GUIDANCE

Scientific guidance on soil phototransformation products in groundwater – consideration, parameterisation and simulation in the exposure assessment of plant protection products

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Abstract

This Guidance Document gives recommendations how to consider transformation products from soil photolysis ('phototransformation products') when modelling the predicted environmental concentrations in groundwater. It describes possible parameterisations of the photolytic pathway (i.e. the photolytic half-life and the corresponding reference irradiation) in a tiered approach using the FOCUS-PELMO model. Following the recommendations of the EFSA guidance (2014), separate half-lives can be derived for the surface processes (k_{fast}) and the biodegradation in the soil matrix (k_{slow}) from field dissipation studies by using biphasic models. From field dissipation studies evaluated with biphasic kinetics, the k_{fast} value can be considered 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.

Summary

The main aim of this Guidance Document is to consider the phototransformation products (photo-TPs) formed by soil photolysis in the groundwater exposure assessment.

First, it should be checked whether photo-TPs have to be considered in the groundwater exposure assessment following the relevance criteria for groundwater metabolites given in European Commission Guidance Document (2000). Furthermore, the occurrence of the transformation product in the irradiated experiment should be at least 5% higher than in the associated dark control in at least one sampling time. This additional criterion is a pragmatic value to distinguish predominantly photolytic/light-exposed surface transformation products from those formed by both microbial and light-exposed surface processes. In case this criterion is not met, the transformation product should be regarded as an ordinary metabolite for which this guidance document is not relevant.

If photo-TPs are observed in a **laboratory** soil photolysis investigation in relevant amounts according to European Commission Guidance Document (2000), 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. Laboratory soil photolysis studies are the only way to identify qualitatively which transformation products may be formed under the influence of light.

If **field studies** are available, the assessor needs to distinguish between studies designed without exclusion of photolysis ('**legacy**' studies), and studies designed to avoid photolysis and other surface processes according to EFSA (2014) ('**tailored**' studies). Only field dissipation studies done without exclusion of photolysis ('legacy' studies) can provide information on the formation of photo-TPs under environmental conditions. If only 'tailored' field studies are available, it is not possible to get information about the maximum occurrence of photo-TPs under field conditions, and then, the identified photo-TPs from the laboratory soil photolysis study have to be considered in groundwater exposure assessment via the photolytic pathway that simulates what happens at the soil surface.

If 'legacy' or tailored field dissipation studies are available and soil photo-TPs have been analysed and the LOQ for the transformation products was sufficient to identify concentration levels that may trigger a groundwater assessment, the following cases are possible:

- conditions during the field studies should ensure that photolysis has occurred (e.g. plant cover in field experiments should be avoided, arithmetic mean irradiance (global solar irradiation) over the first month of the study should be at least 100 W m^{-2})
- when photo-TPs, identified in the laboratory soil photolysis study in relevant amounts, have not been analysed in the field study, the photo-TPs have to be considered in groundwater exposure assessment
- when photo-TPs, identified in the laboratory soil photolysis study in relevant amounts, have been analysed, but not detected in relevant amounts according to European Commission Guidance Document (2000), no further groundwater exposure assessment for the photo-TPs is required
- when photo-TPs, identified in the soil photolysis study in relevant amounts, were also observed in relevant amounts under field conditions according to European Commission Guidance Document (2000), they have to be considered in the groundwater exposure assessment via the photolytic pathway.

The model FOCUS-PELMO (versions more recent than 5.5.3) allows to consider the soil photolysis pathway together with the biodegradation pathway as a higher tier option in the leaching assessment of active substances, and to consider the photo-TPs in the leaching simulation as lower tier approach. FOCUS-PELMO requires two input parameters for the consideration of the photolytic pathway: the **photolytic half-life**, which describes the behaviour of a substance under the influence of natural light, and the **reference radiation** (irradiance) after the application at the field trial, for which the photolytic half-life was determined.

To estimate the **photolytic half-life,** the approach outlined in EFSA guidance (2014) can be used, and then, it is possible to derive separate half-lives from field dissipation studies for the surface processes, e.g. photolysis and volatilisation (k_{fast}), and biodegradation in the soil matrix (k_{slow}) by using biphasic models. The k_{fast} values have to be derived from biphasic kinetics data from field studies according to FOCUS degradation kinetics (FOCUS, 2006). The k_{fast} values from field dissipation studies of photosensitive substances are directly influenced by irradiance at the trials. 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.

Reference radiation data can be retrieved by measurements done directly at the field trial or from a weather station nearby (line distance < 10 km) or 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.

In the modelling approach, both pathways (photolytic degradation and biodegradation) are considered independent from each other and the model determines automatically the daily changing amount of active substance going into each pathway with regard to the scenario parameters irradiance and light interception on the one hand, and temperature and moisture on the other hand. In FOCUS-PELMO 5.5.3 and 6.6.4, the soil photolysis process is simulated until the active substance is 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 transport through the top 1 mm soil layer is simulated in the same way as the transport through the other soil layers. Transportation through the top 1 mm depends on the K_{fast} value of the compound and on the amount of water that moves to the next soil layer. The climate files used for the FOCUS groundwater models include also the daily irradiation values for each FOCUS scenario. In FOCUS-PELMO (versions more recent than 5.5.3), 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.

A tiered approach is recommended for considering photo-TPs in PECgw simulations using FOCUS-PELMO 5.5.3 (and subsequent versions):

Tier 1: Photo-TP as parent substance

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

Tier 2A: Default values in the complete degradation scheme

1) Generate the metabolism scheme in FOCUS-PELMO including the photolytic pathway.
2) The recommended default values of the active substance in Tier 2A are:
   $DT50_{fast} = 0.1$ day @ reference irradiance = 100 W m^{-2}
   $DT50_{slow} = 10$ day @ reference irradiance = 100 W m^{-2}.
3) Conduct two simulations, one for each of the parameters shown in point 2.
4) Conduct additional runs if the number of photo-TPs is two or more.

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

1) Generate the metabolism scheme in FOCUS-PELMO including photolytic pathway (as in Tier 2A).
2) Get radiation data from:

   a) direct measurements at the field trial or
   b) measurements at a weather station nearby (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 FOCUS (2006) 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, switch to Tier 2A.

5) Conduct FOCUS-PELMO simulations with the parameters derived in point 4.

For degradation products for which both simulations (either with the photolytic pathway with Tier 2A or 2B, or with only the biodegradation pathway in the dark) are performed, the highest PECgw for each FOCUS scenario should be considered for the groundwater exposure assessment.

Besides FOCUS-PELMO, also FOCUS-PEARL can simulate the Tier 1 of photolysis scheme. Some further development of the PEARL software package in respect to the use of complete soil photolysis approach can be anticipated to enable also the higher Tiers 2A or 2B. Once a version of FOCUS-PEARL with the features needed is available, it will be possible to use both FOCUS-PELMO and FOCUS-PEARL for Tiers 2A or 2B.

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1.   Introduction

The European Commission Guidance Document (2014) 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 document is based on the requirements and criteria of the Regulation EC (No) 1107/2009. Advanced simulation models, which can calculate predicted environmental concentrations (PEC) of active substances and their transformation products in groundwater, were introduced and evaluated. In addition, a tiered approach was developed to consider extended modelling options in the groundwater exposure assessment.

The refinement procedure of groundwater exposure assessment for active substances is not in the focus of the present Guidance Document and will only be briefly mentioned (see Section 7). The main intention of this Guidance Document is to consider the phototransformation products (photo-TPs) formed by soil photolysis as a standard requirement in the groundwater exposure assessment using the best available models and parameters in accordance with the current guidelines and scientific opinions. Since May 2013, the model FOCUS-PELMO 5.5.3 is available on the FOCUS website (https://esdac.jrc.ec.europa.eu/projects/pelmo). This model and later versions make 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 to consider the photo-TPs in the leaching simulation as 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' (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 FOCUS groundwater scenarios were not selected considering soil photolysis, and then their conservatism related to soil photolysis is unknown. However, 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 the EU (FOCUS-PELMO and FOCUS-PEARL). For FOCUS-PEARL, it is currently 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 can be anticipated to enable also the higher Tiers 2A or 2B. Once a version of FOCUS-PEARL with the features needed is available, it will be possible to use both FOCUS-PELMO and FOCUS-PEARL for higher Tiers 2A or 2B, in cases where the higher Tiers 2A or 2B are necessary.

It has to be highlighted that the present Guidance Document forms an integral part of the groundwater exposure assessment as described in the European Commission Guidance Document (2014), and then if not specifically indicated, the recommendations as provided there should be followed.

2.   Decision tree for consideration of phototransformation products in PEC groundwater simulations

First, it needs to be checked whether photo-TPs have to be considered in the PEC groundwater (PECgw) exposure assessment. It should be noted that consequent to the Commission Regulation (EU) 283/2013, for agricultural practices that involve placing the active substance below the soil surface, the results of a soil photolysis study are not needed and photo-TPs do not need to be included in PECgw simulations. This applies also to active substances with low light absorbance (i.e. when it does not possess substantial absorbance maxima above 290 nm). The decision scheme for consideration of photo-TPs in PECgw simulations for active substances which are not incorporated and that absorb light above 290 nm is provided in Figure 1.

If the photolytic degradation pathway is relevant for an active substance according to the results of a soil photolysis investigation, this pathway can be considered in the groundwater simulation additionally to the biodegradation pathway as a higher tier option and would lead to lower PECgw values of the active substance. This higher tier option regarding the active substance simulation results

is out of the current scope of this Guidance Document and a proposal for this approach is only mentioned in Section 7.

If photo-TPs are observed in a laboratory soil photolysis investigation using a thin soil layer in relevant amounts according to European Commission Guidance Document (2000), and with a relevant difference in comparison to the dark control as set out in the Guidance, these transformation products have to be considered in the lower tier approach of the groundwater exposure assessment following the decision tree provided in Figure 1 – Box 1. The design of a laboratory soil photolysis study with its thin soil layer can result in extreme test conditions concerning temperature and soil dryness (even in study designs aiming to maintain soil moisture). This can minimise the biodegradation pathway compared to the soil surface in the field where the layer where light-induced transformation occurs is connected to the underlying soil which can be a source of soil moisture and also a buffer against large fluctuations in surface temperature, that can be present when dark light cycles are employed in draft OECD guideline laboratory investigations (OECD, 2002a). The consequence is that there may be a higher formation rate of photo-TPs formed under the influence of light under laboratory conditions where typically there is a reduced spectrum of radiation, which is unlikely to be completely representative for environmental conditions (note near IR radiation above 800 nm is limited in laboratory bench test set-ups). Here, the global solar irradiation for summer in Athens (Greece) or Arizona (USA) is the standard measured value used to compare to the laboratory bench test set-up. Usually, UV-Vis wavelengths are considered to be responsible for photodegradation under laboratory conditions. Under conditions that are more realistic in the field, a bigger portion of the active substance may be transformed via biodegradation and a smaller portion transformed by photolysis both at the soil surface. The above detail acknowledges that the conduct of laboratory soil photolysis studies is complex and there are some difficulties in the interpretation of results. However, it is the only tool available to identify qualitatively which novel transformation products may be formed under the influence of light. In practice, it serves as a photolysis transformation product search study.

2.1. Relevant difference in comparison to the dark control

The relevance criteria for groundwater metabolites are given in European Commission Guidance Document (2000). In order to declare a transformation product as a photo-TP needing a groundwater exposure assessment, an additional criterion is established: The occurrence of the transformation product in the irradiated experiment is at least 5% higher than in the associated dark control, in at least one sampling 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. This additional criterion is a pragmatic value to distinguish predominantly photolytic/light-exposed surface transformation products from those formed by both microbial and light-exposed surface processes.

European Commission (2000) gives the following entry criteria for when the steps in the groundwater relevance guidance need to be followed:

'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.'*

Note that the above percentages are on a molar basis. The European Commission (2000) criteria should be assessed in conjunction 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 photo-TP needing a groundwater exposure assessment. Another example: a transformation product had maximum occurrences of 12% and 11% in the irradiated experiment and the dark control, respectively, at the same time. 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 contemporaneous dark control. Hence, this second example would also not qualify as a photo-TP needing a groundwater exposure assessment.

Therefore, a difference of > 5% between the dark and light experiment is proposed as the criterion of a 'relevant difference', for the points in time with an amount according to the European Commission (2000) criteria. This means there is at least one point in time with an amount in the irradiated

experiment and with another amount in the contemporaneous dark control, which is at least 5% lower than in the irradiated experiment.

In case there are replicates, only the arithmetic mean values of the points in time are considered. If data for more than one radiolabelled position of the test substance are available, the arithmetic mean for all labels should be used. In cases, where one of the radioactive labels is on an element that is cleaved from the molecule of interest during transformation process results for such a label (not available values) should not be used to calculate an arithmetic mean.

It should be noted that for the assessment of relevant difference, it does not matter whether it is a moist or dry experiment, as also a natural soil surface can be moist or dry depending on the weather. Moist soil conditions can promote biodegradation, but metabolites from biodegradation can also be prone to phototransformation. Hence, the moist experiment can show other secondary photo-TPs.

2.2.   Details of decision tree

If field studies are available (Box 2 in Figure 1), the assessor needs to distinguish between field dissipation studies with a test design without exclusion of photolysis, like so-called 'legacy' studies (Box 2a in Figure 1) on the one hand, and on the other hand special tailored DegT50matrix field studies (Box 2b in Figure 1) with a test design to avoid photolysis and other surface processes according to EFSA (2014). These special field studies are designed to obtain degradation rates (DegT50matrix) used in exposure modelling and they are not an alternative for triggered standard field dissipation studies. Only field dissipation studies done following the OECD Guidance (2016) without exclusion of photolysis (or maybe 'legacy' studies) can provide information on the formation of photo-TPs under environmental conditions. If only tailored DegT50matrix field studies are available, it is not possible to get information about the maximum occurrence of photo-TPs under field conditions. In this case, following a worst-case assumption, the identified photo-TPs from the laboratory soil photolysis study have to be considered in groundwater exposure assessment via the photolytic pathway that simulates what happens at the soil surface.

The following cases are possible, if 'legacy' or tailored surface applied field dissipation studies are available and soil photo-TPs have been specifically analysed for and that the LOQ for the transformation products was sufficient to identify concentration levels that may trigger a groundwater assessment:

- Conditions during the field studies should ensure that photolysis has occurred. Crop cover and application season can significantly affect the photodegradation process and thus limit or even avoid the formation of photo-TPs. It is suggested to have study designs that avoid significant plant cover in field experiments and achieve arithmetic mean irradiance (global solar irradiation) over the course of the first month of the study of at least 100 W m^{-2}.[1] Studies with significant plant cover or with a mean irradiance below 100 W m^{-2} in the first month should not be evaluated further (Box 3 in Figure 1). Further guidance on irradiance values is provided in Section 4.2 and in Appendices A–C.
- When photo-TPs, identified in the laboratory soil photolysis study in relevant amounts and at a relevant difference, have not been analysed for as residues in the field dissipation study, information about their maximum occurrence under field conditions will not be available. Thus, due to a lack of empiric evidence, the photo-TPs have to be considered in groundwater exposure assessment (Box 4 in Figure 1).
- When photo-TPs, identified in the laboratory soil photolysis study in relevant amounts and at a relevant difference, have been analysed as residues in well-designed field dissipation experiments, but not observed in relevant amounts according to European Commission Guidance Document (2000), these data overwrite the results of the laboratory soil photolysis study. In this case, no further groundwater exposure assessment for the photo-TPs is required (Box 5 in Figure 1). Results from all available reliable studies have to be considered, but evidence from a single study site would be sufficient, provided the irradiance criteria in the first bullet are respected and sampling complied with OECD Guidance (2016).
- When photo-TPs, identified in the soil photolysis study in relevant amounts and at a relevant difference, were also observed in relevant amounts under field conditions according

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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.

to SANCO/221/2000 (European Commission, 2000), they have to be considered in the groundwater exposure assessment via the photolytic pathway (Box 5 in Figure 1).
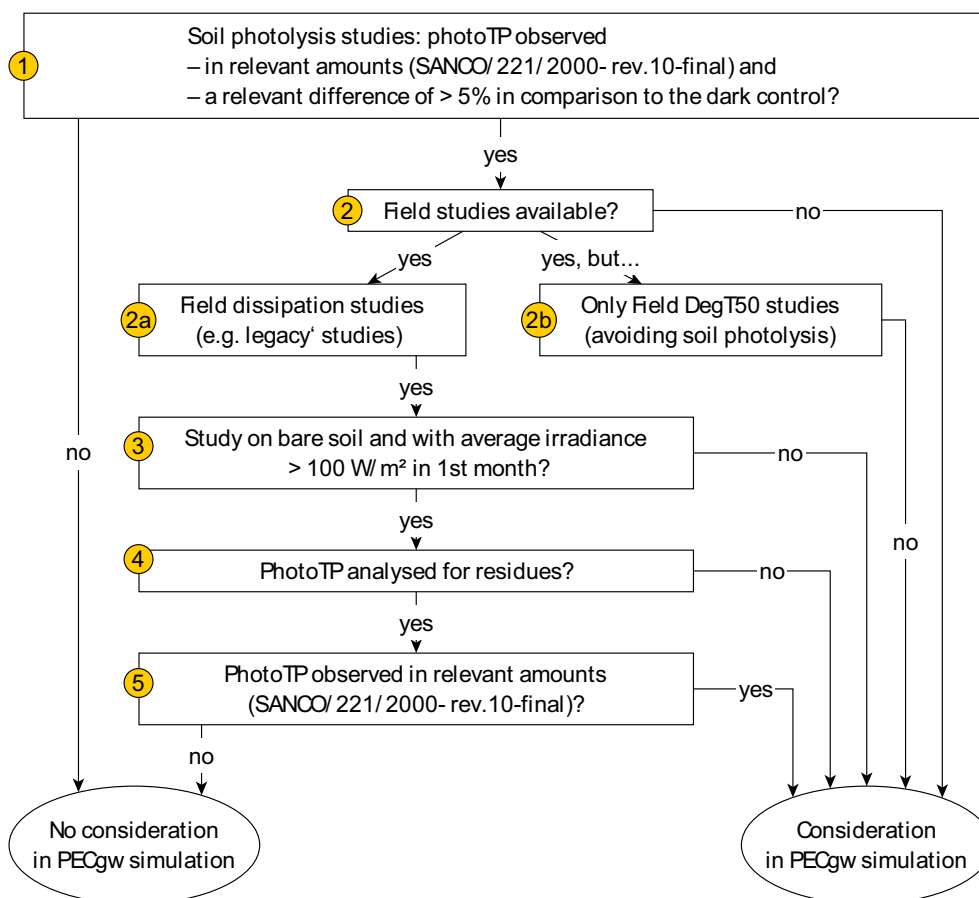

Figure 1: Decision tree for consideration of photo-TPs in PECgw simulations

Aerobic laboratory DegT50 endpoints and field study DegT50 endpoints when available are used for deriving biodegradation rates for phototransformation products in simulations, once these compounds move below the topsoil layer, in the same way that they are used as input in simulations when a transformation product is only formed by biodegradation.

3.   Background information about radiation

The electromagnetic radiation emitted by the sun and reaching the terrestrial atmosphere is mainly composed by 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.
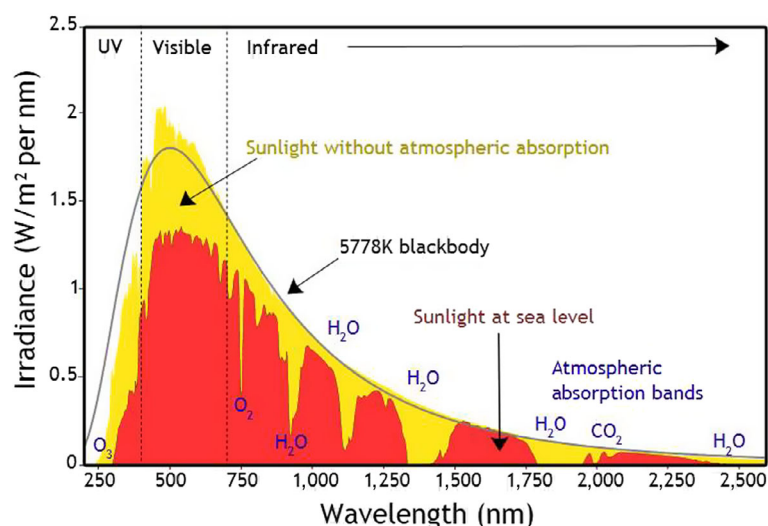
*Source: By Nick84 - https://commons.wikimedia.org/wiki/File:Solar_spectrum_ita.svg, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=24648395, based on the American Society for Testing and Materials (ASTM) Terrestrial Reference Spectra.

Figure 2: Solar radiation spectrum at sea level (red area) covers wavelengths* from 300 to 3,000 nm

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

	Ultraviolet radiation (UV)	**Visible radiation (VIS)**	**Infrared radiation (IR)**
Direct radiation	2%	42%	56%
Diffuse radiation	10%	65%	25%

The global solar irradiation (also called insolation or intensity, see Table 2), i.e. the incident radiation of wavelengths 300–3,000 nm per unit area of a horizontal surface,[2] is expressed as daily irradiation and recorded during a day of 24 h. 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 near IR but not the whole IR radiation spectrum 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

Technical term	Synonyms	Units
Irradiation	Intensity, radiation, insolation (for radiation from sun only)	$kJ\ m^{-2}\ day^{-1}$ $kWh\ m^{-2}\ day^{-1}$
Irradiance	Term reference radiation used in the graphical user interface (GUI) of FOCUS-PELMO 5.5.3 and later versions	Actually mean daily $W\ m^{-2}\ h^{-1}$ (though $W\ m^2$ indicated in GUI)

For the calculation in PELMO, the daily irradiation, which can be provided in different units, needs to be converted into irradiance (entitled as 'Reference radiation' in the PELMO graphical user interface where units of $W\ m^{-2}$ are indicated). To convert the daily irradiation (given in $kJ\ m^{-2}\ day^{-1}$) into irradiance, the value is multiplied by 1,000 and divided by 86,400. To convert the daily irradiation (given in $kWh\ m^{-2}\ day^{-1}$) into irradiance, the value is multiplied by 1,000 and divided by 24. Two examples of conversion are given in Table 3. (Explanation: 1 kWh = 3,600 kJ, 1 kJ = 1,000 Watt seconds and 1 day = 86,400 s). Note

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[2] For comparison: The light from a lamp in a soil photolysis study has often wavelengths between 290 nm and 800 nm. Generally, this range is 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.

that whilst PELMO model interface indicates units of $W\,m^{-2}$ with no time dimension, the value needed that results from these conversions are mean daily $W\,m^{-2}\,h^{-1}$.

Table 3: Two examples for conversion of daily irradiation into irradiance (FOCUS scenario Hamburg)

Date	Daily irradiation $(kJ\,m^{-2}\,day^{-1})$	Daily irradiation $(kWh\,m^{-2}\,day^{-1})$	Irradiance $(W\,m^{-2})$
19 June 01	298,17	8.282	345.1
22 December 01	1,098	0.305	12.7

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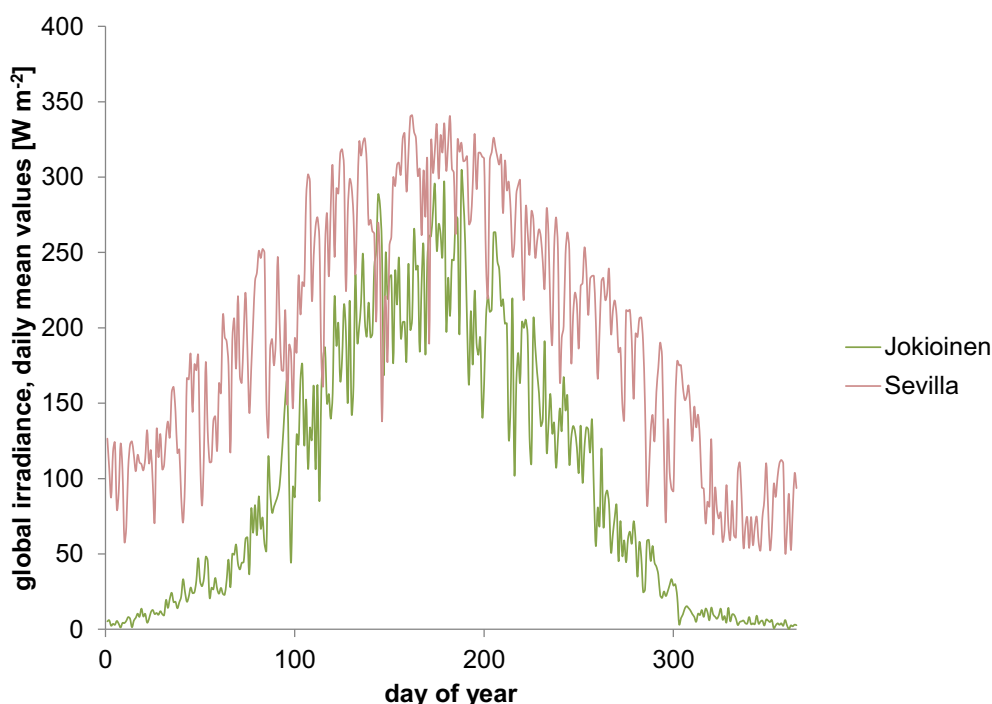

Figure 3: Irradiation $(kJ\,m^{-2}\,day^{-1})$ data in the first climate year of the FOCUS scenarios Jokioinen (file 'J_01.cli') and Sevilla (file 'S_01.cli'), converted to irradiance $(W\,m^{-2})$

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

FOCUS groundwater scenario	Global irradiance $(W\,m^{-2})$ Arithmetic mean	Global irradiance $(W\,m^{-2})$ Minimum	Global irradiance $(W\,m^{-2})$ Maximum
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

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

4. Recommendations for parameterisation of phototransformation products in PECgw simulations

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

Since April 2011, FOCUS-PELMO version 4.4.3 has been available on the FOCUS website, which makes it possible to consider soil photolysis along with 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 allowed both pathways to be simulated 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 the growing stage of the crop. Interception is not considered between harvest and emergence for annual crops (assumption of no vegetation).

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

The model FOCUS-PELMO 5.5.3 and subsequent versions require 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.

FAQ No. 1

Why is the DT50 from a kinetic evaluation of the soil photolysis study not considered in the higher Tier 2B?

Laboratory 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 laboratory soil photolysis studies do not have a harmonised finalised 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 Panel (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, 2007; p. 9).'

Therefore, it is recommended to take information about the occurrence and transformation of photo-TPs 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 (Section 4.2).

4.1. Photolytic half-life

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

Using a modification of the approach outlined in EFSA guidance (2014) (i.e. normalising $DT50_{fast}$ for irradiance), 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, $k2$ can be interpreted as the biodegradation rate and $k1$ as the sum of the biodegradation rate and other dissipation rates. However, as frequent sampling about the hinge point is rarely available and fitting kinetics is in practice an empirical exercise, so such an interpretation is quite theoretical, it is proposed that $k1$ can be used directly as a worst-case estimate of the photolysis and volatilisation rate.
- DFOP: In a DFOP kinetic, $k1$ can also be taken directly, because $k1$ and $k2$ happen at the same time. In case the Chi^2 is similar for DFOP and HS, DFOP is chosen (FOCUS, 2006).
- 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 has the SFO kinetic as the best fit 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 can be considered to represent 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 $> 1 \times 10^{-4}$ 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-TPs 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 (FOCUS, 2006).

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).

4.2. 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) demands measurement of 'hours of sunshine and intensity of solar radiation'.

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

6) measurements directly at the field trial or
7) measurements at a weather station nearby (bee line distance < 10 km) or
8) 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. Appendices 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.[3]

In meteorology, the global solar irradiation (incident radiation of wavelengths 300–3,000 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 290–800 nm is usually most relevant for photodegradation (OECD, 2008). 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.

The term irradiance is a synonym for the term 'reference radiation' used in FOCUS-PELMO 5.5.3 and subsequent versions.

4.3.   Handling of two or more phototransformation products

In the case, that an active substance has two or more photo-TPs, each photo-TP is simulated separately (i.e. one by one) in Tier 1 (including secondary metabolites, if applicable) and in Tiers 2A and 2B (including all dark biodegradates). Though at Tier 2B, it is not recommended to undertake an ambitious kinetic evaluation in order to find a proper split of k_{fast}, i.e. an apportionment between the photo-TPs. Usually the data derived from field studies are influenced by more than only the photolytic process. Hence, it is unlikely to provide a reliable splitting in form of photolysis formation fractions. This does not *a priori* preclude that reliable fitting might be demonstrated. Only in this case would parameterisation of the fitted phototransformation pathway in modelling be justified.

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

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

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

With:

$k_{fast,reference}$: the photolysis rate derived from the field trials (Section 4.1) (day^{-1}).
$irradiance_x$: irradiance at day x from the scenario climate files (w m^{-2}).
$irradiance_{reference}$: the mean irradiance for which $k_{fast,reference}$ was observed (Section 4.2).
interception: the changing interception of the crop (=0 after harvest of annual crops).

For more information, refer to Section 2.5.3.2 in the user manual of PELMO (Klein, 2012).

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

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[3] E.g. https://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.

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

Normally, the measured half-lives from biodegradation studies according to OECD Test Guidelines n° 307 (OECD, 2002b) and Koc values from adsorption studies according to OECD Test Guidelines n° 106 (OECD, 2000) should be used as input parameters for the photo-TPs. If one or both of these values is not available, a default half-life of 1,000 days and/or a Koc value of 0 should be used for leaching simulations of photo-TPs.

5. Tiered approach

5.1. Tier 1: phototransformation product as parent substance

A worst-case approach to assess the leaching behaviour of the photo-TPs (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, when there is a single photo-TP, it is considered separately as a parent substance with the application rate of the active substance corrected by the ratio of molar masses. Where two or more non-volatile novel photo-TPs have been formed in the laboratory photolysis study at levels needing assessment, the same principle is applied except that the application rate can also use the 1- maximum observed value for the other identified photo-TPs approach, at this tier. In case, a secondary metabolite is formed by biodegradation of the photo-TP, a combined simulation of both transformation products in Tier 1 has to be performed. A separate Tier 1 simulation of the secondary biodegradation 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). At Tier 1, whilst groundwater guidance remains that application to soil net of crop interception is simulated with FOCUS tools, this approach is also followed here.

In case, this secondary metabolite of a photo-TP 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-TP (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-TP (and/or their secondary metabolites, respectively) according to European Commission (2000) has to be done or the 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-TPs (and their secondary metabolites) is provided in Figure 4.
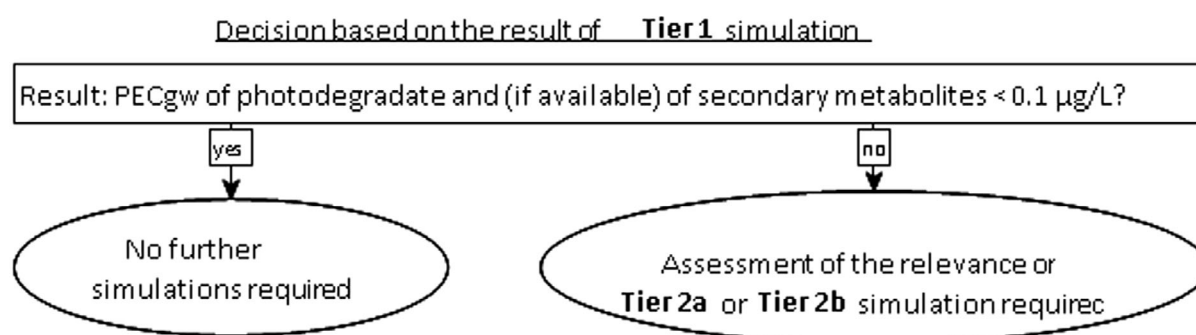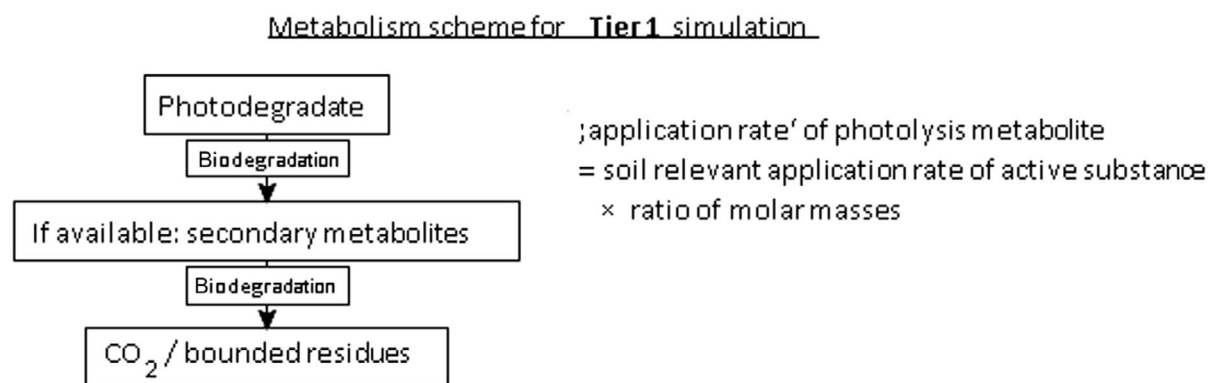
Metabolism scheme for Tier 1 simulation

```
┌─────────────────────┐
│   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

Figure 4: Worst-case approach (Tier 1) to assess the leaching behaviour of photo-TPs (and their secondary metabolites)

FAQ No. 2

Why is the maximum occurrence from soil photolysis studies not considered in Tier 1?

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

5.2. 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 run two simulations using the two default photolytic half-lives at a default reference irradiance reported below. 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.

It has to be emphasised that the PECgw simulation in Tier 2A with the default active substance inputs is only recommended as a conservative parameterisation for the leaching behaviour of photo-TPs, so the results for the active substance and other metabolites from these simulations should not be relied on.

FAQ No. 3

What is the reason for the slow default parametrisation for photolysis in Tier 2A?

In some rare cases, slower photolysis gives higher concentrations for a photo-TP due to very strongly sorped parent compound (e.g. fludioxonil). When such strongly sorped compound is applied in sunny summer, the emerging photo-TP is subject to fast biodegradation under warm conditions. This can lead to rather low PECgw of the photo-TP.

Assuming, photolysis is slower, the active substance that sorps very strongly remains at the soil surface. Once, the crop is harvested in autumn, the irradiance increases suddenly. The emerging photo-TP is subject to slower biodegradation in the colder autumn. This can lead to higher PECgw of the photo-TP. Hence, a pair of default values is presented below.

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

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

Then two sets of calculations should be run using both default values and the highest concentrations should be used for the exposure assessment. If the groundwater concentration of the photo-TP 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 European Commission (2000) has to be done or the more complex leaching simulation according to Tier 2B has to be performed.

5.3. 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 in a laborious procedure from the data of field dissipation studies of the 'legacy' type, in case these data are available.

As mentioned in Section 2, 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 1st month of the study of at least 100 W m^{-2}.

The data have to be normalised according to the daily irradiances (see Section 4.1; 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 (Section 4.2) shall 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 Appendices 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 (see Annex A) will be made available also via Zenodo knowledge junction
See Appendix B for a detailed example.

Table 5: Overview of worksheets in the Excel file 'basic tools for deriving photolysis endpoints' and their purpose

Worksheet	Input	Output	Purpose
AGRI4CAST	–	–	Visualisation 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'	

Worksheet	Input	Output	Purpose
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} day^{-1}	Irradiance values in W m^{-2} day^{-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	k_{fast} normalised to 100 W m^2	Geometric mean or min/max of k_{fast} values from several field studies	

Finally, the following distinction of cases is applied:

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 normalised 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.

With regard to (b), the trial with the maximum normalised photolysis rate (which represents the fastest observed photolysis of the precursor) is usually the worst case for the photo-TPs, but there are exceptions because of the complex situation within a leaching simulation. The trial with the minimum normalised photolysis rate represents the slowest observed photolysis as worst case for the active substance precursor. The simulation results with the higher PECgw values for the photo-TPs are considered relevant for final assessment (see example in Appendix).

If tier 2b simulations do not result in concentrations below the parametric drinking water limit and it has not been possible to demonstrate non-relevance with the necessary effects information, then higher tiers for groundwater exposure assessment (approaches in tiers 3 and 4) as described in European Commission (2014) are approaches that can be followed.

FAQ No. 4

For transformation products, which are formed in parallel, usually formation fractions are derived from degradation studies and then used in the simulations. How could it be explained, that in Tier 2A and 2B, there are no formation fractions between the photo-TP and other metabolites?

Formation fractions determine, which amount of a parent substance is transformed to different transformation products. Formation fractions are only useful within one process (e.g. biodegradation).
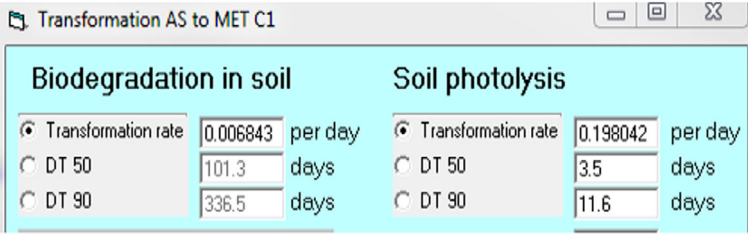
The photolytic routines within PELMO determine automatically the daily-changing transformation rates according to the weather. This means, there is no constant split between photolytic or biodegradation processes.

Imagine the following metaphor: a tank filled with active substance. This tank has two taps. One tap called 'biodegradation' is regulated by the temperature (and also soil moisture), it opens when it is getting warmer (and more humid). The other tap called 'photolysis' is regulated by the sunlight, it opens when it is getting lighter. Be aware, that there can be situations when it is warm but not sunny and vice versa. The taps are controlled independently. Therefore, a sliding controller (like a panoramic potentiometer for audio signals) or constant formation fractions would not be suitable.

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6. Simulation with FOCUS-PELMO 5.5.3 and subsequent versions

In Tiers 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 from the precursor to the novel photolysis metabolite is kept at 0 per day).

Figure 5: Data entry mask in FOCUS-PELMO 5.5.3 (values are entered for Tier 2B of examplamin in Appendix D)

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.

FAQ No. 5

What can I do if a complex degradation scheme does not fit into the space provided by PELMO?

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 99,999 day^{-1} and a very high default sorption of 99,999 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.

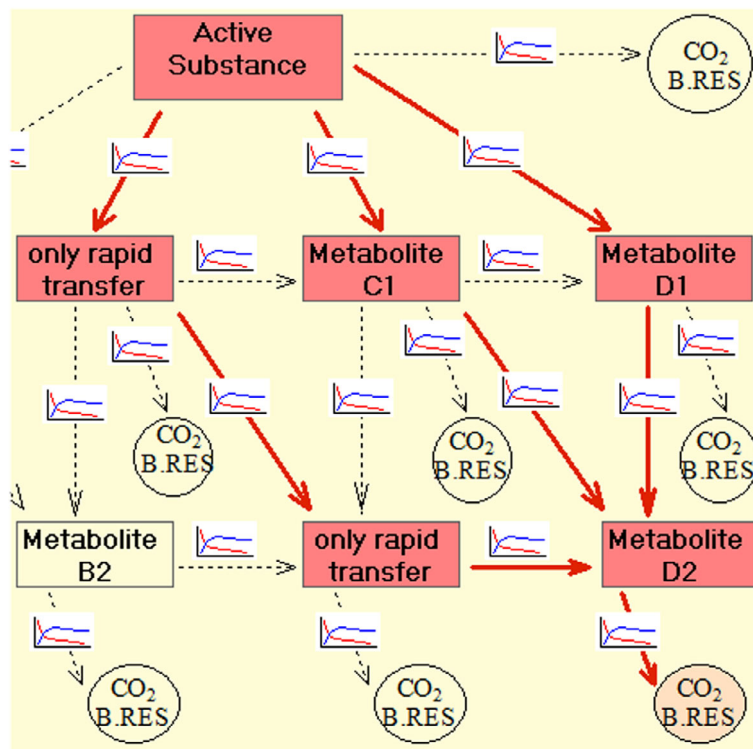
Figure 6: Trick with pseudo metabolites 'only rapid transfer' ($k = 99{,}999$ day^{-1}; Kfoc $= 99{,}999$ L kg^{-1}; same molar mass as precursor substance) in order to represent a complex, branched scheme within PELMO

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

This guidance is intended only for the assessment of photo-TPs. 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-TPs. As this option would exceed the primary scope of this guidance, this option should not be implemented until further discussion devoted to this topic will take place in a possible future revision of the FOCUS groundwater report (European Commission, 2014). 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 document. The parameterisation of this higher tier approach for an active substance is presented only as a proposal for a future revision.

If the photodegradation process is considered to be a significant process for the compound of concern, the derivation of the normalised DT50$_{fast}$ has to be done as described under Sections 4.1, 4.2 and 5.3. It should be considered that the soil photolysis pathway as a higher tier option for active substances would be possible only for non-volatile substances.

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$_{fast}$ derived from the geometric mean, if ≥ 4 field trials are suitable for deriving measured data. If only three field trials are suitable, the lowest normalised k$_{fast}$ should be used in the PECgw simulation for the active substance. If only one to two field trials are suitable for deriving a k$_{fast}$, 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-TPs were formed in relevant amounts during soil photolysis process.

8. Recommendation

For the consideration of photo-TPs as an integral part in groundwater exposure assessment, a tiered approach with FOCUS-PELMO 5.5.3 and subsequent versions is provided. In all tiers, also substance-specific DegT50 values for biodegradation are used in the simulation for soil layers below the very top layer (1 mm in FOCUS-PELMO 5.5.3 and 6.6.4). Details of the selection of the endpoints and recommendations for special cases are shown in Section 4 and 5. Here, a short summary of the required steps is presented:

Tier 1: Photo-TP as parent substance

9) Each photo-TP is considered as an active substance in a separate simulation considering only biodegradation.
10) The application rate of the photo-TP is set to 100% of the application rate of the active substance corrected by the ratio of molar masses of active substance and photo-TP.
11) If a secondary metabolite is formed by the photo-TP, both transformation products have to be simulated together in one run.
12) Conduct the FOCUS PEARL and PELMO simulation for each photo-TP.

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 day @ reference irradiance = 100 W m^{-2} slow: $DT50_{slow}$ = 10 day @ reference irradiance = 100 W m^{-2}
3) Conduct two FOCUS PELMO simulations, one for each of the parameters shown in point 2.
4) Conduct additional runs if the number of photo-TPs is two or more.

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

1) Generate the metabolism scheme in PELMO inclusive photolytic pathway (analogous to Tier 2A)

13) Get radiation data from

   d) measurements directly at the field trial or
   e) measurements at a weather station nearby (bee line distance < 10 km) or
   f) 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.

14) Derive normalised k_{fast} of active substance from biphasic kinetics of data from field dissipation studies according to the recommendations of FOCUS (2006) and EFSA (2014).

15) Case-by-case decision:

   a) If the number of suitable trials is $\geq$ 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.

2) Conduct the FOCUS-PELMO simulations with the parameters derived in point 4

For degradation products for which both simulations (either with the photolytic pathway with Tier 2A or 2B, or with only the biodegradation pathway in the dark) are performed, the highest PECgw for each FOCUS scenario should be considered for the groundwater exposure assessment.

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Abbreviations

DFOP	Double First-Order in Parallel
FOCUS	FOrum for Co-ordination of pesticide fate models and their Use
FOMC	First-Order Multi-Compartment
GW	Groundwater
GUI	Graphical User Interface
HS	Hockey-Stick Model
IR	Infrared Radiation
Photo-TPs	phototransformation products
PEC	Predicted Environmental Concentration
SFO	Simple First Order
UV	Ultraviolet radiation
VIS	Visible radiation

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	16.4.2007	Germany, Netherlands, Belgium, Luxembourg, Switzerland, Austria, Slovenia and partly other countries[1]	After registration https://www.dwd.de (search for 'Pamore') https://webservice.dwd.de/cgi-bin/spp1167/webservice.cgi or upon request, charges apply
COSMO-EU	7	01.12.1999	Europe and partly other continents[2]	
AGRI4CAST	25	1.1.1979	'Covering the EU Member States, neighbouring European countries, and the Mediterranean countries', however some parts of Scandinavia are missing (see Figure A.1)	After registration https://agri4cast.jrc.ec.europa.eu/DataPortal/UserRegistration.aspx see 'Gridded Agro-Meteorological Data in Europe' https://agri4cast.jrc.ec.europa.eu/DataPortal/Index.aspx?o=d free of charge
MARS	< 27.8 (equivalent of 0.25°)	1.1.1989	Whole earth's surface	No registration, here data only for 10-day-periods: https://spirits.jrc.ec.europa.eu/files/ecmwf/int/europe/rad/ daily values upon request https://mars.jrc.ec.europa.eu/mars/Contact-Us free of charge
NASA	< 55.5 (equivalent of 0.5°)	1.7.1983	Whole earth's surface	No registration https://power.larc.nasa.gov/data-access-viewer/ 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.
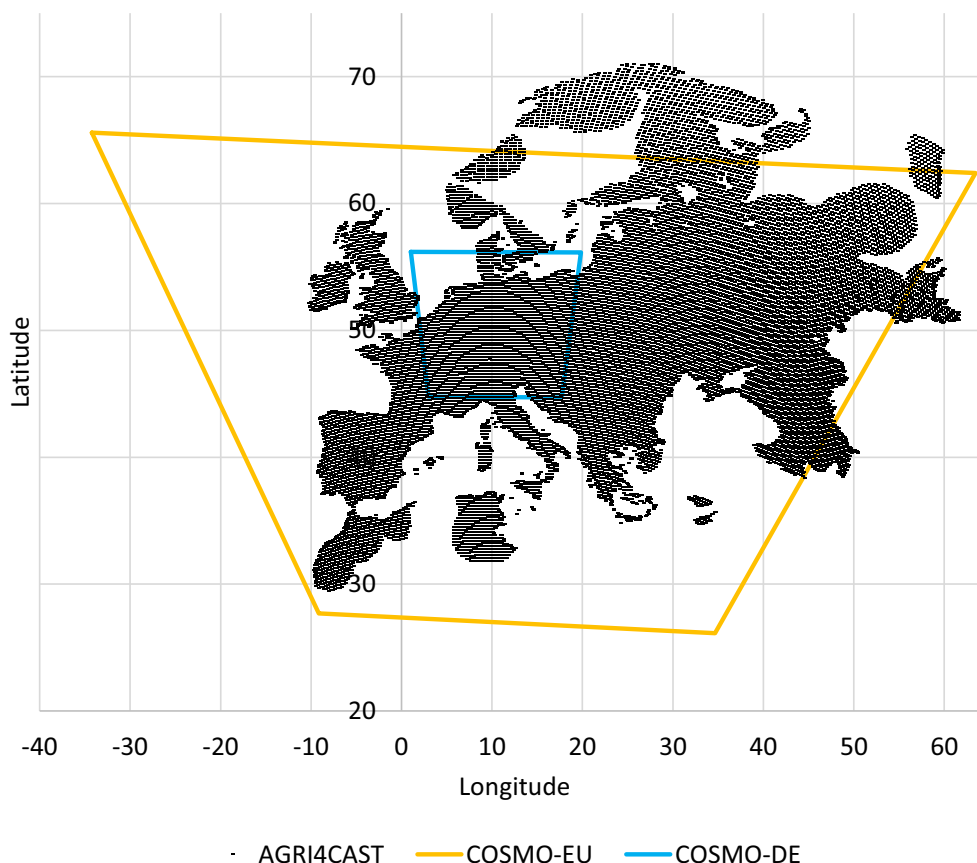
Figure A.1: Spatial availability of different data sources (black dots: AGRI4CAST; orange lines: COSMO-EU; blue lines: COSMO-DE)

The suitability of the different data sources was investigated by means of a comparison of a short time series (Table A.2). As a benchmark measured values from the DWD weather station Wittenberg-Teuchel (51.89°N; 12.65°E) for the period 01.–10. 3.2008 were chosen (see second line in Table A.2). In COSMO rotated coordinates are necessary, which are 45.75°/−24.56° in this case.

In COSMO, this equation for the global irradiance was used as proposed in the literature[4]:

GLOB = ASOB_S/(1 − ALB_RAD)

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

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

with ASWDIR_S: direct shortwave radiation at ground level; ASWDIFD_S: diffuse downward shortwave radiation at ground level − but these data are only available since some day later in 2008.

For the data sources AGRI4CAST and MARS, a spatial interpolation was conducted with the following simple procedure[5]: First calculate the Euclidean distance of the four surrounding grid points, then conduct weighting of the four grid points according to the inverse of the distance. See worksheet 'interpolation' of the Excel file.

---

[4] Literature concerning the COSMO-DE and COSMO-EU databases: Baldauf et al., 2011. Kurze Beschreibung des Lokal-Modells Kürzestfrist COSMO-DE (LMK) und seiner Datenbanken auf dem Datenserver des DWD. DWD Offenbach. https://www.dwd.de/bvbw/generator/DWDWWW/Content/Forschung/FE1/Veroeffentlichungen/Download/LMK__DBbeschr__1104__en,templateId=raw,property=publicationFile.pdf Jan-Peter Schulz and Ulrich Schättler, 2009. Kurze Beschreibung des Lokal-Modells Europa COSMO-EU (LME) und seiner Datenbanken auf dem Datenserver des DWD. DWD Offenbach. https://www.dwd.de/bvbw/generator/DWDWWW/Content/Forschung/FE1/Veroeffentlichungen/Download/LME__DBbeschr__0901__en,templateId=raw,property=publicationFile.pdf/LME_DBbeschr_0901_en.pdf

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

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

$$\text{Bias}_{\text{rel}} = \frac{1}{n} \sum_{i=1}^{n} \frac{O_i - P_i}{O_i},$$

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

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} day^{-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} day^{-1}	43; 73; 52; 100; 136; 63; 64; 47; 114; 150	84	38	–3%
MARS	kJ m^{-2} day^{-1}	48; 51; 78; 111; 130; 96; 87; 79; 123; 143	95	32	–26%
NASA	kWh m^{-2} day^{-1}	58; 82; 57; 104; 126; 80; 95; 81; 128; 157	97	32	–28%

(1): via equation GLOB = ASOB_S/(1 – ALB_RAD).
(2): last value was not retrieved by an oversight, value from weather station instead.
(3): without missing value.
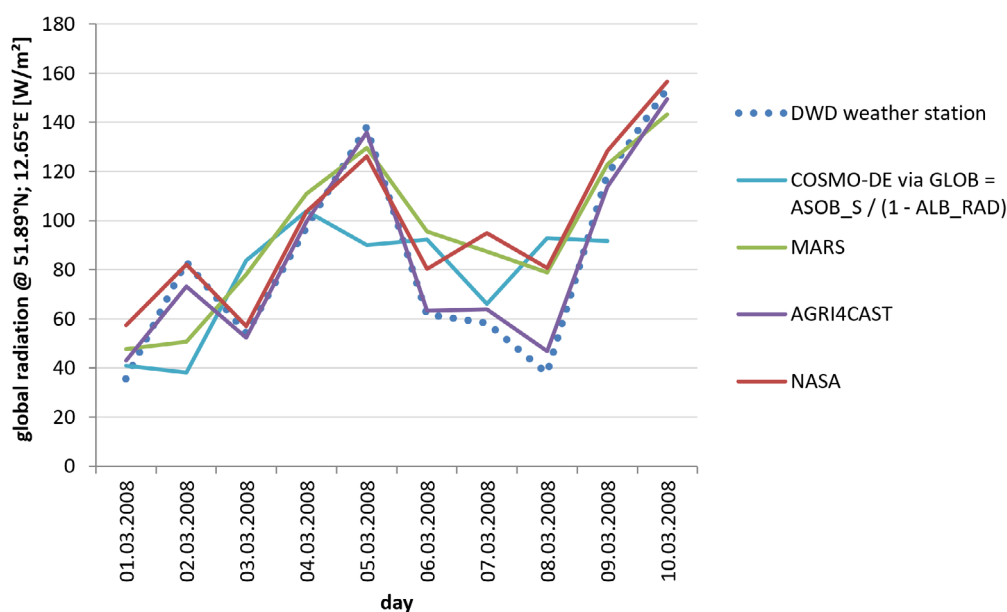
Figure A.2: Graphical comparison of time series

Due to the low relative bias of the AGRI4CAST time series (−3%), this data source can be recommended. Furthermore, AGRI4CAST has the best temporal availability, a spatial availability for big parts of Europe (see Figure A.1) and can be accessed free of charge after registration. However, for trial site locations where AGRI4CAST does not have good spatial coverage, a check should be made on the relative bias for different data sources to select the 'best' data source for the site of the relevant trial location.

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 15.5.1996 in Poitou-Charentes, France (47.0°N; 0.2°W), with a duration of 367 days.

Retrieval of a suitable data set

After registration
https://agri4cast.jrc.ec.europa.eu/DataPortal/UserRegistration.aspx
visit 'Gridded Agro-Meteorological Data in Europe'
https://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/m^2 per day)'.
- Under 'Day' enter 15/5/1996 as the starting date and 17/5/1997 as the ending date.
- Under 'Grid' open 'France'. Under 'Aquitaine-limousin' 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 Section 5.3).

Then enter the coordinates of the field study into the orange cells (see Figure B.1). In case, you have coordinates in the format *degree, minutes, seconds* (e.g. 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.

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

		latitude [°]	longitude [°]		
Enter coordinates of field study →		47.0	-0.2		

CLOSEST GRID POINTS:

ranking	distance [°]	grid_no	latitude [°]	longitude [°]	altitude [m]	
1	0.13	86078	46.95932	-0.32297	100	relevant
2	0.20	86079	46.99009	0.00287	70	
3	0.25	87078	47.18187	-0.36726	70	
4	0.27	87079	47.21279	-0.04007	42	
5	0.27	85078	46.73671	-0.27915	154	optional
6	0.34	85079	46.76733	0.04534	115	
7	0.45	88079	47.43545	-0.08348	40	
8	0.45	86077	46.92757	-0.64845	158	

Figure B.1: Screenshot from the sheet 'grid points' in the file 'basic tools for deriving photolysis endpoints.xlsx'

Interpolation of the irradiance data

The information from the last step and the coordinates of the study site are transferred automatically into the next sheet 'inter, conv, norm' (see upper half of the Figure B.2). As the grid

point no. 86078 has the shortest Euclidean distance to the study site, it will be weighted stronger with 38% in the interpolation procedure.
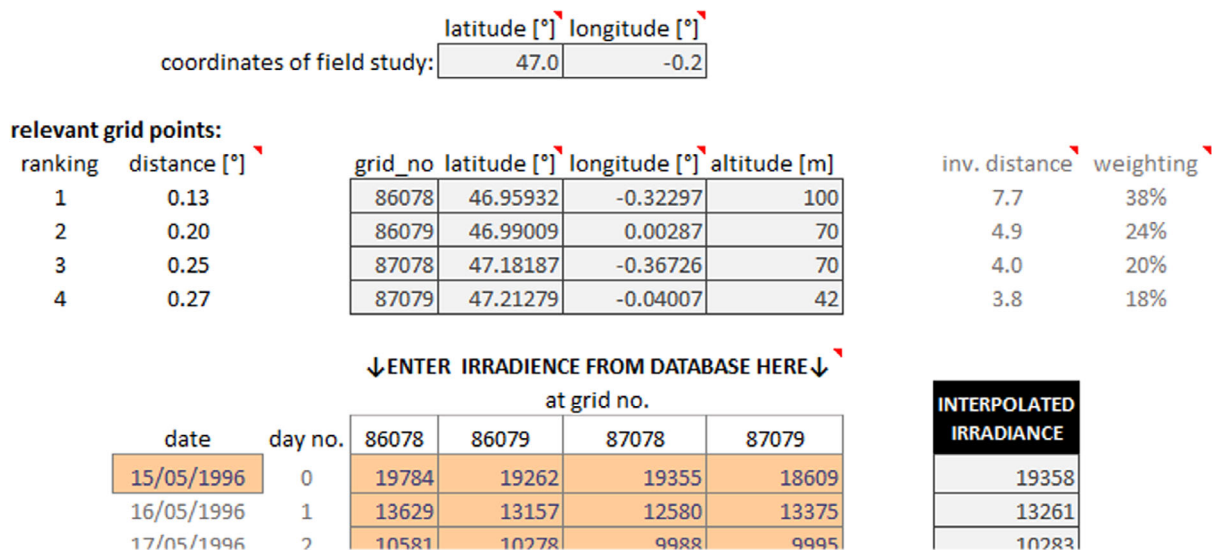
		latitude [°]	longitude [°]
coordinates of field study:		47.0	-0.2

relevant grid points:

ranking	distance [°]	grid_no	latitude [°]	longitude [°]	altitude [m]		inv. distance	weighting
1	0.13	86078	46.95932	-0.32297	100		7.7	38%
2	0.20	86079	46.99009	0.00287	70		4.9	24%
3	0.25	87078	47.18187	-0.36726	70		4.0	20%
4	0.27	87079	47.21279	-0.04007	42		3.8	18%

↓ENTER IRRADIENCE FROM DATABASE HERE↓

		at grid no.					INTERPOLATED IRRADIANCE
date	day no.	86078	86079	87078	87079		
15/05/1996	0	19784	19262	19355	18609		19358
16/05/1996	1	13629	13157	12580	13375		13261
17/05/1996	2	10581	10278	9988	9995		10283

Figure B.2: Screenshot from the sheet 'inter, conv, norm' in the file 'basic tools for deriving photolysis endpoints.xlsx'

Go back to the csv-file from AGRI4CAST in order to transfer the irradiance data for each of the four grid points from column F (see Figure B.3) to the orange cells in the columns D–G of the 'basic tools' (see Figure B.2). For this purpose, a filter function in the software might be useful for selecting only one grid point at a time (see first row in Figure B.3 as it is provided from Microsoft Excel). The days in the csv-file are given in the format *year, month, day* (e.g. 19960515) without any separation.

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

	A	B	C	D	E	F
	GRID_NO	LATITUDE	LONGITUD	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

Figure B.3: Screenshot from the raw data in the csv-file from AGRI4CAST

Conversion of the irradiance data

Irradiance data from AGRI4CAST are given in the unit kJ/m^2 per day. However, PELMO requires the unit W m^{-2}. A conversion takes place in column M (see Figure B.4).

conversion from:
kJ/m^2
to W/m^2 ↓
224
153
119

select→
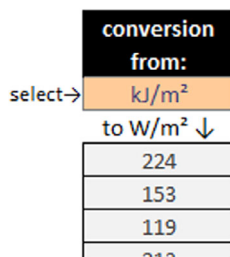
Figure B.4: Screenshot from the sheet 'inter, conv, norm' in the file 'basic tools for deriving photolysis endpoints.xlsx'

Time-step normalisation for field studies

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	

Figure B.5: Screenshot from the sheet 'inter, conv, norm' in the file 'basic tools for deriving photolysis endpoints.xlsx'

In the next step, the sampling time points and the residues of the active substance from the field study have to be entered in column Q and S. In column R, the time points are translated for the reference irradiance of 100 W m^{-2}. Figure B.6 shows the effect of the time-step normalisation in this example.
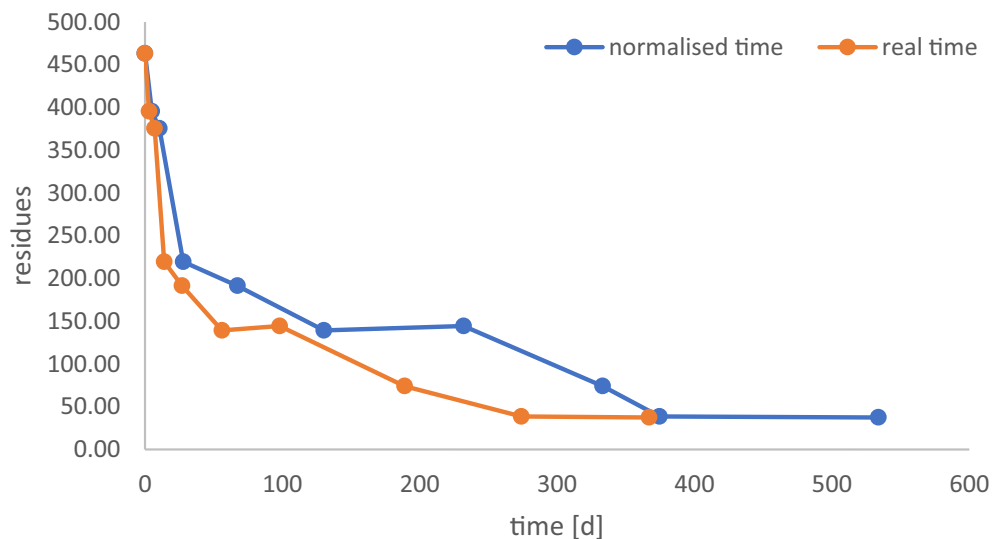
Figure B.6: Effect of the time-step normalisation

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

Table B.1: Results of kinetic evaluation

Kinetic	Chi^2 (%)	Visual fit	k$_1$ (1/day)	k$_2$ (1/day)
DFOP	8.8	Good	0.061	0.0032
HS	7.3	Good	0.026	0.0035

Here, HS was chosen with k$_{fast}$ = k$_1$ = 0.026 (see Section 5.1).

Finally, the geometric mean or the extrema of the k$_{fast}$ values is taken for the Tier 2B simulation as shown below.

Purpose: comparison of the normalised k_{fast} values from different field studies

Summarize the respective k_{fast} from different field studies in the orange cells.

field study	k_{fast} @ 100 W m^{-2} (d^{-1})
Lebien, Germany	0.15
Grisolles, France	0.2
Vitray, Louzy, Poitou-Charentes, France	0.026
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: 0.107

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: 0.026

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

Figure B.7: 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 POWER database can be used.

For this example, open the web page https://power.larc.nasa.gov/data-access-viewer/ and make following inputs in corresponding query fields to extract the data for a fictional field trial which started on 1.4.1992 in Parma (44.8°N; 10.3°E):

1) 'Sustainable Buildings' (if you want to get irradiation values directly as W/m^2, otherwise pick 'Renewable Energy' for kWh/m^2 or 'Agroclimatology' for MJ/m^2 per day values)
2) 'Daily'
3) Latitude of '44.8' and longitude of '10.3' (Parma city coordinates)
4) Start date '1st April 1992', end date '10th April 1992'
5) 'ASCII' (just for this example; you might prefer CSV for actual work; 'GeoJSON' option additionally generates graphs)
6) 'All Sky Surface Shortwave Downward Irradiance'
7) Press 'Submit'

Below you see the screenshot of the POWER Data Access Viewer interface with the abovementioned inputs:
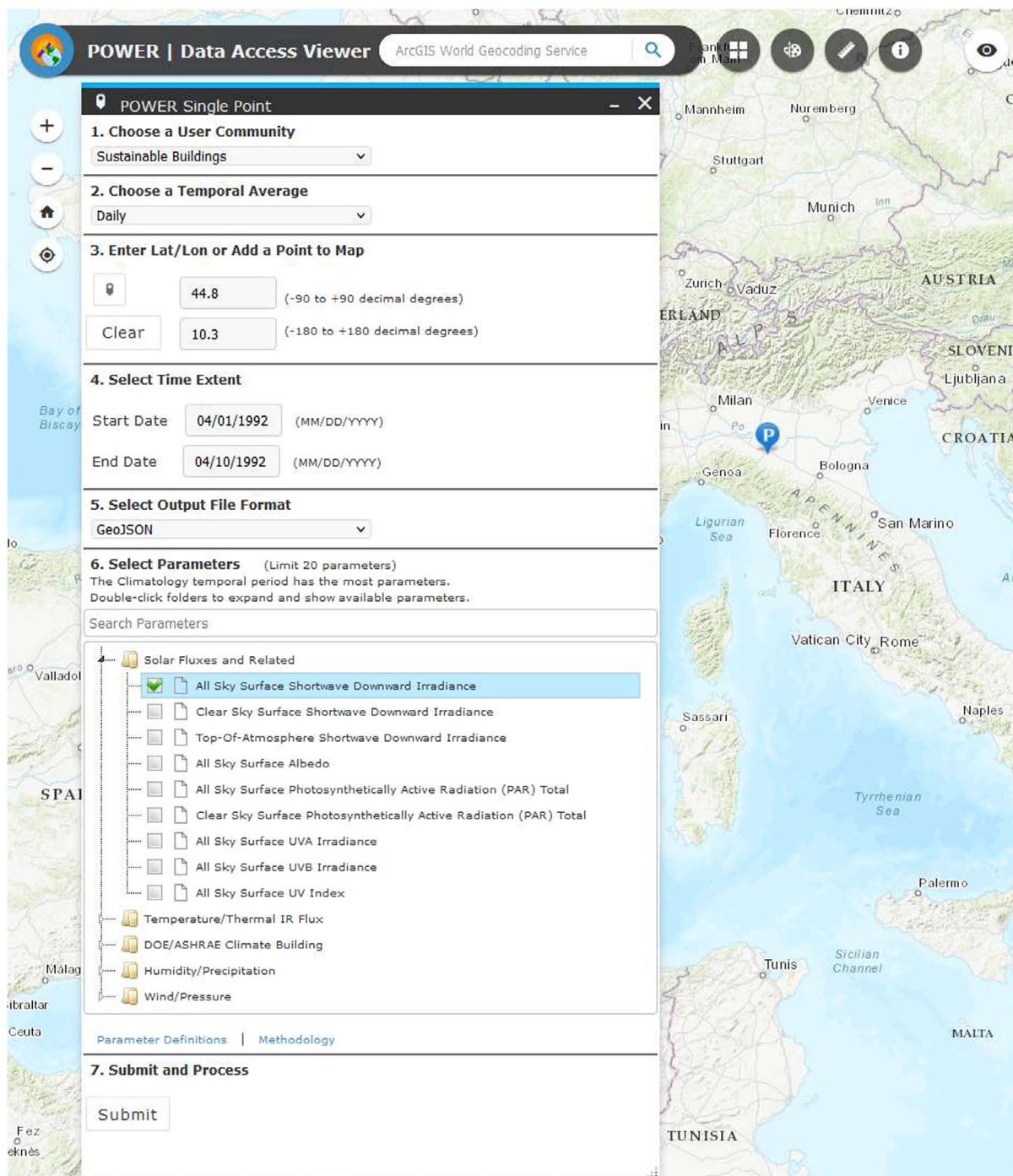
Figure C.1: Screenshot from the NASA POWER Data Access Viewer web page with example inputs selected

After pressing 'Submit' a direct link (a blue button) to the ASCII text file with query results will appear. Downloaded data will look like this, with irradiation values in the column ALLSKY_SFC_SW_DWN:

```
-BEGIN HEADER-
NASA/POWER CERES/MERRA2 Native Resolution Daily Data
Dates (month/day/year): 4/1/1992 through 4/10/1992
Location: Latitude 44.8 Longitude 10.3
Elevation from MERRA-2: Average for 0.5 x 0.625 degree lat/lon region = 170.78
meters
```

```
   Value for missing model data cannot be computed or out of model availability
range: −999
   Parameter(s):
   ALLSKY_SFC_SW_DWN  CERES  SYN1deg  All  Sky  Surface  Shortwave  Downward
Irradiance (W/m^2)
   -END HEADER-
   YEAR MO DY ALLSKY_SFC_SW_DWN
   1992 4   1        73.00
   1992 4   2        240.90
   1992 4   3        114.20
   1992 4   4        129.80
   1992 4   5        101.70
   1992 4   6         82.90
   1992 4   7        139.70
   1992 4   8        133.10
   1992 4   9        209.00
   1992 4   10       282.90
```

Retrieved irradiation data can be used later for the time-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

Parameter	Value
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 photo-TP M002:

Table D.2: Summary of the relevance assessment of the photo-TP M002

Photo-TP	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 day)	12.9% > 5%	Available, but samples were not analysed for M002	Y
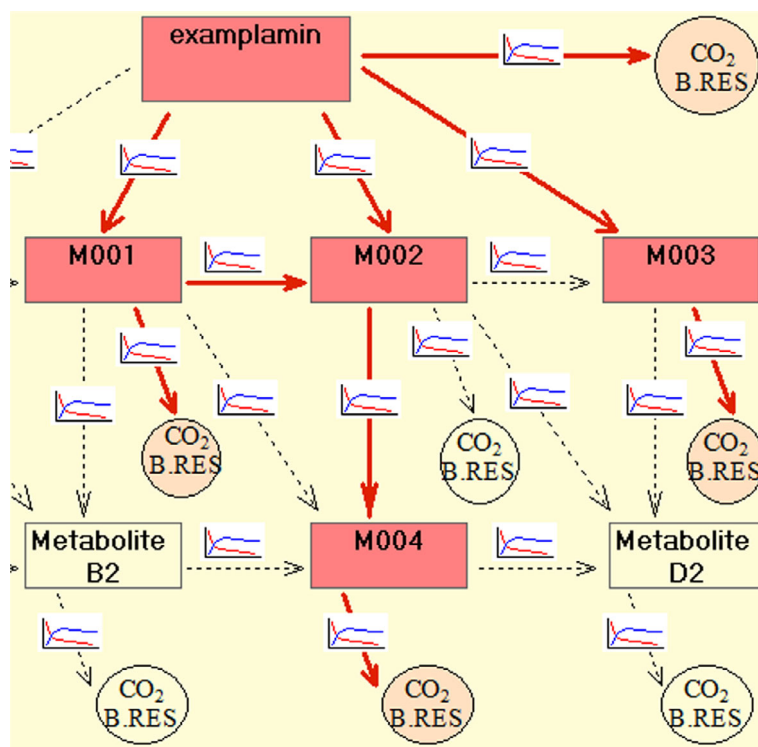
Figure D.1: Metabolism scheme for examplamin and its transformation products in Tiers 2A and 2B (between examplamin and M002 there is biodegradation and photolysis, see Figure 5)

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

Parameter	Value
Active substance	**Examplamin**
Molecular weight (g/mol)	367.3
DT50 in soil (day)	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 (day)	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 (day)	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 (day)	20.8
K_{foc}	33
1/n	0.87

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

for Tier 1:

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

Table D.4: Calculation of the 'application rate' of photo-TP M002 used in the Tier 1 approach of PECgw simulation

	Examplamin	M002
Molecular mass (g/mol)	367.3	163.1
'Application rate' (g/ha)	80	$80 \times 163.1/367.3 = 35.5$
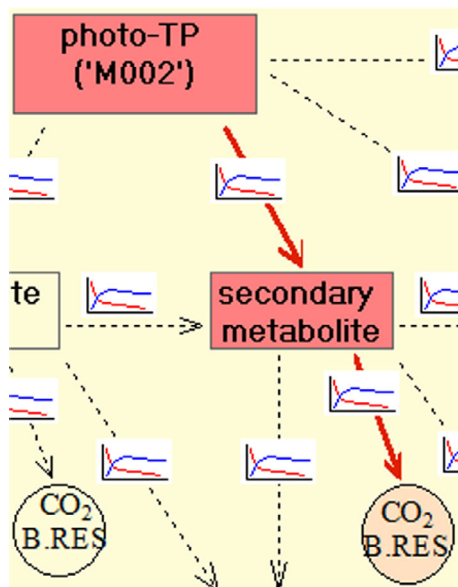
Figure D.2: Metabolism scheme for the photo-TP M002 and its transformation product M004 in Tier 1

for Tier 2A:

usage of default values

for Tier 2B:

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

Table D.5: Summary of suitable photolysis rates of examplamin

Soil	Coordinates	Date of application	Chi^2 error	Kinetic parameters	DT50$_{pho}$ @ 100 W m^{-2} (day)	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$_{fast}$ = 0.094 ln(2)/ k$_{fast}$ = 7.4	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} (day) **Geometric mean over all kinetic evaluations (n = 5)** **[If the number of suitable trials is 3, two simulations with the maximum and minimum photolysis rates from the trials are conducted.]**					5.8	

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

Use	Scenario	80th percentile PECgw at 1 m soil depth (μg L^{-1}) modelled by FOCUS PELMO 5.5.3				
		Examplamin	M001	M002	M003	M004
Winter cereals	Tier 1, Piacenza (combined simulation of photo-TP M002 as parent and its metabolite M004)	–	–	0.412	–	0.920
	Tier 2A, Piacenza, 0.1 day @ 100 W m^{-2} (default)	< 0.001	< 0.001	0.372	< 0.001	0.786
	Tier 2A, Piacenza, 10 day @ 100 W m^{-2} (default)	< 0.001	0.005	0.127	0.026	0.246
	Tier 2B, Piacenza, 6.1 day @ 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 phototransformation products in soil
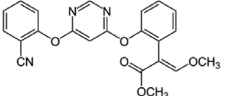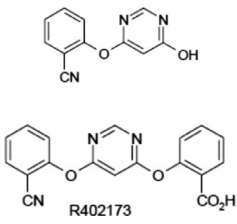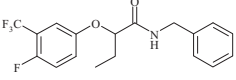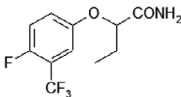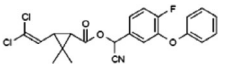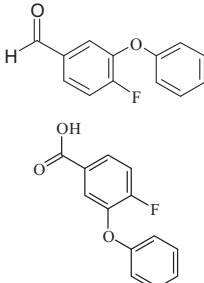
Relevant photo-TPs are defined in Section 2.1.
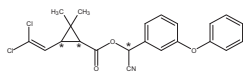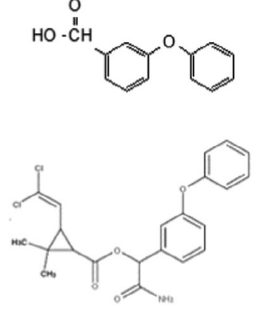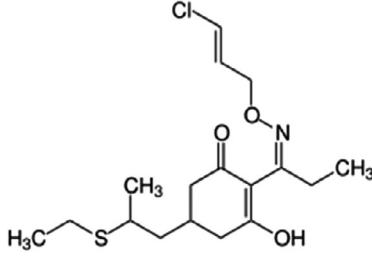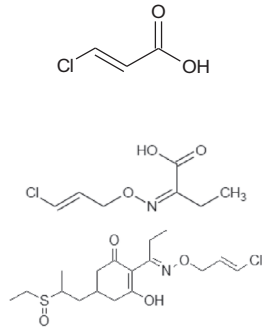
The presence of functional groups such as carbonyl (C = O), nitroaromatic, N-oxide, alkene (C = C), aryl chloride, weak C–H and O–H bonds, sulfides and polyenes increases the likelihood that a substance is labile under photolytic conditions. The photolability arises from the chromophoric properties, e.g. of carbonyl functions, or from the weak covalent bonds, e.g. O–H bonds (Piechocki and Thoma, 2006).[6]
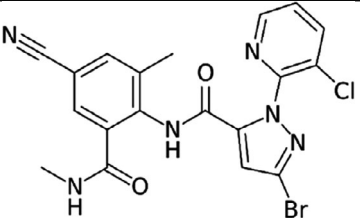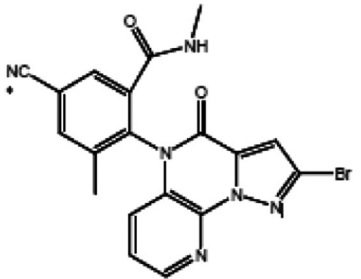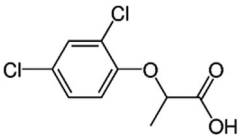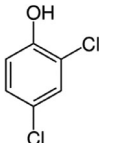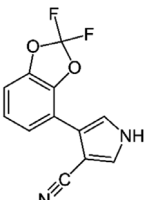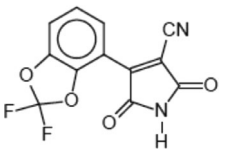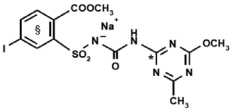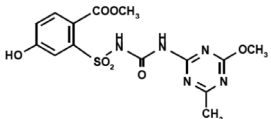
There is empirical evidence, that sorption of photo-TPs is often lower than the sorption of the parent compound (see Table E.1: 10 cases with Koc of photo-TPs < Koc of parent, only three cases with Koc of photo-TPs > Koc of parent, five cases with a lack of published data concerning sorption). This is one more argument for investigating the risk of groundwater contamination by photo-TPs.

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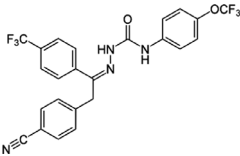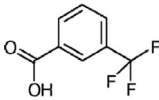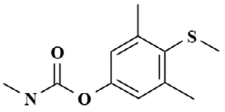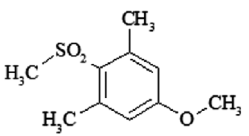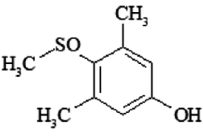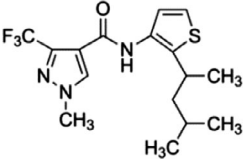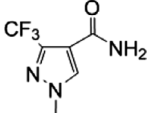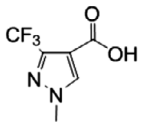
[6] Piechocki JT and Thoma K, 2006. Drugs and the Pharmaceutical Sciences Vol. 163: Pharmaceutical Photostability and Stabilization Technology. *CRC Press*, 1st Edition, New York/London, pp. 79–80.
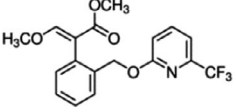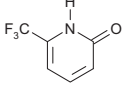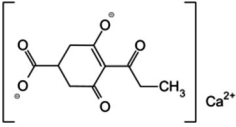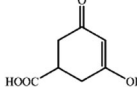
Table E.1: Alphabetic list of known active substances with relevant photo-TPs in soil – which is not intended to be exhaustive! (compiled until April 2018, with data from RAR documents)
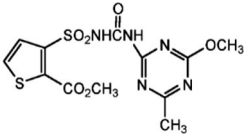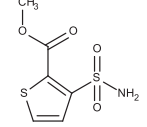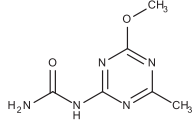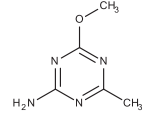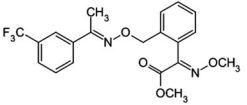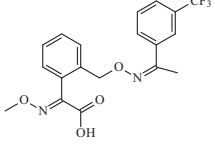
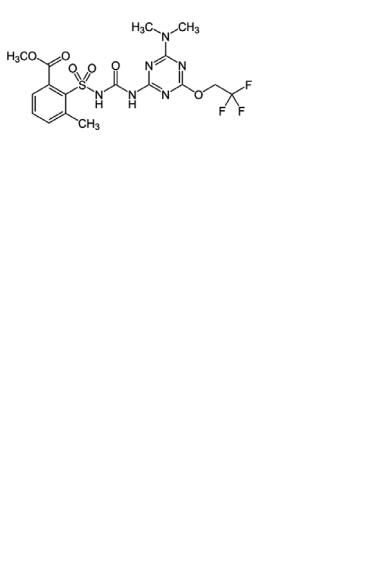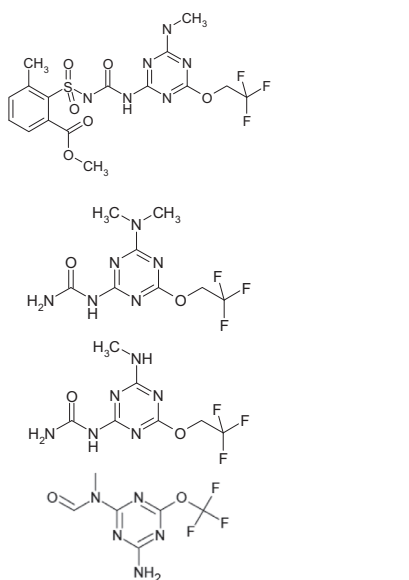| Active substance	Structure of active substance	K_{Foc} of active substance (arithmetic mean)	Relevant photo-TPs in soil photolysis study (max. occ. irradiated/in dark control)	Structure of photo-TPs	K_{Foc} of photo-TPs (arithmetic mean)
Azoxystrobin		423	R401553 (5.0% and 5.7%/no data) R402173 (5.4% and 7.6%/no data) (Data from dark control might show irrelevance as photo-TPs, in case the difference is < 5% compared to irradiated trial.)		203 90
Beflubutamid		1,213	UR-50624 (9.2% and 11.3%/2.6% and 0.3%)		No reliable data
beta-cyfluthrin		112,000	FPB aldehyde (18%/< 3%) FPB-acid (22.3%/< 11.2%)		No data 136

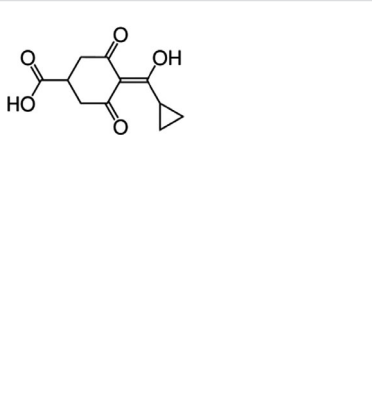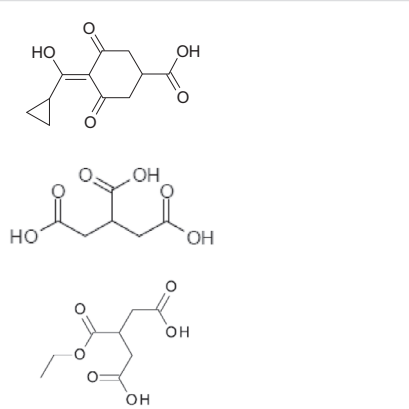| Active substance	Structure of active substance	K_{Foc} of active substance (arithmetic mean)	Relevant photo-TPs in soil photolysis study (max. occ. irradiated/in dark control)	Structure of photo-TPs	K_{Foc} of photo-TPs (arithmetic mean)
beta-cypermethrin		130,031	3-phenoxybenzoic acid (PBA, 'P14') (11.7%/0.4%)		69.8
			cyperamide ('P2') (32.6%/5.8%)		27,058 (QSAR estimate)
Clethodim		22.7	trans-3-chloroacrylic acid (CAA) (18.1% /<< 5%)		2.2 (QSAR estimate) [1.0 used for alkali soil conditions]
			2-[3-chloroallyloxyimino] butanoic acid (18.7%/??)		81.9 (QSAR estimate)
			clethodim sulfoxide (74%/62%)		13.3

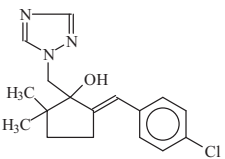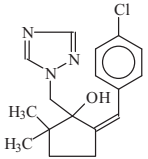| Active substance	Structure of active substance	K_{Foc} of active substance (arithmetic mean)	Relevant photo-TPs in soil photolysis study (max. occ. irradiated/in dark control)	Structure of photo-TPs	K_{Foc} of photo-TPs (arithmetic mean)
cyantraniliprole		193	IN-RNU71 (14.1%/n.d.)		139
Dichlorprop		43.9	2,4–dichlorophenol (23.6%/0.9%)		126 (single value)
Fludioxonil		145,600	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

Active substance	Structure of active substance	K_Foc of active substance (arithmetic mean)	Relevant photo-TPs in soil photolysis study (max. occ. irradiated/in dark control)	Structure of photo-TPs	K_Foc of photo-TPs (arithmetic mean)
metaflumizone		30,714 [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%) methiocarb sulfoxide phenol (M04) (28.8%/ < 3.8%)	 	189 50.7
Penthiopyrad		761	PAM (47%/ n.d.) PCA (36%/ n.d.) [with DM-PCA as successor metabolite]	 	9 2

Active substance	Structure of active substance	K_{Foc} of active substance (arithmetic mean)	Relevant photo-TPs in soil photolysis study (max. occ. irradiated/in dark control)	Structure of photo-TPs	K_{Foc} of photo-TPs (arithmetic mean)
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

Active substance	Structure of active substance	K_{Foc} of active substance (arithmetic mean)	Relevant photo-TPs in soil photolysis study (max. occ. irradiated/in dark control)	Structure of photo-TPs	K_{Foc} of photo-TPs (arithmetic mean)
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		2,379	CGA 373466 (27%/ <3.8%)		88

Active substance	Structure of active substance	K$_{Foc}$ of active substance (arithmetic mean)	Relevant photo-TPs in soil photolysis study (max. occ. irradiated/in dark control)	Structure of photo-TPs	K$_{Foc}$ of photo-TPs (arithmetic mean)
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		
trinexapac-ethyl		60 (minimum)	CGA179500 (M1) (61.5%/ 93.7%) higher in dark control, not relevant		145
			CGA275537 (M4) (10.8% / 2.6%)		1 (surrogate value from CGA300405)
			CGA300405 (M5) (12.5%/ 1.2%)		1 (EPIWIN)

Active substance	Structure of active substance	K_Foc of active substance (arithmetic mean)	Relevant photo-TPs in soil photolysis study (max. occ. irradiated/in dark control)	Structure of photo-TPs	K_Foc of photo-TPs (arithmetic mean)
triticonazole		456	RPA 406203 (10.95%/ 3.99%)		no data

Annex A – Basic tools for deriving photolysis endpoints

Excel file (Basic tools for deriving photolysis endpoints) available on Zenodo knowledge junction at the following link: https://zenodo.org/record/6327650#.Yic2mejMIuU