation rate of photo transformation compounds under laboratory conditions with a reduced spectrum of radiation, which is not representative for environmental conditions. Here, the global solar irradiation is the standard measured value. However, mainly UV-VIS radiation and not IR radiation is responsible for photodegradation. Under conditions that are more realistic a bigger portion of the active substance is transformed via biodegradation and a smaller portion is degraded by photolysis.

3.1 Relevant difference in comparison to the dark control

The relevance criteria for metabolites are given in SANCO/221/2000 rev.10-final. In order to declare a transformation product as a relevant photo transformation compound, an additional criterion is established: The occurrence of the transformation product in the irradiated trial is at least 5 % higher than in the dark control in at least one point in time. In case, this criterion is not met, this transformation product should be regarded just as an ordinary metabolite for which this guidance document is not relevant.

SANCO/221/2000 rev.10-final gives the following relevance criteria:

'a) Metabolites, which account for more than 10 % of the amount of active substance added in soil at any time during the studies; or

b) which account for more than 5 % of the amount of active substance added in soil in at least two sequential measurements during the studies; or

c) for which at the end of soil degradation studies the maximum of formation is not yet reached.'

The SANCO criteria should be assessed in synopsis with the dark control. For example, a soil photolysis study, in which a transformation product had maximum occurrences of 11 % and 12 % in the irradiated trial and the dark control, respectively would not qualify as a relevant photolysis.

Another example: A transformation product had maximum occurrences of 12 % and 11 % in the irradiated trial and the dark control, respectively. Here, it is proposed to check whether the relevant occurrences of a) > 10 %, b) > 5 %, or c) the maximum at the end of the study are at least 5 % higher than in the dark control. Hence, the second example would also not qualify for a relevant photolysis.

Therefore, a difference of > 5 % between the dark and light trial is proposed as the criterion of a 'relevant difference', for the points in time with a relevant amount according to the SANCO criteria. This means, there is at least one point in time with a relevant amount in the irradiated trial and with another amount in the dark control, which is at least 5 % lower than in the irradiated trial.

97 In case, there are replicates, only the arithmetic mean values of the points in time are considered. If
98 data for more than one variant of the test substance with different radioactive labels is available, the
99 arithmetic mean for all labels should be used. Attention should be paid in cases, where one of the
100 radioactive labels disappears from the molecule of interest during transformation process as part of a
101 cleaved fragment. Results for such label (false n.a. values) should certainly not be considered in the
102 calculation of arithmetic means.

103 It should be noted, that for the relevance assessment it does not matter whether it is a moist or dry
104 trial, as also a natural soil surface can be moist or dry depending on the weather. A moist trial has the
105 disadvantage that it promotes biodegradation. On the other side, metabolites from biodegradation
106 can also be prone to photodegradation. Hence, the moist trial can show other secondary photo
107 transformation compounds.

3.2 Details of decision tree

109 If field studies are available (Box 2 in Figure 1), it has to be distinguished between field dissipation
110 studies with a test design without exclusion of photolysis, like so-called 'legacy' studies (Box 2a in
111 Figure 1) on the one hand, and, on the other hand, special tailored $DegT50_{matrix}$ field studies (Box 2b in
112 Figure 1) with a test design to avoid photolysis and other surface processes according to EFSA 2014
113 guidance. These special field studies are designed to obtain degradation rates ($DegT50_{matrix}$) used in
114 exposure modelling and they are not an alternative for triggered standard field dissipation studies.
115 Only 'legacy' field dissipation studies without exclusion of photolysis can provide information on the
116 formation of photo transformation compounds under environmental conditions. If no 'legacy' study
117 or only tailored $DegT_{50 \; matrix}$ field studies are available, it is not possible to get information about the
118 maximum occurrence of photo transformation compounds under field conditions. In this case,
119 following a worst-case assumption, the identified photo transformation compounds from the soil
120 photolysis study have to be considered in ground water exposure assessment via the photolytic
121 pathway.

122 The following cases are possible, if 'legacy' field dissipation studies are available:

123 • Conditions during the field studies should ensure that photolysis has occurred. Crop cover and
124 application season can significantly affect the photodegradation process and thus limit or even
125 avoid the formation of photo transformation compounds. It is suggested to evaluate only studies
126 on bare soil and to demand an average irradiance over the course of study of at least 100 W m$^-$
127 ^{2}.[1] Studies with plants or an average irradiance below 100 W m^{-2} should not be evaluated further
128 (Box 3 in Figure 1). Further guidance on irradiance values is provided in chapter 5.2 and in
129 appendices A-C.
130 • If photo transformation compounds, identified in the soil photolysis study in relevant amounts
131 and at a relevant difference, were not analysed for residues in the field dissipation study, no
132 information about their maximum occurrence under field conditions is available. Thus, the
133 photo transformation compounds have to be considered in groundwater exposure assessment
134 following a worst-case assumption (Box 4 in Figure 1).
135 • If photo transformation compounds, identified in the soil photolysis study in relevant amounts
136 and at a relevant difference, were analysed for residues in the field dissipation study, but not
137 observed in relevant amounts according to SANCO/221/2000 rev.10-final, these data overwrite
138 the results of the soil photolysis study. In this case, no further groundwater exposure assessment
139 for the photo transformation compounds is required (Box 5 in Figure 1).

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[1] The value of 100 W m^{-2} seems to be appropriate in the light of the global annual mean irradiance for the FOCUS groundwater
scenario Jokioinen site, which is the least illuminated of all scenarios, having 100 W m^{-2} too (see Table 4). This minimum
value restricts the suitability of field dissipation studies in Jokioinen to the summer period, whereas studies in winter would
probably have too little irradiance for inducing enough photolysis.

140   • If photo transformation compounds, identified in the soil photolysis study in relevant amounts
141   and at a relevant difference, were also observed in relevant amounts under field conditions
142   according to SANCO/221/2000 rev.10-final, they have to be considered in the groundwater
143   exposure assessment via the photolytic pathway (Box 5 in Figure 1).

144   For the two last mentioned cases, it is a precondition, that soil photo transformation compounds have
145   been specifically analysed for and that the LOQ for the transformation products was sufficient to
146   identify concentration levels that may trigger a groundwater assessment.
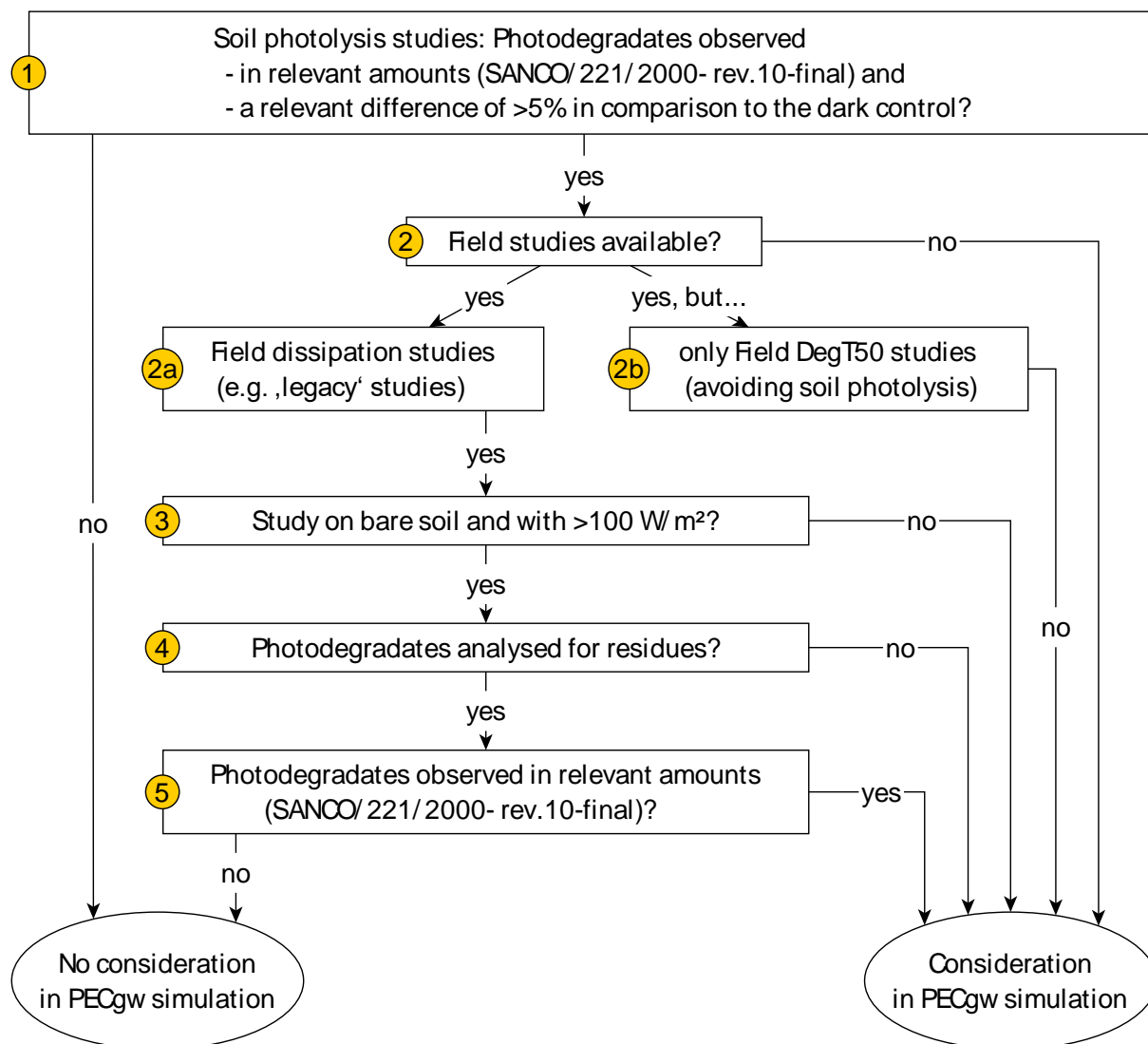

147

148   Figure 1:   Decision tree for consideration of photo transformation compounds in PECgw simulations

4 Background information about radiation

The electromagnetic radiation emitted by the sun is mainly infrared radiation (IR, wavelength > 700 nm), visible radiation ('light', wavelength 400 – 700 nm) and ultraviolet radiation (UV, wavelength < 400 nm). The spectrum at sea level is shown in Figure 2 and Table 1 .

In terms of energy, sunlight at the earth's surface is about 52-55 % IR, 42-43 % visible and 3-6 % UV. These fractions of UV, VIS and IR in the spectrum of radiation vary with meteorological conditions, e.g. with cloud coverage (Table 1). In the direct radiation (i.e. a beam of rays from the sun) the fraction of IR is much higher (56 %) and the fraction of UV much lower (2 %) than in the diffuse radiation (skylight). The natural radiation is a mix of both direct and diffuse radiation.
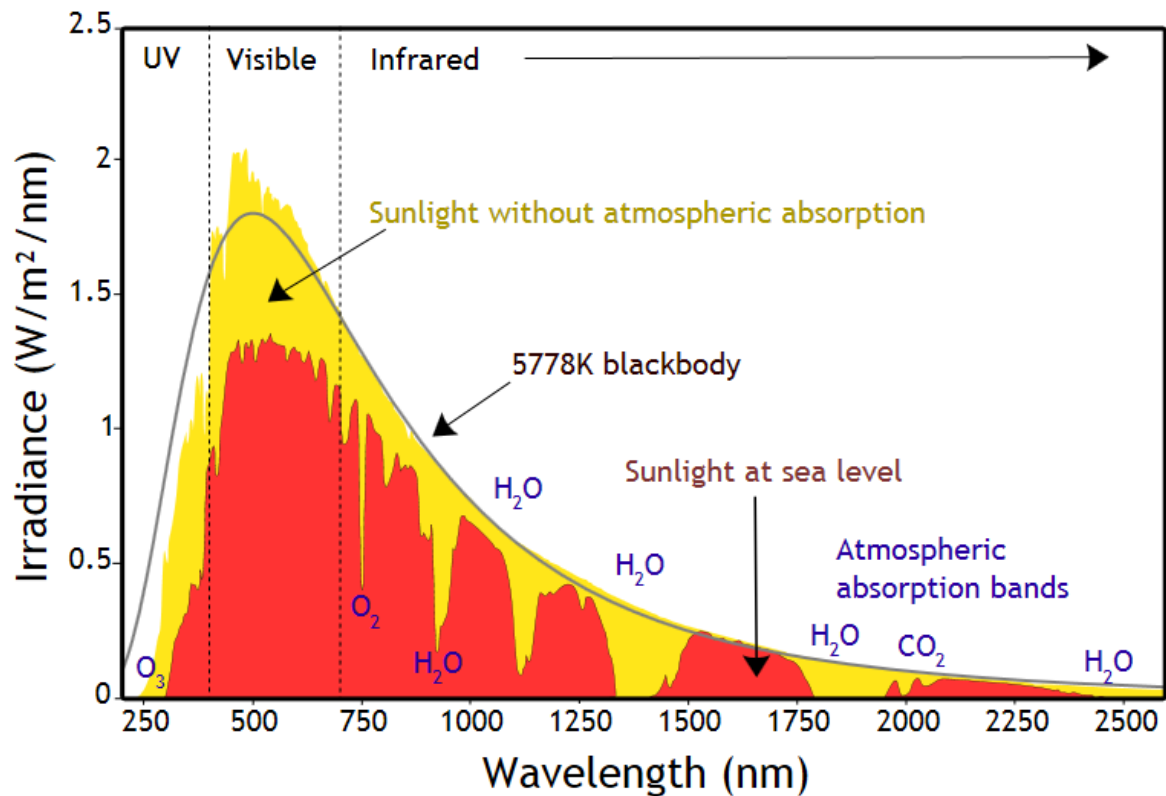

Figure 2:   Solar radiation spectrum at sea level (red area) covers wavelengths from 300 to 3000 nm[2]

Table 1   Mean fractions of UV, VIS and IR in the spectrum of direct and diffuse solar radiation (source: J. L. Monteith (1975): Vegetation and the atmosphere)

direct radiation	2 %	42 %	56 %
diffuse radiation	10 %	65 %	25 %

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[2]   Source: By Nick84 - http://commons.wikimedia.org/wiki/File:Solar_spectrum_ita.svg, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=24648395, based on the American Society for Testing and Materials (ASTM) Terrestrial Reference Spectra

The global solar irradiation (also called insolation or intensity, see Table 3), i.e. the incident radiation of wavelengths 300 – 3000 nm[3] per unit area of a horizontal surface, is expressed as daily irradiation and recorded during a day of 24 hours. The unit of the solar irradiation is kilojoules per square metre ($kJ\ m^{-2}$). In meteorology the global solar irradiation is a standard measured value. Thus, its use is recommended here as a pragmatic approach despite the fact that mainly UV-VIS radiation and not IR radiation is responsible for photodegradation.

As an overview of the technical terms, the most common synonyms are given in Table 2.

Table 2   Technical terms for radiation

irradiation	intensity, radiation, insolation (for radiation from sun only)	$kJ\ m^{-2}\ d^{-1}$ $kWh\ m^{-2}\ d^{-1}$
irradiance	-	$W\ m^{-2}$

For the calculation in PELMO, the daily irradiation, which can be provided in two different units, needs to be converted into the time-independent irradiance (entitled as '*Reference radiation*' in the PELMO program interface). To convert the daily irradiation (given in the unit $kJ\ m^{-2}\ d^{-1}$) into irradiance (given in the unit $W\ m^{-2}$), the value is multiplied by 1000 and divided by 86400. To convert the daily irradiation (given in the unit $kWh\ m^{-2}\ d^{-1}$) into irradiance, the value is multiplied by 1000 and divided by 24. Two examples for conversion are given in Table 3. (Explanation: 1 kWh = 3600 kJ, 1 kJ = 1000 Watt seconds and 1 day = 86400 seconds.)

Table 3   Two examples for conversion of daily irradiation into irradiance

19 June 01	29817	8.282	345.1
22 December 01	1098	0.305	12.7

The exemplary solar irradiance for the 1st climate year of the FOCUS scenarios Jokioinen and Sevilla is shown in Figure 3.

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[3] For comparison: The light from a lamp in a soil photolysis study has often wavelengths between 295 nm and 800 nm. Generally, the range of 295 – 400 nm is most relevant for photodegradation. The specific wavelength(s) leading to a photodegradation in a given molecule can be seen from the absorption spectrum in the UV-VIS-spectrogram.
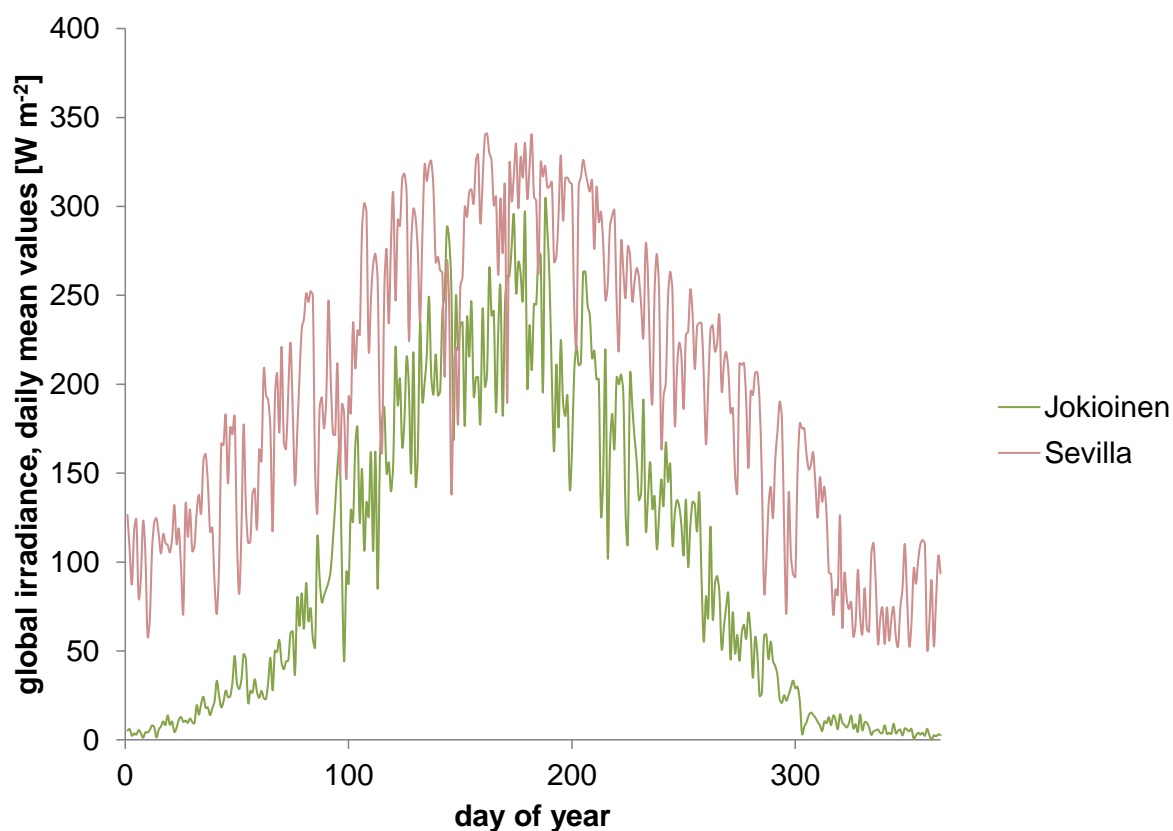
global irradiance, daily mean values [W m⁻²]

day of year

Jokioinen
Sevilla

184

185 Figure 3:   Irradiation (kJ m^{-2} d^{-1}) data in the 1st climate year of the FOCUS scenarios Jokioinen (file 'J_01.cli')
186   and Sevilla (file 'S_01.cli'), converted to irradiance (W m^{-2})

187

188 Table 4   Comparison of the FOCUS groundwater scenarios with regard to global irradiance. Statistic for first
189   climate year.

Châteaudun	138.4	21.3	335.2
Hamburg	117.6	12.7	345.1
Jokioinen	100.0	0.1	302.9
Kremsmünster	127.7	20.2	319.7
Okehampton	119.7	13.6	317.1
Piacenza	151.0	6.9	331.4
Porto	171.1	39.7	355.6
Sevilla	195.5	51.8	341.1
Thiva	172.4	45.3	295.9

190

191 Member states should check individually, whether the existing FOCUS groundwater climate files (see
192 Table 4) are representative for the solar conditions on their territory.

5   Recommendations for parameterisation of photo transformation compounds in PECgw simulations

With regard to harmonisation and for pragmatic reasons a tiered approach is recommended for consideration of photo transformation compounds in PECgw simulations.

Since April 2011, FOCUS PELMO version 4.4.3 software has been provided on the FOCUS website, which makes it possible to consider soil photolysis beside biodegradation as a higher tier option in the leaching assessment of active substances. The soil photolysis process is simulated until the active substance has been completely transported from the soil surface (1 mm) into the soil matrix by rainfall or irrigation. Finally, FOCUS-PELMO 4.4.3 allows simulating both pathways for the active substance in one scheme under the conditions of the intended use and the climate scenario. Crop vegetation is considered by reducing irradiance according to the interception caused by growing stage of the crop. No interception is assumed between harvest and emergence for annual crops.

A further update of FOCUS-PELMO was provided resulting in the new version FOCUS-PELMO 5.5.3 (February 2012), which included the possibility to simulate the leaching behaviour of photo transformation compounds.

The model FOCUS PELMO 5.5.3 and subsequent versions requires two input parameters for the consideration of the photolytic pathway of an active substance. The first parameter is a photolytic half-life, which is representative and conservative enough to describe the behaviour of a substance under the influence of natural light. The second, causally connected parameter, is the reference irradiance after the application at the geographical location of the field trial, for which the photolytic half-life was determined.

Soil photolysis studies are designed as route studies in order to get information about the relevance of this transformation process and the potential transformation products. Furthermore, at the moment soil photolysis studies are not harmonised by an agreed OECD guideline and they are considered not to be suitable in order to derive kinetic parameters for modelling purposes, because the test conditions are rather artificial.

EFSA PPR 2010 says:

'OECD (2002a) developed a guideline for measuring soil photolysis in the laboratory. […]This OECD study is commonly considered to be a "route study" rather than a "rate study", i.e. it is considered suitable for identifying photodegradates that are formed at the soil surface but it has not been designed to generate photodegradation rates that can be used to predict such rates under field conditions (EFSA, 2007b; p 9).'

Therefore, it is recommended to take information about the occurrence and transformation of photo transformation compounds from soil photolysis studies and to derive the kinetic parameters as input values in PECgw simulation from field dissipation studies evaluated according to EFSA guidance (2014).

Outlook: In case, a new or revised OECD guideline for soil photolysis studies is established, the statement above might be revised, i.e. soil photolysis studies might be more suitable for a kinetic evaluation (which would be easier than for field dissipation studies with changing irradiances). Special attention should be paid to the artificial, filtered spectrum of lamps in soil photolysis studies, which hinders the determination of a 'natural' global irradiance as a reference (chapter 5.2).

5.1 Photolytic half-life

In order to consider photo transformation compounds in a FOCUS PELMO simulation, it is necessary to estimate the photolytic half-life of the active substance under realistic conditions.

According to EFSA guidance (2014), it is possible to derive separate half-lives from field dissipation studies for the surface processes, e.g. photolysis and volatilisation (DT50$_{fast}$), and biodegradation in the soil matrix (DT50$_{slow}$) by using biphasic models (DFOP, HS).

- HS: In a HS kinetic, k_2 can be interpreted as the biodegradation rate and k_1 as the sum of the biodegradation rate and other dissipation rates. Hence, it is recommended to calculate $k_{photo} = k_1 - k_2$.
- DFOP: In a DFOP kinetic, k_1 can be taken directly, because k_1 and k_2 happen at the same time. In case the Chi² is similar for DFOP and HS, DFOP is chosen (cf. FOCUS Deg. Kin., chapter 7.1.1).
- FOMC: A FOMC kinetic is not suitable in order to derive a rate of the fast, initial phase, as a photolysis endpoint.
- SFO: In case, a field study shows a SFO kinetic instead of a biphasic kinetic, it is also not suitable.

For substances with a low vapour pressure below 1×10^{-4} Pa at 20 °C, only little volatilisation occurs under natural conditions. For these non- or semi-volatile substances, the DT50$_{fast}$ or the corresponding k_{fast} value represents the photolytic degradation, and it should be used as input parameter for the photolysis pathway in FOCUS PELMO 5.5.3 and subsequent versions. For substances with a vapour pressure > 1×10^{-4} Pa the volatilisation pathway cannot be excluded and therefore the k_{fast} value is not representative only for the photolytic half-life. For volatile substances the k_{fast} values can be influenced by photolysis and volatilisation and would be overestimated indeed, but the formation of photo transformation compounds would also be overestimated and so it could be accepted as a worst-case approach in Tier 2B also for volatile substances. Hence, all tiers can be used also for volatile active substances.

The k_{fast} values have to be derived from biphasic kinetics of data from field studies according to FOCUS degradation kinetics.

The k_{fast} values from field dissipation studies of photosensitive substances are directly influenced by irradiance at the trials during the time window of soil photolysis. Degradation rates k_{fast} normalised to a specific irradiance would describe the photolytic process best. Therefore, a time-step normalisation according to the daily irradiances is introduced. Hence, the time-step normalisation is similar to what is already performed in order to deduce biodegradation rates from field studies according to changing soil moisture and temperature.

The easier normalisation of biodegradation rates with constant values of soil moisture and temperature is only appropriate for laboratory studies under controlled conditions. Likewise, a normalisation of photolysis rates with a constant irradiance would only be appropriate for a soil photolysis study, but not for a field study with strongly fluctuating daily irradiances.

A time-step normalisation can improve the fit of the photolysis fast phase, because variations of the irradiance are transferred to the time axis. (The fit of the slow phase will probably not improve - however, here we are only interested in the photolysis fast phase.)

The breakpoints can differ between both procedures, with and without a time-step normalisation. Without a time-step normalisation, the breakpoint can be determined just by random changes of the irradiance, e.g. a cloudy period. Instead, we are interested in the breakpoint when the active substance penetrates into the soil, when photolysis diminishes.

For the purpose of this time-step normalisation the worksheet 'inter, conv, norm' in the 'basic tools for deriving photolysis endpoints' can be used (see Table 5).

5.2 Irradiance

Generally, radiation information was not part of the study protocols of former field dissipation studies. In prospective field dissipation studies with photodegrading substances, the measurement of insolation values at the specific study trial is preferable. Accordingly, OECD (2016) ('Guidance Document for Conducting Pesticide Terrestrial Field Dissipation Studies') demands measurement of 'hours of sunshine and intensity of solar radiation'.

This is the proposed priority in order to retrieve radiation data:

1. measurements directly at the field trial or
2. measurements at a weather station nearby (bee line distance < 10 km) or
3. interpolated values from a data source for radiation values (e.g. AGRI4CAST or NASA) according to the longitude and latitude of the trial location and for the study time after the application date.

Different data sources for radiation values are presented in Appendix A.

Appendix B and C give examples for determining radiation values from the AGRI4CAST and the NASA web pages.

The coordinates of the trial location can be retrieved via internet[4].

In meteorology the global solar irradiation (incident radiation of wavelengths 300 nm – 3000 nm on a horizontal surface) is available as a standard measured value. Thus, its use is recommended here despite the fact that only the range of 295 – 400 nm is most relevant for photodegradation. The global solar irradiation in field trials is not constant over time and photodegradation at different sites can be quite different. Conversely, in a laboratory test, the radiation from a xenon lamp is constant and calculation of quantum yield is easier in laboratory tests.

Values from NASA have to be converted by the factor 1000/24 from the insolation (irradiation in the unit $kWh\ m^{-2}\ d^{-1}$) to a time-independent irradiance ($W\ m^{-2}$). The term irradiance is a synonym for the term 'reference radiation' used in FOCUS-PELMO 5.5.3 and subsequent versions.

5.3 Handling of two or more photo transformation compounds

In case, an active substance has two or more photo transformation compounds, each phototransformation compound is simulated separately in Tier 1 (including secondary metabolites, if applicable) and in Tier 2A and 2B (including all biodegradates). In Tier 2B, it is not recommended to undertake an ambitious, shaky kinetic evaluation in order to find a proper split of k_{fast}, i.e. an apportionment between the photo transformation compounds. It seems doubtful, whether the data derived from field studies and influenced by more than only the photolytic process can provide such a reliable splitting in form of photolysis formation fractions. Hence, each photo transformation compound has to be simulated in a separate run, one by one.

5.4 Implementation of the photolysis pathway in FOCUS-PELMO 5.5.3 and subsequent versions

The photolytic degradation is a time dependent process under changing environmental conditions at the soil surface. The kinetic parameter $DT50_{photo}$ for the active substance is derived from irradiance-

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[4] e.g. http://itouchmap.com/latlong.html - here type in the wanted location name in the 'address' field. Zoom out of the map in order to make sure you got the right location, as a lot of names are given to different places (e.g. there is also a London in Canada). One decimal place of the coordinates is enough.

318 normalised data, in contrast to the kinetic parameters for biodegradation that were derived from
319 normalised data according to soil temperature and soil moisture. In the modelling approach both
320 pathways are considered independent from each other and the model determines automatically the
321 daily changing amount of active substance going into each pathway with regard to the scenario
322 parameters irradiance and light interception on the one hand, and temperature and moisture on the
323 other hand. At a sunny winter day, photolysis might be higher than biodegradation, and vice versa at
324 a cloudy summer day.

325 The daily changing photolysis rate for day x ($k_{fast,x}$) in FOCUS-PELMO 5.5.3 and subsequent versions is
326 calculated according the following equation:

327
$$k_{fast,x} = \frac{k_{fast,reference} \cdot irradiance_x}{irradiance_{reference}} \cdot (1 - interception)$$

328 with

329 $k_{fast,reference}$ the photolysis rate derived from the field trials (chapter 5.1)

330 $irradiance_x$ irradiance at day x from the scenario climate files

331 $irradiance_{reference}$ the mean irradiance for which $k_{fast,reference}$ was observed (chapter 5.2)

332 interception   the changing interception of the crop (=0 after harvest of annual crops)

333 For more information, please refer to chapter 2.5.3.2 in the user manual (Michael Klein, 2012).

334 The soil photolysis process is simulated until the active substance is completely transported from the
335 soil surface (1 mm) into the soil matrix by rain fall or irrigation. The top layer of 1 mm is a normal soil
336 compartment in PELMO similar to the deeper soil layers. The transport through the top 1 mm soil layer
337 is simulated in the same way as the transport through the other soil layers (the first layer is only
338 thinner). Transportation through the top 1 mm depends on the K_f value of the compound and on the
339 amount of water that moves to the next soil layer.

340 The resolution in the soil core is a parameter in the scenario file (*.sze). All FOCUS scenarios have a
341 spatial resolution of 5 cm. Independent of this resolution in the soil core, there is a 1 mm top layer
342 where volatilisation from soil surface and soil photolysis is calculated. To keep the overall soil depth of
343 the scenario, the first soil layer in the scenario files is internally reduced by 1 mm (no user input).
344 Hence, the first FOCUS layer in the soil matrix is actually only 4.9 cm thick (5 cm - 1 mm).

345 Normally, the measured half-lives from biodegradation studies according to OECD 307 and Koc values
346 from adsorption studies according to OECD 106 should be used as input parameters for the photo
347 transformation compounds. If one or both of these values is not available, a default half-life of 1000 d
348 and/or a Koc value of 0 should be used for leaching simulations of photo transformation compounds.

6 Tiered approach

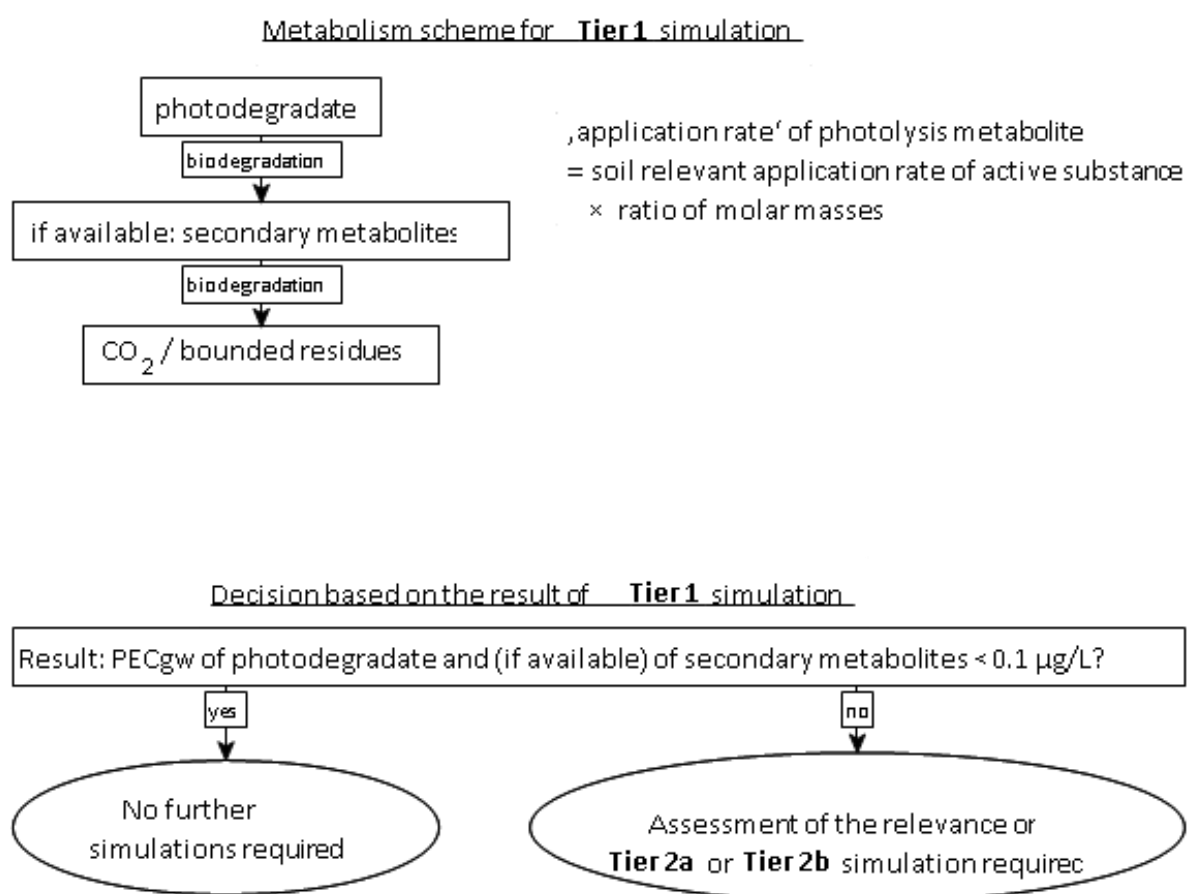## 6.1 Tier 1: Photo transformation compound as parent substance

A worst-case approach to assess the leaching behaviour of the photo transformation compounds (and, in case they occur, their secondary metabolites) can be a common PECgw simulation, either with FOCUS-PELMO or FOCUS-PEARL, without a photolytic pathway. Here, each phototransformation compound is considered separately as a parent substance with the application rate of the active substance corrected by the ratio of molar masses. In case, a secondary metabolite is formed by biodegradation of the photo transformation compound, a combined simulation of both transformation products in Tier 1 has to be performed. A separate Tier 1 simulation of the secondary metabolite can violate the tiered approach in some cases (PECgw value of the secondary metabolite in Tier 2 may be higher than in Tier 1).

In case, this secondary metabolite of a photodegradate is formed parallel via biodegradation from other metabolites, Tier 1 cannot be used and the simulations start with Tier 2A or 2B.

If the groundwater concentration of the photo transformation compound (and their secondary metabolites, if applicable) does not exceed 0.1 µg/L in Tier 1, the exposure assessment is finalised and no further steps are necessary. Otherwise, a relevance assessment for the photo transformation compound (and/or their secondary metabolites, respectively) according to SANCO/221/2000 rev.10-final has to be done or the more complex leaching simulations according to Tier 2A or Tier 2B have to be performed.

As Tier 2A is not much more work than Tier 1 (because it is based on the degradation scheme already parameterised for the biodegradation products), it is also possible to start with Tier 2A directly.

The worst-case approach (Tier 1) to assess the leaching behaviour of photo transformation compounds (and their secondary metabolites) is provided in Figure 4.

373

Metabolism scheme for **Tier 1** simulation

```
┌─────────────────────┐
│   photodegradate    │
└─────────────────────┘
        │ ┌──────────────┐
        │ │ biodegradation│
        ▼ └──────────────┘
┌──────────────────────────────┐
│ if available: secondary metabolites│
└──────────────────────────────┘
        │ ┌──────────────┐
        │ │ biodegradation│
        ▼ └──────────────┘
┌─────────────────────┐
│ CO₂ / bounded residues│
└─────────────────────┘
```

‚application rate' of photolysis metabolite
= soil relevant application rate of active substance
  × ratio of molar masses

Decision based on the result of **Tier 1** simulation

Result: PECgw of photodegradate and (if available) of secondary metabolites < 0.1 µg/L?

yes — No further simulations required

no — Assessment of the relevance or **Tier 2a** or **Tier 2b** simulation required

374

375   Figure 4:   Worst case approach (Tier 1) to assess the leaching behaviour of photo transformation compounds
376   (and their secondary metabolites)

377   Initially it was also envisaged to consider the maximum occurrence of the photo transformation
378   compounds in the soil photolysis study in addition to the ratio of molar masses for Tier 1. However,
379   this option was discarded, as it might lead to the cases, in which the tiered approach would be violated
380   (PECgw in Tier 1 < PECgw in Tier 2).

6.2 Tier 2A: Default values in the complete degradation scheme

The PECgw of the active substance and its transformation products are simulated according to the complete degradation scheme including the photolytic and biodegradation pathway in FOCUS-PELMO 5.5.3 and subsequent versions.

In order to avoid the laborious procedure of identifying realistic photolysis endpoints for an active substance (see Tier 2B), it is recommended in Tier 2A to use default photolytic half-lifes at a default reference irradiance. This approach gives lower, more realistic PECgw values than the Tier 1 approach. As it cannot be guaranteed that these default values represent the fastest photolysis, which is possible for active substances in plant protection products, the Tiers 2A and 2B serve as alternative paths in the tiered approach. In case, a faster photolysis is found for an active substance, the default values might be revised.

It has to be emphasised, that the PECgw simulation in Tier 2A with the default inputs is only recommended as a conservative parameterisation of leaching behaviour for photo transformation compounds, not for the active substance and other metabolites.

There are rare cases, in which a slower photolysis parameterisation gives counterintuitively higher concentrations for a photo transformation compound. These rare cases are linked to active substances that sorb very strong (e.g. fludioxonil). When such a substance is applied in sunny summer, the emerging photo transformation compound is subject to fast biodegradation under warm conditions. This can lead to rather low PECgw of the photo transformation compound.

Assuming, photolysis is slower, the active substance that sorbs very strong is stuck at the soil surface. Once, the crop is harvested in autumn, the irradiance increases suddenly. The emerging photo transformation compound is subject to slower biodegradation in the colder autumn. This can lead to higher PECgw of the photo transformation compound. Hence, a second pair of default values is presented below.

The recommended default values of the active substance in Tier 2A are:

- fast: $DT50_{fast}$ = 0.1 d @ reference irradiance = 100 W m^{-2}
- slow: $DT50_{slow}$ = 10 d @ reference irradiance = 100 W m^{-2}

If the groundwater concentration of the photo transformation compound does not exceed 0.1 µg/L in Tier 2A, the exposure assessment is finalised and no further step is necessary. Otherwise, a relevance assessment according to SANCO/221/2000 rev.10-final has to be done or the more complex leaching simulation according to Tier 2B has to be performed.

6.3 Tier 2B: Measured values in the complete degradation scheme

In this approach measured input parameters, both half-life and irradiance values, from suitable field dissipation studies are necessary, instead of default values. The photolytic half-life of the active substance has to be derived from the data of field dissipation studies of the 'legacy' type, in case this data is available.

As mentioned in chapter 3, conditions during the field studies should ensure that photolysis has occurred. It is suggested to evaluate only studies on bare soil and to demand an average irradiance over the course of study of at least 100 W m^{-2}.

The data has to be normalised according to the daily irradiances (see 5.1; the procedure is described in Appendix B). Be aware, that this involves significant effort in comparison to the rather straightforward Tiers 1 and 2A. The irradiance values (point 5.2) can be based on measured insolation values at the field trial during the study. If these data are not available from the study report, relevant databases (e.g. AGRI4CAST or NASA database) can provide the required information (see Appendix A-C).

The kinetic evaluation of the data with the preceding time-step normalisation produces degradation rates, which can be compared and analysed statistically.

An Excel tool for determination of input parameters for consideration of the photolysis pathway in FOCUS-PELMO 5.5.3 and subsequent versions is provided together with this guidance (see Appendix F). It includes the worksheets given in Table 5.

Note: The Excel tool should be published together with the guidance. It is envisaged that the excel tool will be made available via Zenodo knowledge junction.

See Appendix B for a detailed example.

Table 5   Worksheets in the Excel file 'basic tools for deriving photolysis endpoints' and their purpose

Worksheet	Input	Output	Purpose
AGRI4CAST	-	-	visualization of spatial availability of AGRI4CAST data set
grid points	coordinates of a field study	identification of the relevant grid points in the solar database 'AGRI4CAST'	
inter, conv, norm			includes these three steps
1. interpolation	irradiance data of relevant grid points	spatial interpolation of irradiance values	
2. conversion	irradiance values in kJ m^{-2} d^{-1}	irradiance values in W m^{-2} d^{-1}	
3. normalisation	irradiance values and real time points	time-step normalisation for field studies	then a kinetic evaluation has to be performed with appropriate software
comparison	kfast normalised to 100 W m²	geometric mean or min/max of kfast values from several field studies	

436   Finally, the following distinction of cases is applied:

437   a)   If the number of suitable trials is ≥ 4, one simulation is conducted with the geometric mean of
438   the photolysis rates

439   b)   If the number of suitable trials is 3, two simulations with the maximum and minimum
440   photolysis rates from the trials are conducted

441   c)   If the number of suitable trials is only 1 or 2, Tier 2B is not applicable. You can switch to Tier
442   2A.

443   With regard to b), the trial with the maximum ratio (which represents the fastest observed photolysis)
444   is usually the worst-case for the photo transformation compounds, but there are exceptions because
445   of the complex situation within a leaching simulation. The trial with the minimum ratio represents the
446   slowest observed photolysis as worst-case for the active substance. The simulation results with the
447   higher PEC_{gw} values for the photo transformation compounds are considered relevant for final
448   assessment (see example in Appendix).

7 Simulation with FOCUS-PELMO 5.5.3 and subsequent versions

In Tier 2A and 2B, for all photosensitive substances both the biodegradation and the photolytic pathway have to be considered in the PELMO simulation. Therefore, the parameterisation of both pathways is necessary and possible in one scheme. In Appendix D the parameterisation of both pathways is shown for an exemplary active substance (called 'examplamin'), in all tiers of the tiered approach.

If a transformation product is formed both via biodegradation and soil photolysis from the active substance, both pathways have to be represented in one flow (see data entry mask in Figure 5). If a transformation product is formed only via soil photolysis, only the data for soil photolysis need to be entered in PELMO (the biodegradation transformation rate is kept at 0 per day).

Figure 5:   Data entry mask in FOCUS-PELMO 5.5.3 (values are entered for Tier 3 of examplamin in Appendix C)

The application of the following trick is not restricted to metabolism schemes including photolysis, but it can also be useful for schemes involving only biodegradation:

In PELMO simulations, it should be avoided that the same substance is represented by different boxes in the scheme. Otherwise, PELMO would assume different substances which do not compete for sorption places - sorption would be overestimated for all substances with $1/n < 1$. There is a trick to avoid such defective representations with the help of 'pseudo' metabolites.

Imagine the task to represent a metabolite, which is formed by the active substance and two metabolites in a PELMO scheme (or similar complex, branched problems). Without the pseudo metabolites 'only rapid transfer' shown in Figure 6 this task would be impossible to solve. These pseudo metabolites have a very high default degradation rate of 99999 d^{-1} and a very high default sorption of 99999 $l\ kg^{-1}$. These extreme values guarantee a very fast transfer and negligible leaching during transfer. It is important that these pseudo metabolites have the same molar mass as the precursor substance. It could be demonstrated that such pseudo metabolites do not alter the PECgw results.

476

477
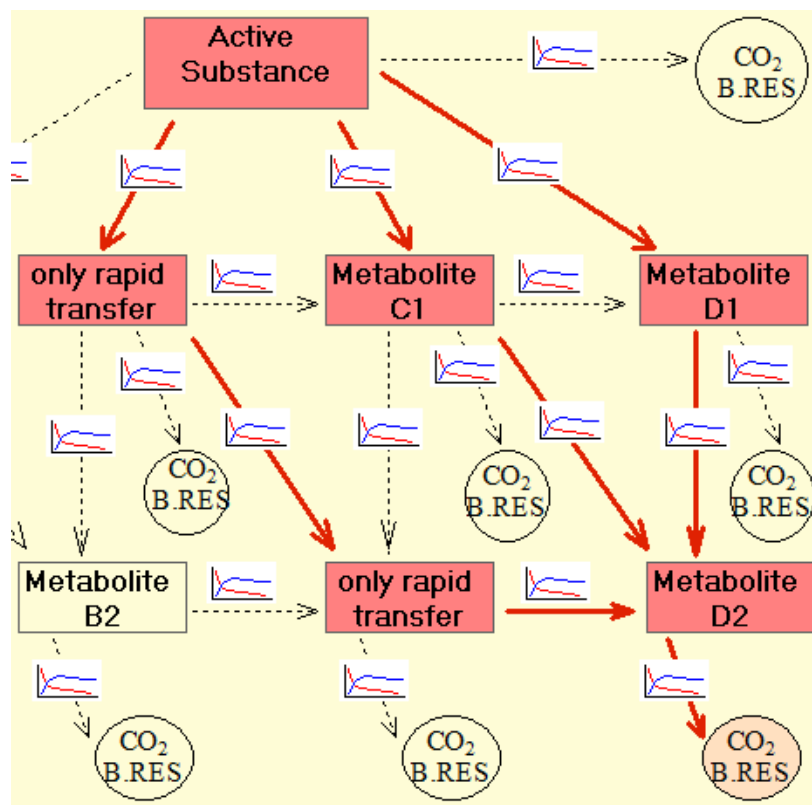
478 Figure 6: Trick with pseudo metabolites 'only rapid transfer' ($k = 99999$ d^{-1}; Kfoc = 99999 L kg^{-1}; same molar
479 mass as precursor substance) in order to represent a complex, branched scheme within PELMO

8 Consideration of the soil photolysis pathway as a higher tier option for active substances

Outlook: This guidance is intended only for the assessment of photo transformation compounds. However, it is conceivable to use the Tier 2B also as a higher tier assessment for the active substance and other metabolites, since their concentrations can be diminished by the formation of photo transformation compounds. As this option would exceed the primary scope of this guidance, this option should be discussed in a future revision of the FOCUS groundwater report. It is also conceivable to integrate this guidance in the FOCUS groundwater report.

In principal, the refinement procedure of ground water exposure assessment for active substances by considering the photolytic pathway on soil surfaces is not the subject of this paper. The parameterisation of this higher tier approach for an active substance is presented only as a proposal for a future revision.

If the photo degradation process is considered to be a significant process for the compound of concern, the derivation of the normalised $DT50_{photo}$ has to be done as described under Point 5.1, 5.2 and 6.3.

Only a proposal for parameterisation similar to Tier 2B is provided. The consideration of photolysis pathway additionally to the biodegradation pathway as higher tier option in the groundwater simulation will always lead to lower PECgw values of the active substance in comparison with the lower tier approach without inclusion of photolytic pathway and it should be conservative.

Hence, it is recommended to use the normalised $DT50_{photo}$ derived from the geometric mean, if ≥ 4 field trials are suitable for deriving measured data. If only 2-3 field trials are suitable, the lowest normalised k_{fast} should be used in the PECgw simulation for the active substance. If only one field trial is suitable for deriving a k_{photo}, there is a lack of knowledge regarding the representativeness and this higher tier option should not be used.

This consideration of photolysis pathway as higher tier approach for active substances has also consequences for the estimation of ground water concentrations of the metabolites formed by biodegradation and could lead to lower concentrations of these metabolites in the groundwater.

If the soil photolysis is not considered significant for the active substance during the exposure assessment, the described higher tier option for the active substance is invalid, whether or not photo transformation compounds were formed in relevant amounts during soil photolysis process.

9 Summary of the tiered approach

For the consideration of photo transformation compounds as an integral part in groundwater exposure assessment a tiered approach with FOCUS-PELMO 5.5.3 and subsequent versions is provided. Details of the selection of the endpoints and recommendations for special cases are shown in chapter 5 and 6. Here a short summary of the required steps is presented:

Tier 1: Photo transformation compound as parent substance

1. Each photo transformation compound is considered as an active substance in a separate simulation considering only biodegradation.
2. The application rate of the photo transformation compound is set to 100 % of the application rate of the active substance corrected by the ratio of molar masses of active substance and phototransformation compound.
3. If a secondary metabolite is formed by the phototransformation compound, both transformation products have to be simulated together in one run.
4. Conduct the FOCUS PELMO simulation for each photo transformation compound

Tier 2A: Default values in the complete degradation scheme

1. Generate the metabolism scheme in PELMO including the photolytic pathway.
2. The recommended default values of the active substance in Tier 2A are:
   fast: $DT50_{fast}$ = 0.1 d @ reference irradiance = 100 W m^{-2}
   slow: $DT50_{slow}$ = 10 d @ reference irradiance = 100 W m^{-2}
3. Conduct two FOCUS PELMO simulations.

Tier 2B: Measured values (if available) in the complete degradation scheme

1. Generate the metabolism scheme in PELMO inclusive photolytic pathway (analogue to Tier 2A)
2. Get radiation data from:
   a) measurements directly at the field trial or
   b) measurements at a weather station nearby (bee line distance < 10 km) or
   c) interpolated values from a data source for radiation values according to the longitude and latitude of the trial location and the time after the application date.
3. Derive normalised k_{fast} of active substance from biphasic kinetics of data from field dissipation studies according to the recommendations of FOCUS degradation kinetics (2006/2011) and EFSA (2014).
4. Case-by-case decision:
   a) If the number of suitable trials is ≥ 4, one simulation is conducted with the geometric mean of the photolysis rates
   b) If the number of suitable trials is 3, two simulations with the maximum and minimum photolysis rates from the trials are conducted
   c) If the number of suitable trials is only 1 or 2, Tier 2B is not applicable. You can switch to Tier 2A.
5. Conduct the FOCUS-PELMO simulations with the parameters derived in point 4.

10   References

EFSA (2007b): Opinion on a request from EFSA related to the default Q10 value used to describe the temperature effect on transformation rates of pesticides in soil. EFSA Journal, 622, 1-32.

EFSA PPR (2010): EFSA Panel on Plant Protection Products; Guidance for evaluating laboratory and field dissipation studies to obtain DegT50 values of plant protection products in soil. EFSA Journal 2010; 8(12):1936. doi:10.2903/j.efsa.2010.1936 (www.efsa.europa.eu)

EFSA (2013): EFSA PPR Panel (EFSA Panel on Plant Protection Products and their Residues), 2013; Scientific Opinion on the report of the FOCUS Groundwater Working Group (FOCUS, 2009): assessment of higher tiers. EFSA Journal 2013; 11(6):3291. doi:10.2903/j.efsa.2013.3291

EFSA (2014): EFSA Guidance Document for evaluating laboratory and field dissipation studies to obtain $DegT_{50}$ values of active substances of plant protection products and transformation products of these active substances in soil. EFSA Journal 2014:12(5):3662, 37 pp.

European Commission (2014): 'Assessing Potential for Movement of Active Substances and their Metabolites to Groundwater in the EU' Report of the FOCUS Ground Water Work Group, EC Document Reference SANCO/13144/2010 version 3, 613 pp.

FOCUS (2006, 2011): Guidance document on estimating persistence and degradation kinetics from environmental fate studies on pesticides in EU registration –Report of the FOCUS work group on degradation kinetics, EC document reference SANCO/10058/2005 version 2.0, 434 pp.

Michael Klein (2012): User Manual PELMO (Pesticide Leaching Model) Version 4.01 https://esdac.jrc.ec.europa.eu/public_path/projects_data/focus/gw/par/FOCUS_PELMO_paramete2.0.pdf

OECD (2016): Guidance Document for Conducting Pesticide Terrestrial Field Dissipation Studies, Series on Testing & Assessment N0.232 Series on Pesticides No. 82 ENV/JM/MONO(2016)6

OECD (2002): Proposal for a new guideline - phototransformation of chemicals on soil surfaces

Appendix A: Data sources for radiation values

Different data sources for radiation values and their availability are presented in Table A 1.

Table A 1   Data sources for radiation values

Data source	Resolution of grid [km]	Temporal availability since	Spatial availability	Availability online
COSMO-DE	2.8	16.04.2007	Germany, Netherlands, Belgium, Luxembourg, Switzerland, Austria, Slovenia and partly other countries [1]	after registration http://www.dwd.de (search for 'Pamore') https://webservice.dwd.de/cgi-bin/spp1167/webservice.cgi
COSMO-EU	7	01.12.1999	Europe and partly other continents [2]	or upon request, charges apply
AGRI4CAST	25	01.01.1975	'covering the EU Member States, neighbouring European countries, and the Mediterranean countries' (see Figure A 1)	after registration http://agri4cast.jrc.ec.europa.eu/DataPortal/UserRegistration.aspx see 'Gridded Agro-Meteorological Data in Europe' http://agri4cast.jrc.ec.europa.eu/DataPortal/Index.aspx?o=d free of charge
MARS	< 27.8 (equivalent of 0.25°)	01.01.1989	whole earth's surface	no registration, here data only for 10-day-periods: http://spirits.jrc.ec.europa.eu/files/ecmwf/int/europe/rad/ daily values upon request http://mars.jrc.ec.europa.eu/mars/Contact-Us free of charge
NASA	< 55.5 (equivalent of 0.5°)	01.07.1983	whole earth's surface	no registration http://power.larc.nasa.gov/cgi-bin/cgiwrap/solar/timeseries.cgi free of charge

[1] lower left corner: 02.98°E; 44.77°N
lower right corner: 17.72°E; 44.72°N
upper left corner: 01.04°E; 56.20°N
upper right corner: 19.84°E; 56.14°N

[2] lower left corner: 09.14°W; 27.70°N
lower right corner: 34.67°E; 26.12°N
upper left corner: 34.24°W; 65.58°N
upper right corner: 63.47°E; 62.40°N
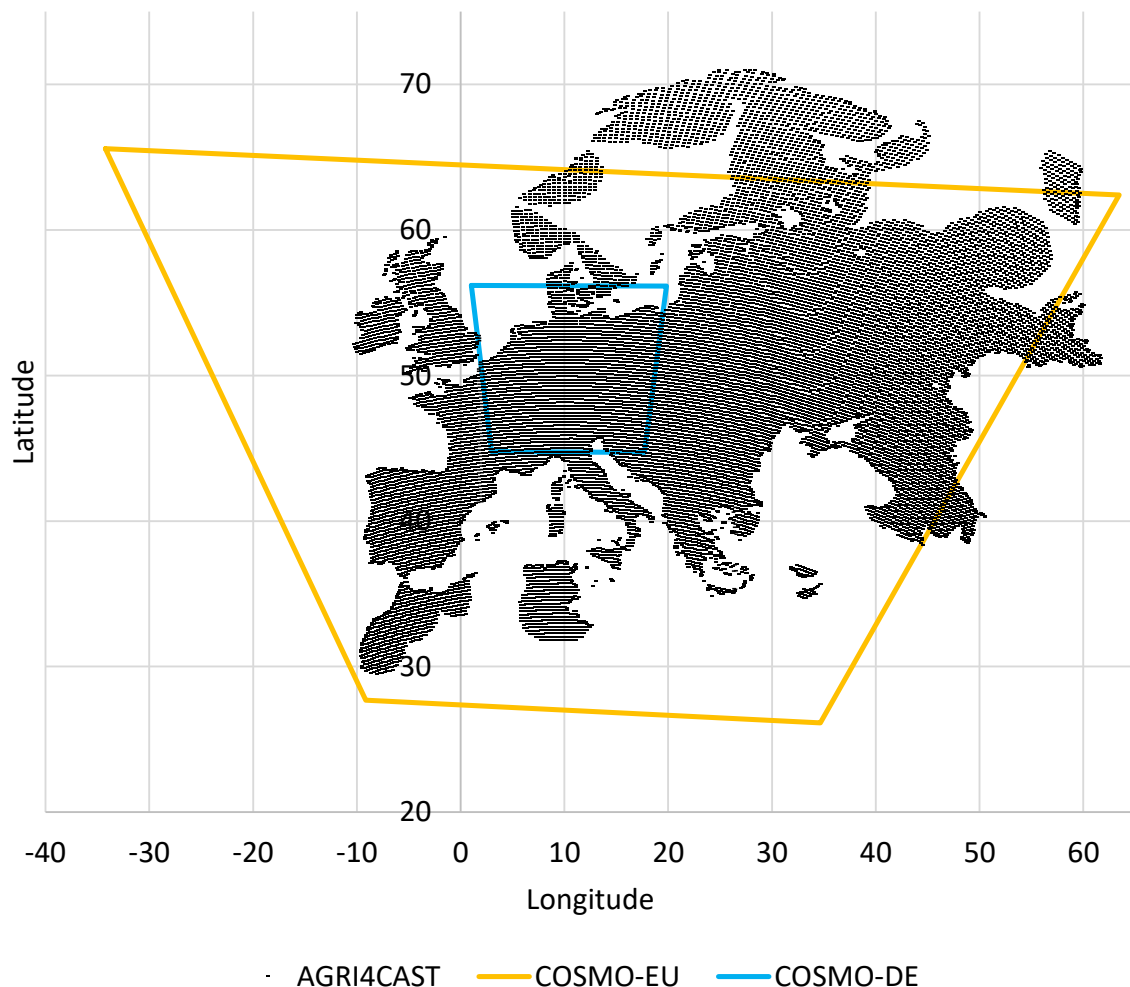
576 Figure A 1: Spatial availability of different data sources (black dots: AGRI4CAST; orange lines: COSMO-EU; blue lines:
577 COSMO-DE)

578

579 The suitability of the different data sources was investigated by means of a comparison of a short time
580 series (Table A 2). As a benchmark measured values from the DWD weather station Wittenberg-
581 Teuchel (51.89°N; 12.65°E) for the period 01.–10.03.2008 were chosen (see second line in Table A 2).
582 In COSMO rotated coordinates are necessary, which are 45.75° / -24.56° in this case.

583 In COSMO this equation for the global irradiance was used as proposed in the literature[5]:

584 GLOB = ASOB_S / (1 - ALB_RAD)

---

[5] Literature concerning the COSMO-DE and COSMO-EU databases:

M. Baldauf et al. (2011): Kurze Beschreibung des Lokal-Modells Kürzestfrist COSMO-DE (LMK) und seiner Datenbanken auf
  dem Datenserver des DWD. DWD Offenbach.

http://www.dwd.de/bvbw/generator/DWDWWW/Content/Forschung/FE1/Veroeffentlichungen/Download/LMK__DBbesc
  hr__1104__en,templateId=raw,property=publicationFile.pdf

Jan-Peter Schulz, Ulrich Schättler (2009): Kurze Beschreibung des Lokal-Modells Europa COSMO-EU (LME) und seiner
  Datenbanken auf dem Datenserver des DWD. DWD Offenbach.

http://www.dwd.de/bvbw/generator/DWDWWW/Content/Forschung/FE1/Veroeffentlichungen/Download/LME__DBbesc
  hr__0901__en,templateId=raw,property=publicationFile.pdf/LME_DBbeschr_0901_en.pdf

585   with ASOB_S: short wave radiation at ground level; ALB_RAD: albedo of ground surface.

586   Alternatively, this equation can be used: GLOB = ASWDIR_S + ASWDIFD_S

587   with ASWDIR_S: direct short wave radiation at ground level; ASWDIFD_S: diffuse downward short
588   wave radiation at ground level - but this data is only available since some day later in 2008.

589   For the data sources AGRI4CAST and MARS a spatial interpolation was conducted with the following
590   simple procedure[6]: First calculate the Euclidean distance of the four surrounding grid points, then
591   conduct weighting of the four grid points according to the inverse of the distance. See worksheet
592   'interpolation' of the Excel file.

593   The relative bias compared to the data of the weather station was calculated as follows:

594

$$Bias_{rel} = \frac{1}{n} \sum_{i=1}^{n} \frac{O_i - P_i}{O_i}$$

595   with n number of days of time series; O_i observed value at weather station; P_i predicted (interpolated)
596   value from respective data source

597   Table A 2:   Comparison of time series

data source	unit in database	example time series for 01.-10.03.2008 @ 51.89°N; 12.65°E (location of DWD weather station Wittenberg-Teuchel) [W m^{-2}]	mean [W m^{-2}]]	standard deviation [W m^{-2}]]	relative bias [%]
weather station	J cm^{-2} d^{-1}	36; 83; 54; 97; 138; 62; 58; 38; 119; 154	84	42	-
COSMO-DE	W m^{-2} [1]	41; 38; 84; 104; 90; 92; 66; 93; 92 (154 [2])	85	33	-19 % [3]
AGRI4CAST	kJ m^{-2} d^{-1}	43; 73; 52; 100; 136; 63; 64; 47; 114; 150	84	38	-3 %
MARS	kJ m^{-2} d^{-1}	48; 51; 78; 111; 130; 96; 87; 79; 123; 143	95	32	-26 %
NASA	kWh m^{-2} d^{-1}	58; 82; 57; 104; 126; 80; 95; 81; 128; 157	97	32	-28 %

598   [1] via equation GLOB = ASOB_S / (1 - ALB_RAD)
599   [2] last value was not retrieved by an oversight, value from weather station instead
600   [3] without missing value

[6] there are a lot of other interpolation procedures available, see
https://www.ncl.ucar.edu/Document/Functions/interp.shtml

601   Figure A 2 gives a graphical representation of the time series.

602
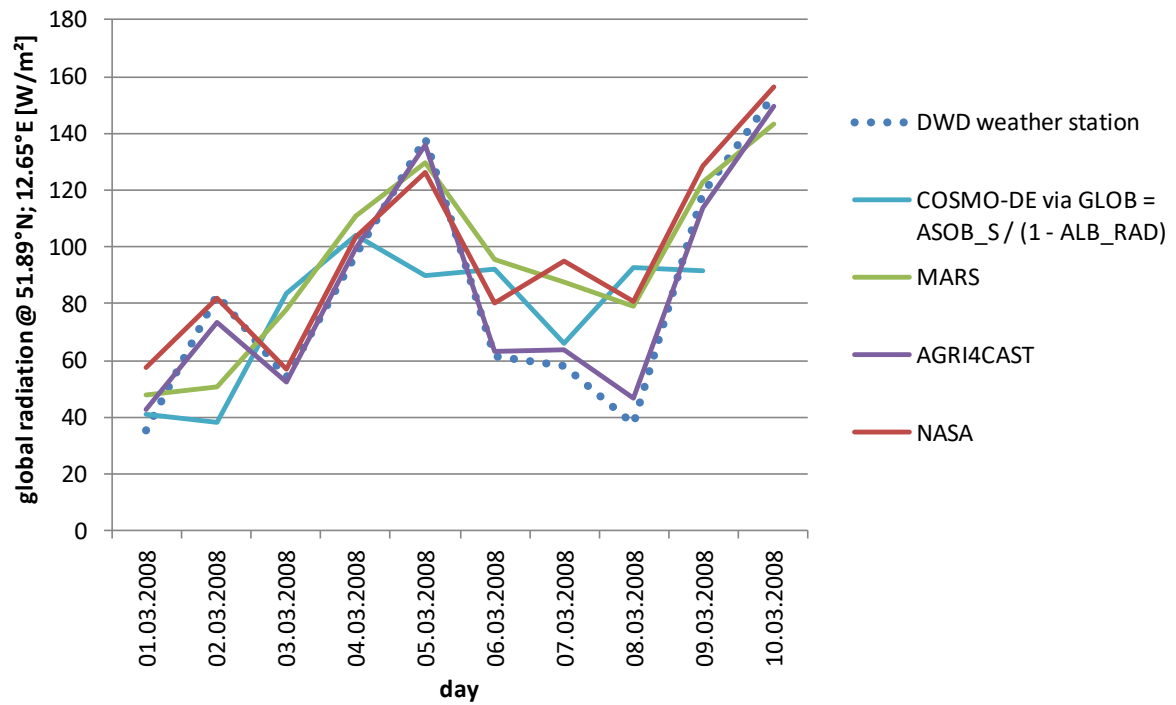
603   Figure A 2:   graphical comparison of time series

604

605   Due to the low relative bias of the AGRI4CAST time series (-3 %) this data source can be recommended.
606   Furthermore AGRI4CAST has the best temporal availability, a spatial availability for big parts of Europe
607   (see Figure A 1) and can be accessed free of charge after registration.

Appendix B: Example for determining radiation values from AGRI4CAST

As an example, the task is to retrieve the global irradiance values for a field trial which started on 15.05.1996 in Poitou-Charentes, France (47.0 °N; 0.2 °W), with a duration of 367 days.

Retrieval of a suitable data set

After registration

http://agri4cast.jrc.ec.europa.eu/DataPortal/UserRegistration.aspx

visit 'Gridded Agro-Meteorological Data in Europe'

http://agri4cast.jrc.ec.europa.eu/DataPortal/SignIn.aspx?idResource=7&o=d

Here the following adjustments have to be performed:
- Under 'Variables' choose 'total global radiation (KJ/m2/day)'.
- Under 'Day' enter 15/05/1996 as the starting date and 17/05/1997 as the ending date.
- Under 'Grid' open 'France'. Under 'Ouest' select 'Poitou-Charentes'.
- Under 'Submit your request' enter a filename like Poitou_1996 and submit the request.

In case, the trial site is less than 30 km away from a regional or national border, it might be necessary to download also the data for the adjacent region.

After some time (from few minutes to few hours), an email notification on available download will be sent. Download and unzip the file. The csv-file can be opened with a spreadsheet like OpenOffice Calc or Microsoft Excel.

Identification of the relevant grid points

For the identification of the relevant grid points first use the sheet 'grid points' in the file 'basic tools for deriving photolysis endpoints.xlsx' which is provided together with this guidance document (see chapter 6.3).

Then enter the coordinates of the field study into the orange cells. In case, you have coordinates in the format *degree, minutes, seconds* (eg. 47° 23' 32''), a conversion to a decimal value is necessary at least for the minutes.

The four nearest grid points are considered as the most relevant grid points. The AGRI4CAST database does not contain radiation values for ocean surfaces. Hence, for field trials near the coastline or near the boundaries of the spatial coverage (see Figure A 1), some of the nearest grid points can be a bit further away.

639   Figure A 3:   Screenshot from the sheet 'grid points' in the file 'basic tools for deriving photolysis endpoints.xlsx'

640   The relevant grid points have the numbers 86078, 86079, 87078, and 87079.

641   **Interpolation of the irradiance data**

642   The information from the last step and the coordinates of the study site are transferred automatically
643   into the next sheet 'inter, conv, norm' (see upper half of the Figure A 4). As the grid point no. 86078
644   has the shortest Euclidean distance to the study site, it will be weighted stronger with 38 % in the
645   interpolation procedure.

647   Figure A 4:   Screenshot from the sheet 'inter, conv, norm' in the file 'basic tools for deriving photolysis
648   endpoints.xlsx'

649

650   Go back to the csv-file from AGRI4CAST in order to transfer the irradiance data for each of the four
651   grid points from column F (see Figure A 5) to the orange cells in the columns D-G of the 'basic tools'
652   (see Figure A 4). For this purpose, a filter function in the software might be useful for selecting only

653 one grid point at a time (see first row in Figure A 5 as it is provided from Microsoft Excel). The days in
654 the csv-file are given in the format *year*, *month*, *day* (e.g. 19960515) without any separation.

655 The interpolated irradiance in column I in the 'basic tools' uses a weighting according to the inverse of
656 the distance in geographical degrees.

657

GRID_NO	LATITUDE	LONGITUDE	ALTITUDE	DAY	RADIATION
86078	46.95932	-0.32297	100	19960515	9508
86078	46.95932	-0.32297	100	19960516	14019
86078	46.95932	-0.32297	100	19960517	12171
86078	46.95932	-0.32297	100	19960518	16591
86078	46.95932	-0.32297	100	19960519	20141
86078	46.95932	-0.32297	100	19960520	16265
86078	46.95932	-0.32297	100	19960521	19784
86078	46.95932	-0.32297	100	19960522	13629
86078	46.95932	-0.32297	100	19960523	10581
86078	46.95932	-0.32297	100	19960524	19214
86078	46.95932	-0.32297	100	19960525	9579
86078	46.95932	-0.32297	100	19960526	9828
86078	46.95932	-0.32297	100	19960527	9854
86078	46.95932	-0.32297	100	19960528	18280
86078	46.95932	-0.32297	100	19960529	28442

658

659 Figure A 5:   Screenshot from the raw data in the csv-file from AGRI4CAST

660

Conversion of the irradiance data

662 Irradiance data from AGRI4CAST is given in the unit kJ/m²/day. However, PELMO requires the unit W
663 m^{-2}. A conversion takes place in column M.

conversion from:
select→ kJ/m²
to W/m² ↓
224
153
119
212

664

665 Figure A 6:   Screenshot from the sheet 'inter, conv, norm' in the file 'basic tools for deriving photolysis
666   endpoints.xlsx'

667

668

Time-step normalisation for field studies

670 In column O the time is stretched, as if there was a continuous irradiance of 100 W m^{-2}.

study location: Poitou-Charentes, France
reference irradiance, W/m²: 100.00

normalised database time	real study time [d]	normalised study time	residues	
0.00	0	0.00	463.33	← should
2.24	3	4.97	395.49	be used for
3.78	7	10.46	375.45	kinetic
4.97	14	27.86	219.49	evaluation
7.09	27	67.29	191.41	
8.20	56	130.26	139.21	

671

672 Figure A 7: Screenshot from the sheet 'inter, conv, norm' in the file 'basic tools for deriving photolysis
673 endpoints.xlsx'

674

675 In the next step, the sampling time points and the residues of the active substance from the field study
676 have to be entered in column Q and S. In column R, the time points are translated for the reference
677 irradiance of 100 W m^{-2}. Figure A 8 shows the effect of the time-step normalisation in this example.

678
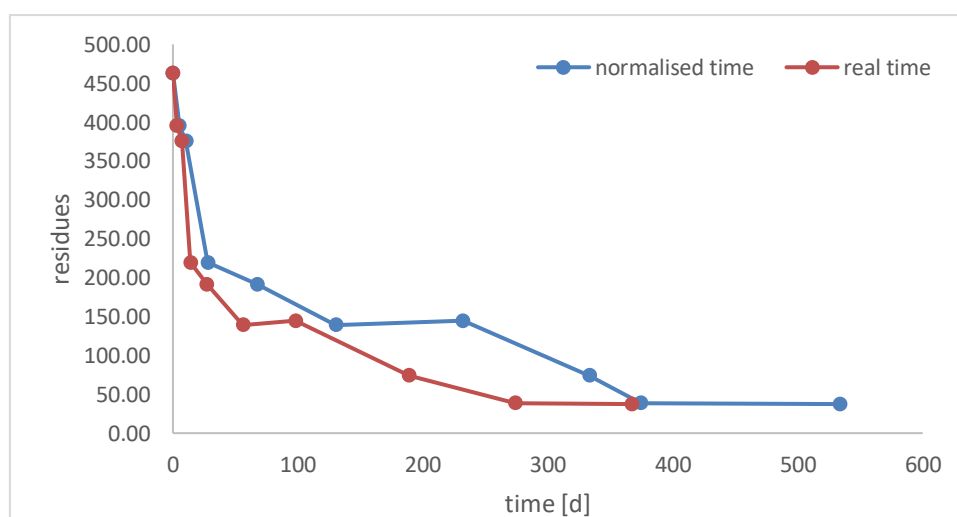
679 Figure A 8: Effect of the time-step normalisation

680

681 The columns R and S give the data set for the kinetic evaluation (e.g. with gmkin, CAKE or KinGUII).

682

Kinetic	Chi² (%)	visual fit	k_1 (1/d)	k_2 (1/d)
DFOP	8.8	good	0.061	0.0032
HS	7.3	good	0.026	0.0035

683

684 Here, HS was chosen with $k_{photo} = k_1 - k_2 = 0.026 - 0.0035 = 0.0225$ (see chapter 5.1).

685

686 Finally, the geometric mean or the extrema of the k_{photo} values is taken for the Tier 2B simulation as
687 shown below.

688

field study	k_{fast} @ 100 W m^{-2} (d^{-1})
Lebien, Germany	0.15
Grisolles, France	0.2
Vitray, Louzy, Poitou-Charentes, France	0.1
Maidenhead Berkshire, UK	0.17

number of k_{fast} values: 4

a) in case >= 4 k_{fast} values are available: one simulation with geometric mean

geometric mean: 0.150

b) in case 3 k_{fast} values are available: two simulations with fastest and slowest observed photolysis

fastest observed photolysis: possible worst-case for photodegradates: 0.200

slowest observed photolysis: worst-case for active substance: 0.100

c) in case only 1 or 2 k_{fast} value are available: Tier 2B is not applicable!

689

690   Figure A 9:   Screenshot from the sheet 'comparison' in the file 'basic tools for deriving photolysis endpoints.xlsx'

Appendix C: Example for determining radiation values from NASA web page

The database AGRI4CAST covers the EU Member States, neighbouring European countries, and the Mediterranean countries' (see Figure A 1). In case, irradiance values outside of Europe are needed, the NASA database can be used.

On the NASA web page:

http://power.larc.nasa.gov/cgi-bin/cgiwrap/solar/timeseries.cgi?email=daily@larc.nasa.gov

the term '*insolation on horizontal surface (kWh m⁻² d⁻¹)*' has to be selected.

the term '*insolation on horizontal surface ($kWh\ m^{-2}\ d^{-1}$)*' has to be selected.

Input for a field trial which started on 01.04.1992 in Parma (44.8 °N; 10.3 °E), in this example only for 10 days, may look as follows:

Figure C 1:   Screenshot from NASA web page, selecting the needed data

After 'Submit', data is presented in a diagram:

Daily Averaged Insolation Incident On A Horizontal Surface

Lat: 44.8 Lon: 10.3 Begin: 4/1/1992 End: 4/10/1992
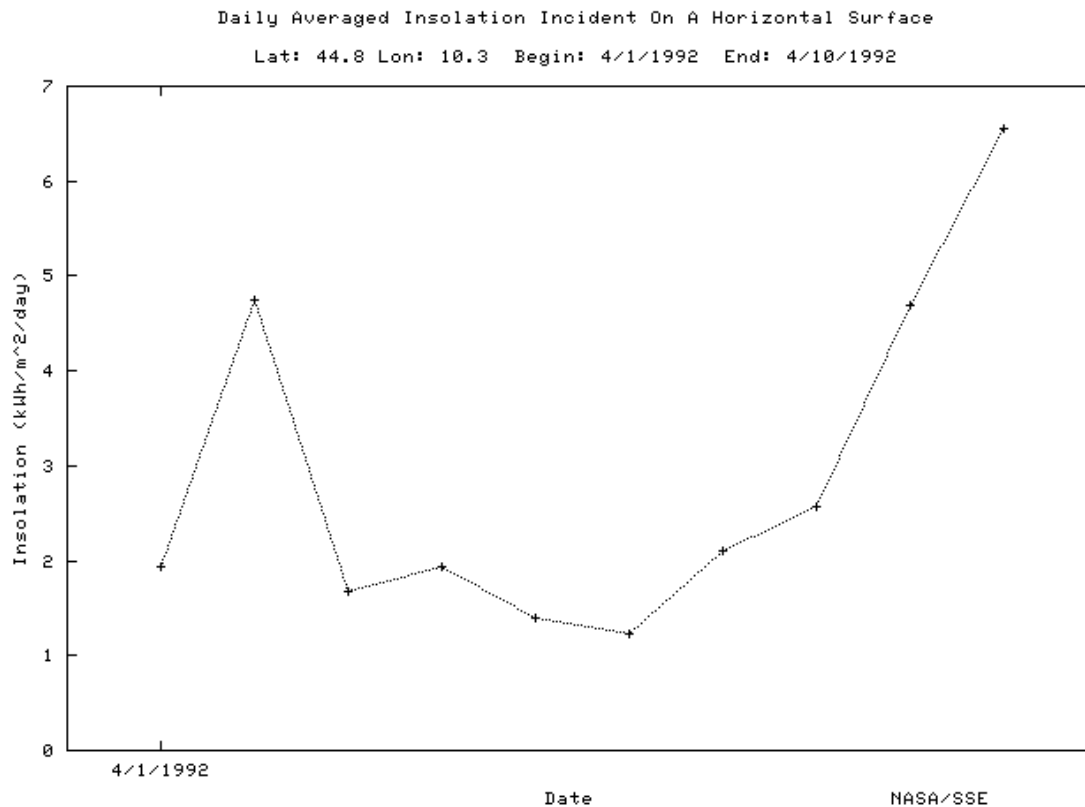
Tue May 20 08:30:46 2014

705 Figure

706 Figure C 2:   data from NASA web page, presented in diagram

707

708 Clicking on 'Download a text file' provides the raw data:

709 NASA/POWER Near Real-time Daily Averaged Data (Evaluation Version)

710 Dates (month/day/year): 04/01/1992 through 04/10/1992

711 Location: Latitude 44.8   Longitude 10.3

712 Elevation (meters): Average for one degree lat/lon region = 452   Site = na

713 Climate zone: 4 (reference Briggs et al, http://www.energycodes.gov)

714 Methodology Documentation:

715 http://power.larc.nasa.gov/common/BuildingMethodology/Building1d0_Methodolo
716 gy_Content.html

717 Parameter(s):

718 swv_dwn   Average Insolation Incident On A Horizontal Surface (kWh/m^2/day)

719

720 YEAR MO DY swv_dwn

721 1992 04 01   1.93

722 1992 04 02   4.75

723 1992 04 03   1.68

724 1992 04 04   1.93

33

725   `1992 04 05    1.40`

726   `1992 04 06    1.23`

727   `1992 04 07    2.11`

728   `1992 04 08    2.56`

729   `1992 04 09    4.70`

730   `1992 04 10    6.56`

731   Figure C 3:   data from NASA web page, presented as text

732 Then these daily values in column 'swv_dwn' have to be converted by the factor 1000/24. For the time-
733 step normalisation for field studies, see Appendix B.

Appendix D: Example for carrying out photolysis simulations in the exposure assessment for authorisation

In the following tables an example is provided based on the groundwater exposure assessment of an active substance degrading via soil photolysis. The tables provide the required input parameter for all Tiers, including Tier 2B with data from field trials. The following tables summarise the results of the different steps. Table D 1 below gives the details about the exemplary indication.

Table D 1:   Input parameters related to indication for PECgw modelling with FOCUS PELMO 5.5.3

Application rate (kg a.s./ha)	1×0.1
Crop (crop rotation)	winter cereals (winter wheat)
Date of application	03.01.
Interception (%)	20 (BBCH 20)
Soil moisture	100 % FC
Q_{10}-factor	2.58
Moisture exponent	0.7
Plant uptake	0
Simulation period (years)	26

Active substance 'examplamin'

The exemplary active substance examplamin degrades via biodegradation resulting in CO_2/ bound residues and three biodegradation metabolites. One of these metabolites (M002) is also formed via biodegradation from metabolite M001 and by photolysis from the active substance. M002 is further transformed via biodegradation into a secondary metabolite (M004). For details see Figure D 1. Thus, the formation of M004 is indirectly influenced by photolysis. Therefore, a Tier 1 calculation has to be conducted for M004 as well. For details see Figure D 2.

The following table summarises the relevance assessment of the photodegradate M002:

Table D 2   Summary of the relevance assessment of the photodegradate M002

Photo-degradate	Soil photolysis study	Max. occurrence, irradiated (at day)	Occurrence at same day in dark control	Difference of occurrences	Field dissipation study, 'legacy' type	Relevance (y/n)
M002	Author (1986)	32.3 % (day 30)	19.4 % (30 d)	12.9 % > 5 %	Available, but samples were not analysed for M002	y

752
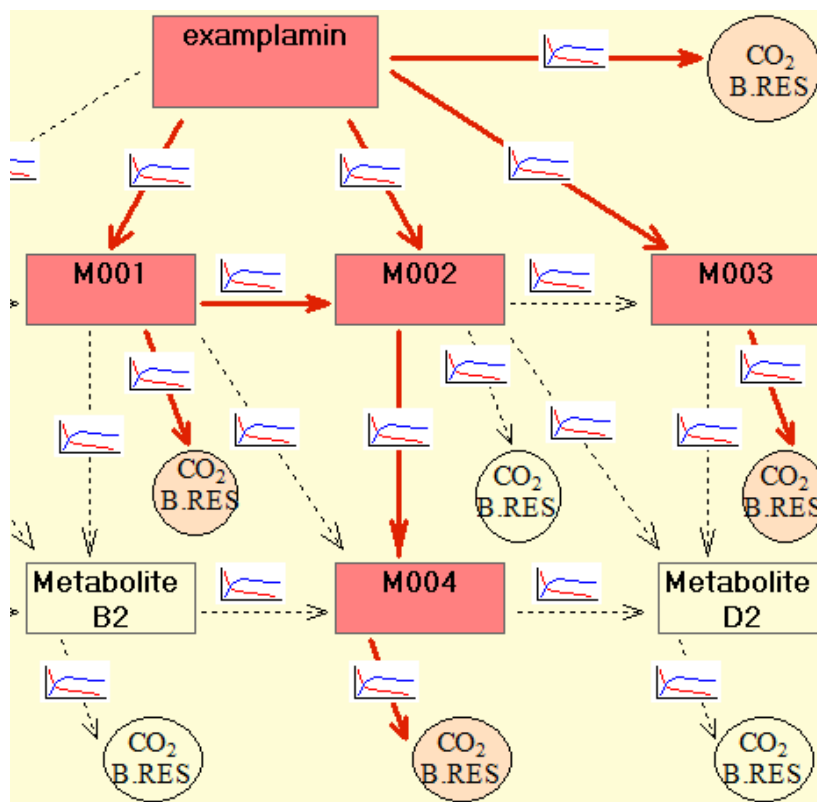
Figure D 1   Metabolism scheme for examplamin and its transformation products in Tier 2A and 2B (between examplamin and M002 there is biodegradation and photolysis, see Figure 5)

755

756   Table D 3   Input parameters related to the biodegradation pathway and sorption of examplamin and its metabolites for PECgw modelling

Active substance	Examplamin
Molecular weight (g/mol)	367.3
DT50 in soil (d)	30.4
K_{foc}	898
1/n	0.97
Transformation product	**M001**
Molecular weight (g/mol)	353.3
Formation fraction	0.03
DT50 in soil (d)	19.5
K_{foc}	27
1/n	0.96
Transformation product	**M002**
Molecular weight (g/mol)	163.1
Formation fraction a.s. -> M002/ M001 -> M002	0.3/ 0.75
DT50 in soil (d)	21.5
K_{foc}	13
1/n	0.83
Transformation product	**M003**
Molecular weight (g/mol)	297.2
Formation fraction	0.39
DT50 in soil (d)	20.8

36

K_{foc}	33
1/n	0.87
Transformation product	**M004**
Molecular weight (g/mol)	177.13
Formation fraction	1.0
DT50 in soil (d)	19.1
K_{foc}	13
1/n	0.83

758

759 for Tier 1:

760 Calculation of so-called 'application rate' by means of the ratio of the molecular masses.

761 Table D 4   Calculation of the 'application rate' of photodegradate M002 used in the Tier 1 approach of PECgw
762   simulation

	Examplamin	M002
Molecular mass (g/mol)	367.3	163.1
'Application rate' (g/ha)	80	80 * 163.1/367.3 = 35.5

763
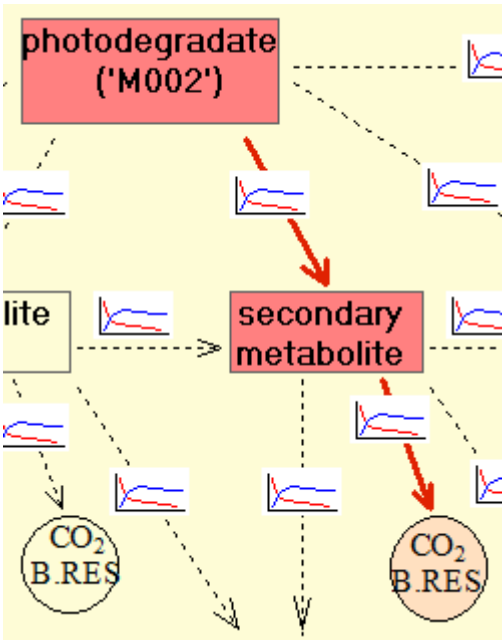
764

765 Figure D 2:   Metabolism scheme for the photodegradate M002 and its transformation product M004 in Tier 1

766

767 for Tier 2A:

768 usage of default values

769

770   for Tier 2B:

771   Summary of the recalculation of field studies in order to derive photolysis rates for the active substance
772   examplamin. This is done for the fast, initial phase of the experimental time after a timestep-
773   normalisation according to the daily irradiances (for a detailed example see Appendix B):

774   Table D 5   Summary of suitable photolysis rates of examplamin

Soil	Coordinates	Date of application	Chi^2 error	Kinetic parameters	DT50$_{photo}$ @ 100 W m^{-2} (d)	Method of calculation
S1, silty clay loam	43.8 °N; 1.3 °E	21.05.1996	10.0 %	M_0: 704.6 k_{fast}: 0.218 k_{slow}: 0.015 g: 0.30	ln(2)/ k_{fast} = 3.2	DFOP
S2, sandy loam	47.0 °N; -0.2 °E	15.05.1996	8.8 %	M_0: 471.2 k_{fast}: 0.0901 k_{slow}: 0.0047 g: 0.60	ln(2)/ k_{fast} = 7.7	DFOP
S3, sandy clay loam	51.5 °N; -0.7 °E	07.06.1996	10.5 %	M_0: 792.1 k_{fast}: 0.0436 k_{slow}: 0.0040 g: 0.57	ln(2)/ k_{fast} = 15.9	DFOP
S4, sandy loam	53.5 °N; 10.5 °E	29.04.1997	11.6 %	M_0: 720.8 k_{fast}: 0.094 k_{slow}: 0.022 t_b: 11.4	k_{photo} = k_{fast} − k_{slow} = 0.072 ln(2)/ k_{photo} = 9.6	HS
S5, sandy clay loam	51.4 °N; -0.8 °E	29.05.1997	15.2 %	M_0: 741.4 k_{fast}: 0.317 k_{slow}: 0.007 g: 0.76	ln(2)/ k_{fast} = 2.2	DFOP
DT50$_{photo}$ @ 100 W m^{-2} (d) Geometric mean over all kinetic evaluations (n=5) [If the number of suitable trials is 2-3, two simulations with the maximum and minimum photolysis rates from the trials are conducted.]					6.1	

775

Table D 6   PECgw at 1 m soil depth of examplamin and its metabolites M001, M002, M003 and M004

| Use No. | Scenario | 80th percentile PECgw at 1 m soil depth ($\mu g\ L^{-1}$) modelled by FOCUS PELMO 5.5.3 | | | | |
		Examplamin	M001	M002	M003	M004
winter cereals	Tier 1, Piacenza (combined simulation of photodegradate M002 as parent and its metabolite M004)	-	-	0.412	-	0.920
	Tier 2A, Piacenza, 0.1 d @ 100 W m^{-2} (default)	< 0.001	< 0.001	0.372	< 0.001	0.786
	Tier 2A, Piacenza, 10 d @ 100 W m^{-2} (default)	< 0.001	0.005	0.127	0.026	0.246
	Tier 2B, Piacenza, 6.1 d @ 100 W m^{-2} (geom.)	< 0.001	0.004	0.192	0.021	0.341
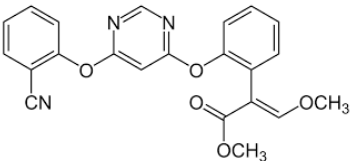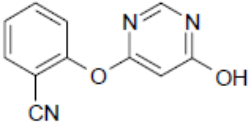
Appendix E: Non-exhaustive list of active substances with relevant photo transformation compounds in soil

Relevant photo transformation compounds are defined as those, which occur with at least 10 % higher occurrence than in the dark control (see section 3).
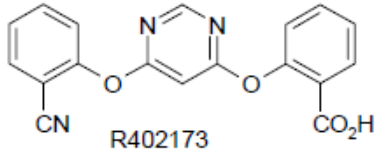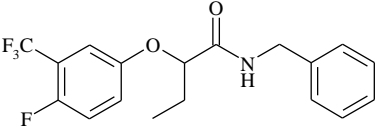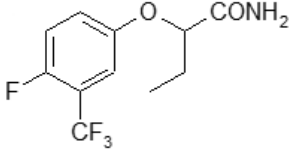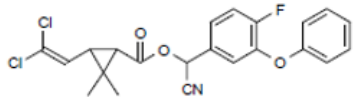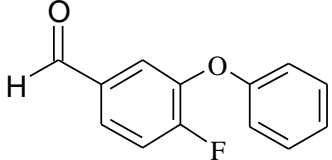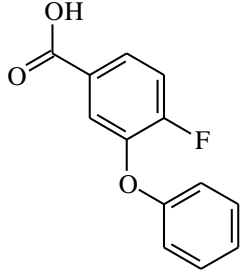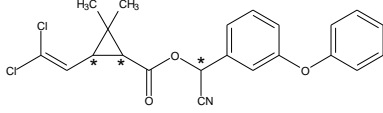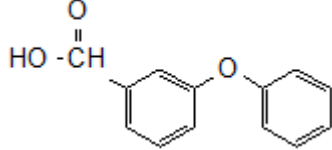
The presence of functional groups such as carbonyl (C=O), nitroaromatic, N-oxide, alkene (C=C), aryl chloride, weak C–H and O–H bonds, sulfides, and polyenes increases the likelihood that a substance is labile under photolytic conditions. The photolability arises from the chromophoric properties, e.g. of carbonyl functions, or from the weak covalent bonds, e.g. O–H bonds (Piechocki and Thoma, 2006)[7].
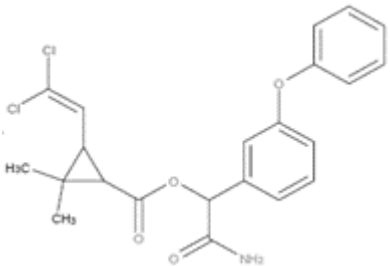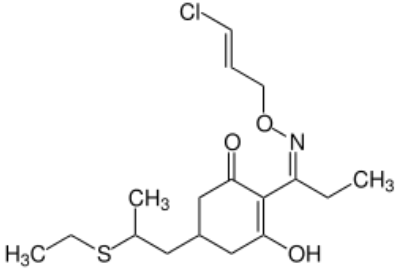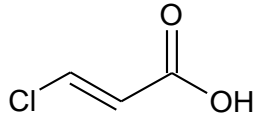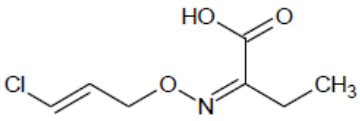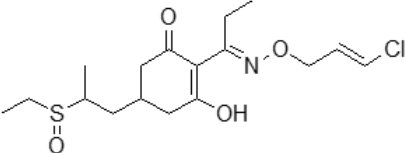
There is empirical evidence, that sorption of photo transformation compounds is often lower than the sorption of the parent compound (see Table E 1: 10 cases with Koc of photo transformation compounds < Koc of parent, only 3 cases with Koc of photo transformation compounds > Koc of parent, 5 cases with a lack of published data concerning sorption). This is one more argument for investigating the risk of groundwater contamination by photo transformation compounds.
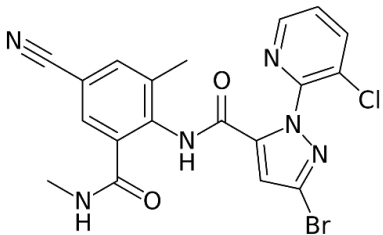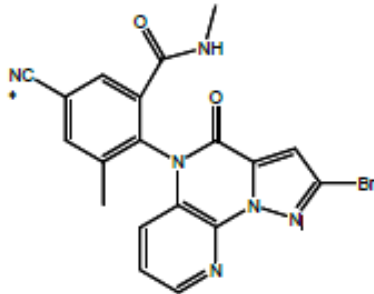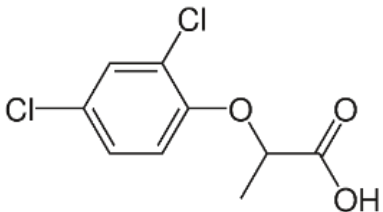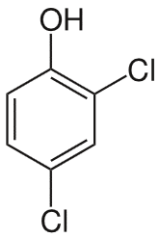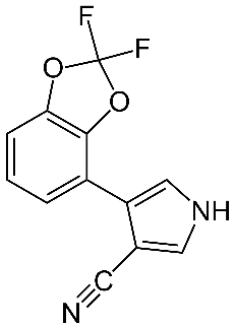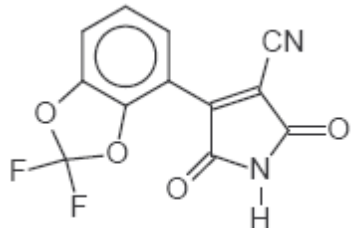
Table E 1   Alphabetic list of known active substances with relevant photo transformation compounds in soil – which is not intended to be exhaustive!
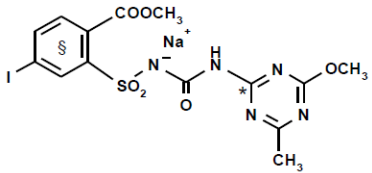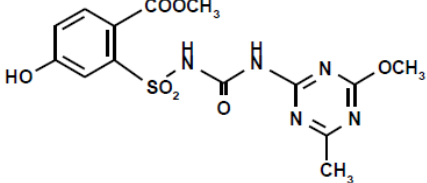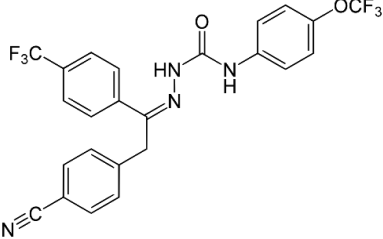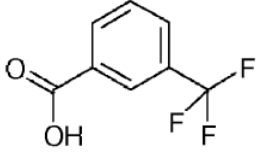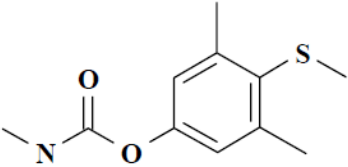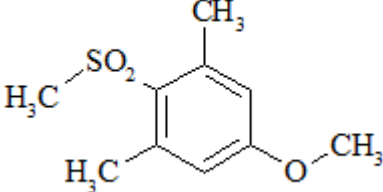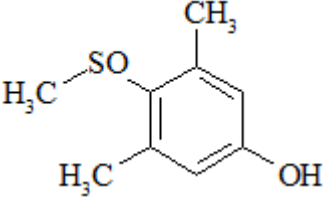
Active substance	Structure of active substance	K_{Foc} of active substance (arithmetic mean)	Relevant photo transformation compounds in soil photolysis study (max. occ. irradiated/ in dark control)	Structure of photo transformation compounds	K_{Foc} of photode-degradates (arithmetic mean)
azoxystrobin		423	R401553 (5.0 % and 5.7 %/ no data)		203
			R402173 (5.4 % and 7.6 %/ no data)		90
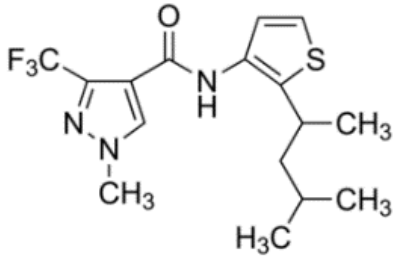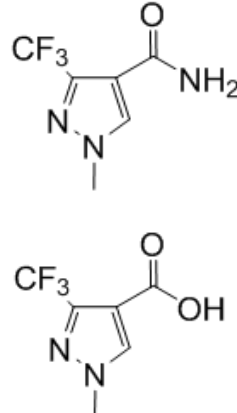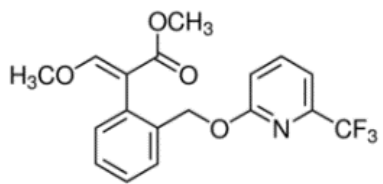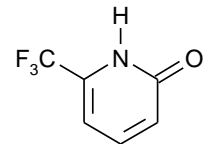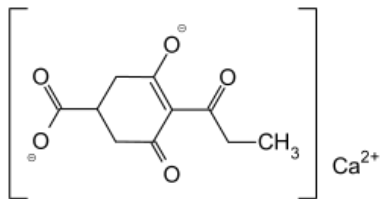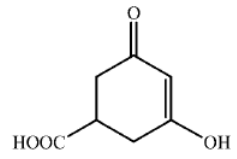
[7] Piechocki, J. T.; Thoma, K. (2006) Drugs and the Pharmaceutical Sciences Vol. 163: Pharmaceutical Photostability and Stabilization Technology *CRC Press*, 1st Edition, New York/ London, page 79-80.
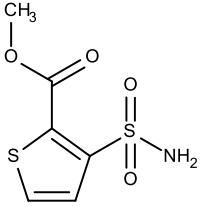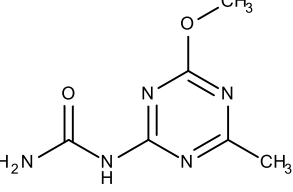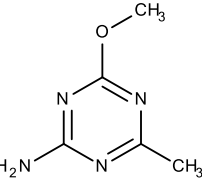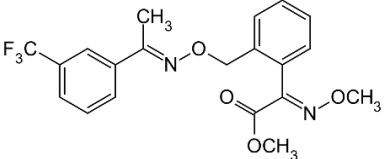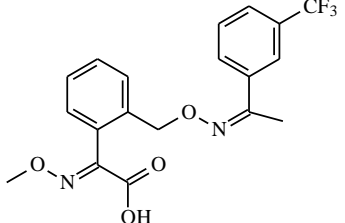
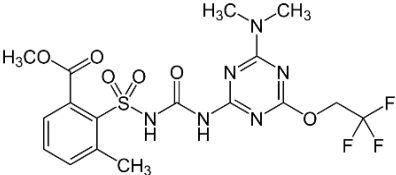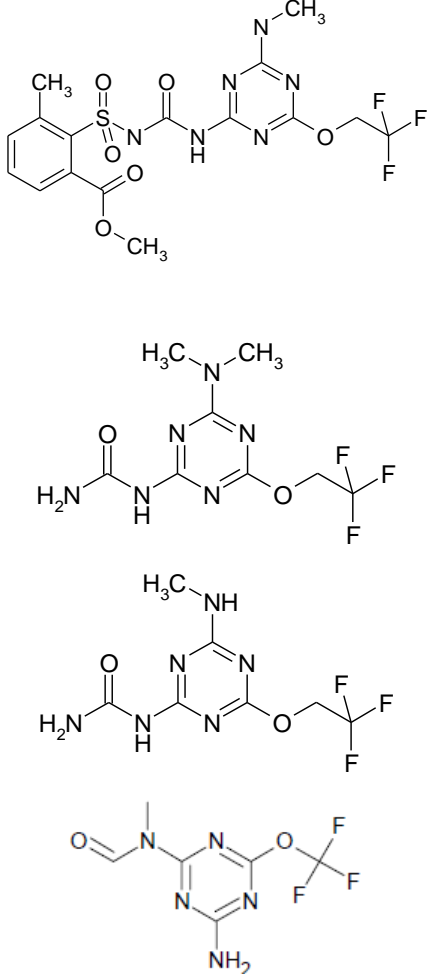|					
			(Data from dark control might show irrelevance as photo-degradates, in case the difference is < 5 % compared to irradiated trial.)	R402173	
beflubutamid		1213	UR-50624 (9.2 % and 11.3% / 2.6 % and 0.3 %)		No reliable data
beta-cyfluthrin		112000	FPB aldehyde (18 % /<3 %) FPB-acid (22.3 % /<11.2 %)		No data 136
beta-cypermethrin		130031	3-phenoxybenzoic acid (PBA, 'P14') (11.7 %/ 0.4 %)		69.8

			cyperamide ('P2') (32.6 %/ 5.8 %)		27058 (QSAR estimate)
clethodim		22.7	trans-3-chloroacrylic acid (CAA) (18.1 % /<< 5 %) 2-[3-chloroallyloxyimino] butanoic acid (18.7 %/ ??) clethodim sulfoxide (74 %/ 62 %)		2.2 (QSAR estimate) [1.0 used for alkali soil conditions] 81.9 (QSAR estimate) 13.3
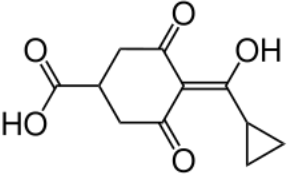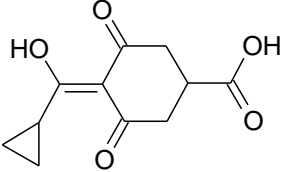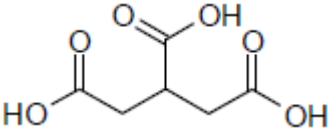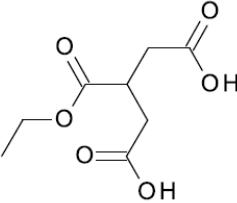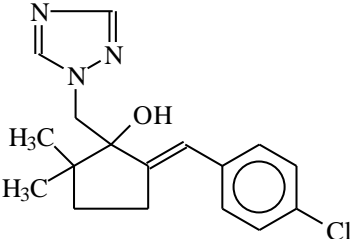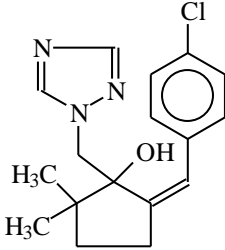
cyantraniliprole		193	IN-RNU71 (14.1 %/ n.d.)		139
dichlorprop		43.9	2,4–dichlorophenol (23.6 %/ 0.9 %)		126 (single value)
fludioxonil		145600	CGA 265378 (12.3 %/ no data)		68.3 [unstable, rough estimate]

iodosulfuron-methyl-sodium		50.6	AE 0002166 (at day 9: 16.2 %/ 4.1 %)		no data
metaflumizone		30714 [linear Koc]	M320I29 (21.1 %/ < 5 %) M320I06 (8.4 % and 6.4 %/ 2.0 % and 3.5 %) - differences 6.4 % and 2.9 %, the latter being < 5 %, hence not relevant		24.8
methiocarb		660	methiocarb sulfoxide (M10) (57.2 %/ < 20.7 %)		189

			methiocarb sulfoxide phenol (M04) (28.8 %/ < 3.8 %)		50.7
penthiopyrad		761	PAM (47 %/ n.d.)		9
			PCA (36 %/ n.d.) [with DM-PCA as successor metabolite]		2
picoxystrobin		898	M03 (or R403814; IN-QDK50 and IN-QFA75 (tautomers)) (28.3 %/ n.d.)		13
prohexadione calcium		204.5	despropionyl-prohexadione (15.21 %/ 4.86 %)		No data

thifensulfuron-methyl		9 (median)	IN-A5546 (27.7 %/ n.d.)		49 (arithmetic mean)
			IN-V7160 (9.6 %/ n.d.)		101.4 (arithmetic mean)
			IN-A4098 (32.3 %/ 19.4 %)		45.5 (median)
trifloxystrobin		2379	CGA 373466 (27 %/ <3.8 %)		88

triflusulfuron methyl		40	IN-66036 (12.2 %/ 2.5 % on same day) (also in aqueous photolysis)		see Hawkins et al. (1992), Singles et al. (2003)
			IN-JL000 (5.4 % and 7.1 %/ n.d.) (also in aqueous photolysis)		
			IN-JM000 (13.5 %/ n.d.)		
			Only in aqueous photolysis: IN-EOQ47		

		60 (minimum)	CGA179500 (M1) (61.5 %/ 93.7 %) higher in dark control, not relevant		145
trinexapac-ethyl			CGA275537 (M4) (10.8 % / 2.6%)		1 (surrogate value from CGA300405)
			CGA300405 (M5) (12.5 %/ 1.2 %)		1 (EPIWIN)
triticonazole		456	RPA 406203 (10.95 %/ 3.99 %)		no data

788

789

Appendix F: Basic tools for deriving photolysis endpoints

See attached Excel file (Basic tools for deriving photolysis endpoints).