Guidance on selection of kinetic input parameters for MAMPEC for PT21 exposure assessments

Background

This guidance document has been developed following discussion between members of the TM PT21 e-consultation group and presentation of draft versions at TMIII2011 and TMII2013. It specifically addresses the selection of kinetic input parameters for MAMPEC exposure modelling of Product Type 21 uses.

The guidance reflects final agreed positions. However, since the area of PT21 environmental risk assessments is constantly developing, it is expected that this guidance document may need to be updated over time as experience in this area increases. Where existing PT21 assessments are in the process of being finalised in the EU review, the approach to selecting kinetic parameters may deviate from this guidance. In this situation it is recommended that additional justification be provided to support the approach used. This justification should demonstrate that the approach used would not result in an unrealistic simulation of any of the fate processes and would not lead to an underestimation of predicted exposure levels.

Summary bullet points from the guidance (see main text for further details):-

- *The first tier approach is to set the abiotic and photolytic rate constants in MAMPEC to zero and derive a single first order (SFO) whole system DT_{50} from the available aerobic aquatic simulation studies. This value should be used as the degradation rate input parameter in MAMPEC by entering the rate in the biological degradation rate input field for the main degrading compartment (water or sediment) and the biological degradation rate for the other compartment should be set to a conservative default of 1000 d (0.000693 1/day)[1].*
- *Where appropriate, the input parameter should be the geomean of all acceptable SFO DT_{50} values.*
- *The biological degradation rate for the OECD shipping lane scenario should be corrected down by a factor of 3 to reflect the lower rate of biodegradation in these environments.*
- *Higher tier refinements are possible as follows; e.g. following the recommendations of the FOCUS kinetics guidance a Level P-II assessment of water sediment studies can be performed (see Chapter 10.3.3 of FOCUS kinetics for full details of the Level P-II approach); estimating a sediment dissipation DT_{50} value from the time point of peak observed residues onwards; including phototransformation using the advanced photolytic routines of MAMPEC where data from appropriate studies supports the use of such routines for the environments being simulated.*

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[1] the separation of abiotic, photolytic and biological degradation rates is required as separate inputs are needed in the MAMPEC model.

- *Wherever it is technically feasible to do so, the outputs from the different tiers of the MAMPEC exposure assessments should be compared, at least qualitatively, with data from the real environment (e.g. monitoring data which is of sufficient quality and quantity to allow a comparison to be undertaken).*

Additional refinement options are possible where these are adequately supported by the underlying data and are clearly reported in regulatory submissions. All refinements should ideally be presented in a step wise manner to enable evaluation of each refinement step.

1. **Introduction**

The selection of appropriate kinetic input parameters for MAMPEC simulations is important to ensure consistent and robust exposure assessments for PT21 substances. In MAMPEC, the kinetic input parameters are chemical reaction rates or half lives.

For any PT21 substance there will be a core data set of abiotic studies addressing hydrolysis or aqueous phototransformation in sterile buffers or natural waters along with a range of simulation studies in aerobic or anaerobic natural waters with or without sediment to determine the extent of degradation. Studies performed in the presence of sediment may also allow the potential for partitioning between phases to occur. Since the range of available study types will differ for each substance, and the importance of different degradation and partitioning processes is also substance specific, careful consideration of the entire database will be necessary to gain a full understanding of the likely environmental fate and behaviour and to inform the selection of kinetic input parameters. However this guidance aims to provide general advice on how to select parameters that will be applicable to all substances.

The aim of kinetic input parameter selection should be to identify realistic parameters which represent behaviour expected in the real environment for use with the agreed OECD ESD scenarios and MAMPEC model routines. Ideally there should not be any exclusion of processes which are relevant to the exposure profile of substances and their degradation products in such environments. For reasons of pragmatism relatively simplistic approaches may be taken at the first tier. However these should be modified at subsequent refined higher tiers to reflect all of the processes which are applicable. This is reflected in a tiered approach recommended by this guidance. In addition, wherever it is technically feasible to do so, the outputs from the different tiers of the MAMPEC exposure assessments should be compared, at least qualitatively, with data from the real environment (e.g. monitoring data which is of sufficient quality and quantity to allow a comparison to be undertaken). Further guidance on this is provided in Appendix III.

Derivation of appropriate kinetic parameters from some of the studies that are likely to be available is relatively straightforward (for example the derivation of total degradation rates in single phase test systems such as aqueous hydrolysis, aqueous phototransformation or aerobic aquatic degradation studies without sediment). In addition the calculation of total system degradation rates and individual sediment or water phase dissipation rates from water sediment studies is comparatively straightforward. Note that for consistency with the definitions used in the FOCUS kinetics guidance (FOCUS, 2006) the term 'degradation' is used for any process where a substance is broken down to degradation products (e.g. hydrolysis, photolysis, microbial degradation). Dissipation is used to describe the process leading to the eventual disappearance of a substance from an environmental compartment. Dissipation does not differentiate between degradation processes and transfer processes and can therefore include partitioning to sediment or suspended matter and volatilisation as well as degradation. However the derivation of true water and sediment degradation rates from water sediment studies is relatively complex if the full recommendations of the FOCUS kinetics guidance is followed (FOCUS, 2006, Chapter 10). Much of the complexity arises from the need to determine separate kinetic parameters for both the degradation and partitioning (or transfer) reactions that occur within and between both phases of the water sediment test systems.

The MAMPEC model offers the possibility to enter separate biological, hydrolytic and photolytic degradation rate constants for both the water phase and the sediment phase as input parameters provided that these can be reliably and separately determined. The specific requirements of the MAMPEC model lead to the possibility of erroneously double counting certain processes if the kinetic parameters are not selected appropriately. Since the MAMPEC model simulates partitioning to suspended matter and subsequent deposition to the sediment layer at the sea bottom, it is important to ensure that the rate constants inputted to MAMPEC reflect true individual degradation processes (i.e. biological, hydrolytic or photolytic) and do not include a contribution via partitioning to sediment for example.

The following figures illustrate the possible fate processes occurring in the marine environment (Figure 1) as well as those processes specifically included in the MAMPEC v 2.5 model (Figure 2).
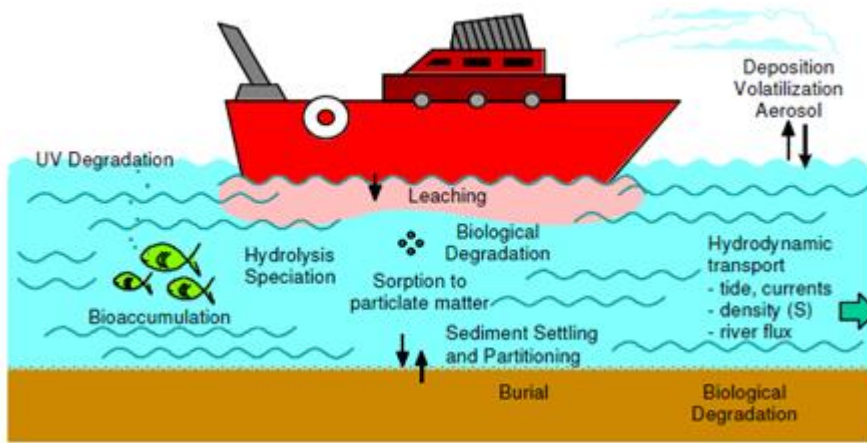
Figure 1. Illustration of the possible fate processes in the marine environment (discussed in MAMPEC report from Hattum et al., 2002). Please note that not all processes are included in version 2.5 of the model.
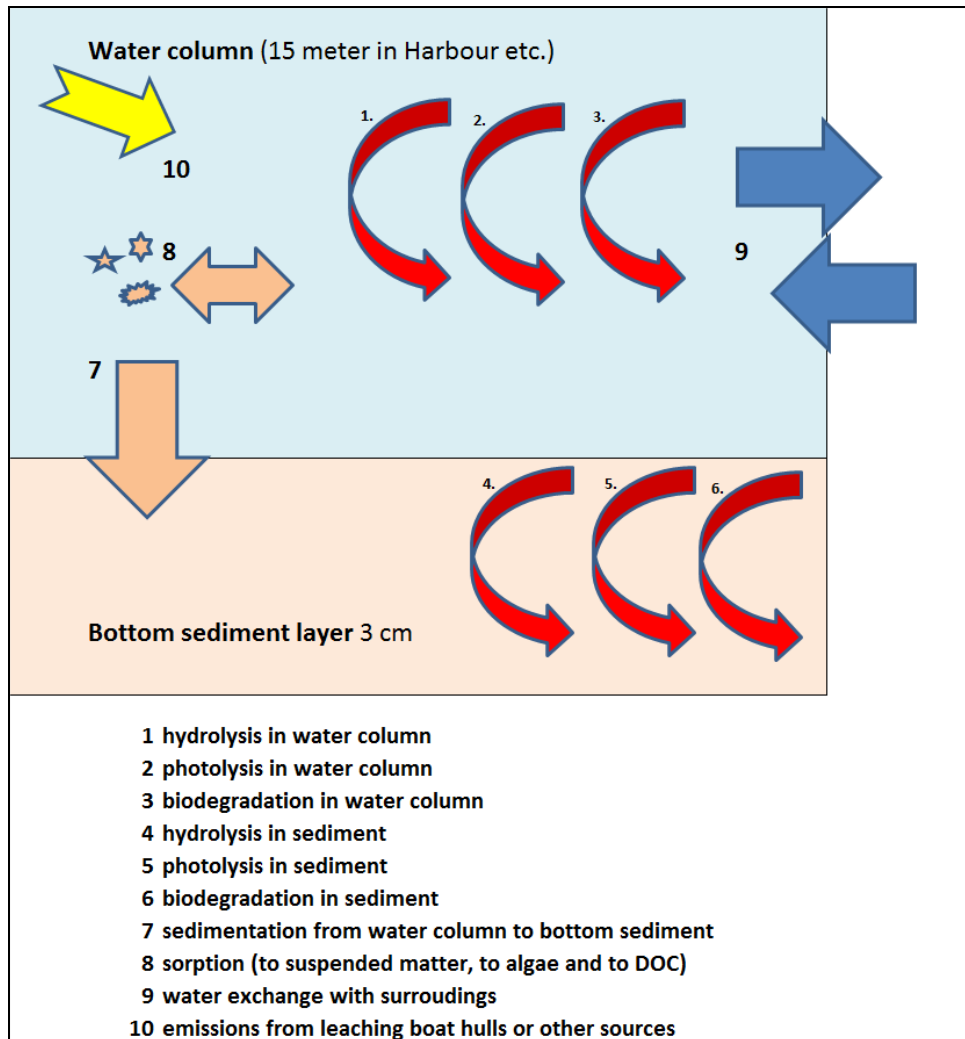

Figure 2.   Illustration of the fate processes actually included in MAMPEC v 2.5

To minimise the risk of double counting specific processes the following guidance is proposed as a first tier approach.

2   First tier approach

*Summary: Set abiotic and photolytic[2] rate constants to zero for water and sediment; derive a single first order[3] whole system DT50 from the aerobic aquatic mineralisation studies (e.g. OECD 309) and use this as the degradation rate input parameter in MAMPEC by entering the rate in the biological degradation rate input field for water and set the biological rate for sediment to 1000 d (0.000693 1/day) by default **or** derive a single first order whole system DT50 from the water-sediment studies (e.g. OECD 308) as the input parameter for the biological degradation rate of the main degrading compartment (water or sediment) and set biological degradation rate to 1000 d (0.000693 1/day) in the other compartment.*

When a range of studies are available (e.g. hydrolysis, aqueous phototransformation and aquatic simulation studies with or without sediment) it is proposed that the core hydrolysis and phototranformation studies are not used directly in the derivation of first tier kinetic input parameters and both rate constants for these processes in water and sediment should be set to zero by default. The exclusion of hydrolysis studies ensures that double counting the contribution via abiotic hydrolytic breakdown is prevented. Quantification of phototransformation in potentially turbid water bodies such as simulated by the MAMPEC commercial harbour or marina is likely to be difficult without detailed information on absorption characteristics, and therefore it is appropriate to exclude this process from the simple first tier assessment. However phototransformation could be of relevance to some substances on a case by case basis and further information on how to incorporate this is considered in the higher tier refinements section. Where novel photolysis products are formed in these studies at significant levels such that formation under natural conditions cannot be excluded, a consideration of the potential exposure levels and associated risks from these photolysis products should still be performed at the first tier. This ensures the simple first tier exposure assessment covers all realistic worst case situations with regard to influence of photolysis. It should also be noted that information from these abiotic studies may be used qualitatively in determining the appropriate rate constant to use for water and sediment phases from the range of simulation studies available. This is detailed below.

Following the first tier approach of excluding hydrolysis and phototransformation, a biological[4] degradation rate constant can be derived from either an aerobic aquatic mineralisation study (e.g. OECD 309) or a

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[2] The terms abiotic, photolytic and biological are used here for consistency with the separate kinetic input parameters that may be used in the MAMPEC model.
[3] where an acceptable fit to single first order kinetics cannot be achieved for the whole system data bi-phasic models (e.g. FOMC, DFOP or HS kinetics) should be tested. Where bi-phasic models do result in acceptable fits, appropriate work arounds as detailed by FOCUS kinetics should be used to ensure an appropriately conservative pseudo SFO DT50 is derived for the purposes of the MAMPEC simulations (e.g. slow phase of DFOP or HS kinetic, FOMC DT90/3.322).
[4] although this is referred to as a 'biological' degradation rate constant for consistency with the terminology used in the MAMPEC model, as it will ultimately be derived from the whole system data it could constitute a lumped rate constant containing both abiotic and biotic degradation processes

water-sediment study (e.g. OECD 308). Where a range of simulation studies are available the selection of appropriate study types from which to derive the biological degradation rate should be carefully assessed and fully justified in the exposure assessment (e.g. Doc IIB). In general preference should be given to utilising information from aerobic marine test systems to most closely resemble the MAMPEC scenarios. The use of information from aerobic marine systems is consistent with the first tier sediment dweller risk assessment which is intended to reflect exposure and effects in the upper most sediment layers where biological activity will be predominantly aerobic in the uppermost layer with increasingly anaerobic conditions in deeper layers. This situation is typically reflected in aerobic water sediment studies conducted in accordance with OECD 308. The use of data from completely anaerobic test systems is not normally recommended for assessments for the purposes of Annex I listing. However useful supporting information may still be obtained from anaerobic systems. In addition conditions in such anaerobic studies may better reflect specific regional conditions (e.g. areas with large anaerobic bottom waters such as The Baltic Sea or Norwegian fjords) and may therefore be useful for refined specific National assessments. Further discussion on this aspect of marine sediment is included in Section 4.2.3.2 of the TGD.

Since the MAMPEC model essentially consists of two compartments (water and sediment) in which the PECwater is calculated independently of sediment processes it could be argued that the endpoint of an aerobic water only aquatic test without a sediment layer (OECD 309) better mimics the processes and conditions addressed in the model calculations. See Figure 2 for an illustration of the fate processes simulated and Figure 3 for a screenshot of the MAMPEC kinetic input parameter tab.

Figure 3.   MAMPEC 2.5 input form for compound definition.
Please note that "*degradation rate - abiotic*" in MAMPEC refers to hydrolysis rate.

Conversely using information from a water-sediment study may have the advantage that it would allow derivation of input parameters for both water and sediment from the same test system to be derived which should ensure consistent endpoint selection. However some assessment of the relevance of the water-sediment test system for the marine environment is required. For example, OECD 308 was intended to principally mimic freshwater ditch conditions both in terms of water and sediment composition as well as dimensions (particularly the water: sediment ratio). The water sediment test setup can be characterized by relatively high organic matter content and a relatively high bacterial cell density that may not be representative of all marine environments. In particular it should be noted that the OECD 308 cautions against application of test results to simulate transformation in the open sea. A further disadvantage of using water sediment studies is that it becomes more difficult to derive true water phase and sediment phase degradation rates in two phase systems. To avoid some of these difficulties it may be preferable to make use of information from an aerobic mineralisation study (e.g. OECD 309), however the environmental conditions of all test systems should still be detailed and considered in relation to their relevance to the range of coastal and open sea marine environments simulated with the standard MAMPEC scenarios. When using an aerobic aquatic mineralisation study the whole system DT50 can be used directly as the biological degradation rate for the water phase in MAMPEC. The biological degradation

rate for sediment can be conservatively set to a DT_{50} of 1000 d[5] (0.000693 1/day) by default.

When an aerobic aquatic mineralisation study is not available, the biological degradation rate constant should be derived from the available water-sediment studies. Since MAMPEC is a marine antifoulant model, results from marine test systems should preferably be used in such simulations. For simplicity at the first tier these studies should be kinetically evaluated to derive a whole system degradation DT_{50} values (i.e. derived from the total sum of active substance residues in water and sediment phases at each time point). Expert discussion at TMII2013 confirmed that kinetic fitting should follow the detailed recommendations of the FOCUS kinetics guidance. An advantage of this approach is that the whole system DT_{50} from the water sediment study is relatively easy to derive with freely available software (e.g. FOCUS kinetics MS Excel spreadsheets). In addition the visual and statistical goodness of fit criteria (e.g. visual plots and chi^2 error percentage as well as t-test or consideration of confidence intervals) are easy to determine. The fitting process is also consistent with fitting of degradation rates in other environmental compartments (e.g. soil). This whole system degradation DT_{50} can be used as a simple and conservative surrogate for degradation in the main degrading compartment. A disadvantage with using water sediment studies is that it can be difficult to determine the main degrading compartment. However for PT21 active substances this may be achieved by examining the active substance and metabolite profiles in water and sediment phases along with information on partitioning potential derived from the standard adsorption studies (e.g. OECD 106) as well as any relevant physico-chemical data on solubility etc. Additionally where the separate hydrolytic degradation rates within relevant pH ranges of the water sediment study show abiotic degradation rates comparable to the whole system DT_{50} rates this may be used as further evidence to support the use of the whole system rate for the aqueous phase. After considering all available information the main degrading compartment may still not be easily identified. In this case it is proposed to make a pragmatic choice based on likely sorption behaviour. For example, for substances with a Koc < 100 L/kg sorption to sediment may be considered minimal, and therefore the main degrading compartment can be assumed to be the aqueous phase to which the whole system DT_{50} should be assigned. For substances with a Koc > 2000 L/kg sorption to sediment can be considered significant, and this can be assigned as the main depredating compartment. In either situation, the other compartment should be conservatively assigned a DT_{50} of 1000 d. The reasons for assigning the whole system degradation rate to a particular compartment (water or sediment) should be clearly detailed in the evaluation. A worked example is included in Appendix I to this guidance to assist evaluators. For substances with a Koc between 100 and 2000 L/kg it may be necessary to run simulations with both combinations for ascribing the whole system DT_{50} and 1000 d default and selecting the combination that give the highest concentrations for the purposes of a first tier risk assessment[6].

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[5] the recommendation for a 1000 d default DT50 has been taken from the FOCUS kinetics guidance
[6] the recommendation to use Koc triggers for selecting the main degrading compartment comes from the generic guidance for FOCUSsw (version 1.1, March 2012)

Where acceptable SFO DT_{50} values have been derived from multiple test systems (e.g. two or more contrasting water-sediment test systems for example) the kinetic input parameter should usually be the geometric mean of all acceptable values[7]. The proposal to use the geometric mean is based on the assumption that the vulnerability of the overall exposure assessments should lay primarily within the description of the scenarios rather than the individual substance parameters. Hence the use of a mean value rather than a worst case value is considered appropriate. In accordance with FOCUS kinetics, when several entire SFO degradation curves are averaged, the curve corresponding to the geometric mean of the half-lives represents the best SFO fit to the averaged data points. Using the geometric mean also has the advantage that the same result is obtained from averaging first order degradation rate constants and averaging corresponding half lives. However in certain cases the use of a mean value may not be justified. For example, the degradation rates may be observed to be highly dependent on environmental conditions, such as pH, or strongly correlated with concentration. In these cases it may be justified to use a single conservative DT_{50} value to reflect the likely degradation behaviour under realistic worst case conditions at the first tier. Where large variation in DT_{50} values from different test systems is observed, some consideration of the possible reasons behind the variation should be included in the assessment report. Users should refer to Section 11.2 of the FOCUS kinetics guidance for further information on averaging kinetic parameters.

Whatever study has been used to derive the biological degradation rate, where this has been derived from water representative of either estuarine or coastal waters, a correction factor of 3 should be applied for the biological degradation rate inputted to the shipping lane scenario to reflect the potential for lower biodegradation in more distant marine environments (i.e. the biological degradation rate constant should be reduced by a factor of 3[8]). Where degradation can be shown to be primarily abiotic (e.g. due to rapid hydrolytic breakdown) this correction factor for shipping lane scenarios need not be applied. Where the study used to derive the biological degradation rate has used samples from open water areas reflective of conditions in the open sea, no correction procedure should be applied and these values can be conservatively used to predict behaviour in the coastal scenarios (e.g. Marina and Commercial Harbour).

Discussion at TM level on the appropriate exposure endpoints for the sediment dweller risk assessments have concluded that the first tier assessment should be based on the $PEC_{suspended\ matter}$ value derived in MAMPEC (see also Section 2.3.8.4 of the TGD). An advantage of this conclusion in terms of kinetic input parameter selection is that the $PEC_{sediment}$ will not be used as the basis of first tier risk assessments for sediment dwellers. Since only the $PEC_{sediment}$ value is sensitive to the sediment DT_{50}

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[7] note that where DT_{50} values are derived from different test systems at contrasting temperatures, these values should be normalised to 20°C prior to calculation of the geometric mean.

[8] the proposed factor of 3 to reflect slower degradation in marine environments more distant from the coastline (such as the shipping lane scenario) is taken from Section 4.2.3.4 of the TGD.

values inputted, and since these values will not be used in the risk assessment, a simple 1000 d default value can be used for the sediment phase in order to run first tier MAMPEC simulations when the biological degradation rate from the aerobic aquatic studies to the water-sediment studies has been assigned to the water phase. The use of such simple defaults will therefore not lead to an overestimation of $PEC_{suspended\ matter}$ concentrations because they are independent of the inputted sediment DT_{50}. It should be noted that the proposal to use a 1000 d default for sediment is a simplistic approach to enable to models to be run without requiring complex kinetic analysis at the first tier. It is not intended to represent a realistic simulation of sediment behaviour, nor should such a value be used when performing an assessment against the PBT criteria. If a more accurate $PEC_{sediment}$ value is required, either for the purposes of a refined sediment dweller risk assessment or to enable comparison with monitoring data or performing reality checks of the MAMPEC exposure concentrations versus the expected behaviour of individual substances, further options to refine the kinetic input parameter for this compartment are provided below in the higher tier refinement section. ~~Finally it should be noted that sediment dweller risk assessments are only required for substances occurring in sediment at greater than 10% applied radioactivity. In the absence of reliable information from water sediment studies to confirm actual levels of sediment partitioning, the sediment exposure and risk assessment should be retained for all active substances and aquatic metabolites by default.~~

These first tier proposals should also be applied to any metabolites included in the exposure assessment. Where a whole system DT_{50} needs to be calculated for a metabolite, this should be based on the whole system metabolite data from the time point of peak occurrence onwards as a simple first tier in order to estimate a conservative dissipation DT_{50}. More complex two-compartment kinetic models could be fitted to the whole system active and metabolite data sets to derive a whole system degradation rate where required. These proposals are in line with level M-I approach detailed in the Section 10.4.2 of the FOCUS kinetics guidance. Where no reliable DT_{50} can be estimated for a metabolite (e.g. when no decline phase was observed in the available studies) a conservative DT_{50} of 1000 d should be set for the biological degradation rate in both water and sediment at the first tier.

Where acceptable risks are identified based on the first tier approach outlined above, there should be no need to consider higher tier refinements. However the first tier approach is recognised as being relatively simplistic and therefore a range of option to refine the input parameters are listed below.

3. Higher tier refinements

The proposals outlined above for a first tier approach are intended to represent a simple pragmatic method to deriving robust and conservative kinetic input parameters for the purposes of a first tier MAMPEC simulation. This first tier approach has been proposed as it is recognised that deriving true separate abiotic, photolytic and biological degradation rate constants for MAMPEC that do not double count certain processes is often very difficult.

However the simple first tier approach does not attempt to describe all relevant processes in detail. It is recognised that the kinetic input parameters may be some of the most important parameters in the surface water exposure assessment for PT21 substances and refinements at subsequent tiers to reflect all of the applicable processes may be important. These possible refinements are therefore described in this section.

The first option to refine the first tier would be to adopt the recommendations of the FOCUS kinetics guidance document with respect to deriving modelling endpoints from the aerobic water sediment studies (i.e. the Level P-II assessment scheme described in Section 10.3.3 of the FOCUS kinetics guidance; a brief overview of the Level P-II assessment approach is also provided in Appendix II). The advantage of this first option would be to ensure a robust kinetic assessment of the underlying data sets and allow calculation of true water and sediment degradation rates for input to the MAMPEC simulations which should represent a refinement over the first tier for both phases. The disadvantage is that this approach requires dedicated kinetic modelling software in order to validate the fits. A further disadvantage is that experience of this scheme for pesticides has tended to show that the specific acceptance criteria for determining acceptable kinetic fits are often found to be extremely difficult to pass. Acceptance criteria include basic visual and statistical criteria as per any kinetic assessment, but also include additional criteria such as demonstrating that degradation in both water and sediment phases are statistically different from zero. In addition the back-transfer rate (i.e. the rate of transfer from sediment to water) must also be shown to be statistically different from zero according to the FOCUS guidance. The final Fsed test criteria which is intended to demonstrate that kinetically derived transfer rates are consistent with the known properties of the substance has also been shown to be difficult to pass. According to the FOCUS guidance, when the fit is not considered acceptable because of the failure of any one of the criteria, a default approach is proposed using a combination of the whole system degradation rate for one compartment and a default DT_{50} of 1000d for the other compartment. Effectively this is the simple first tier approach already outlined above. Due to the complexity of this approach a worked example has been included in Appendix I.

A simpler refinement option for the sediment compartment only would be to derive a sediment dissipation DT_{50} using data from the time point where peak sediment residues are observed onwards. The advantage of this refinement would be the simplicity and the ease of determining the goodness of fit criteria. The refinement over the simple first tier would be that the sediment DT_{50} value should be closer to the actual true sediment degradation rate. One possible disadvantage would be that technically the sediment dissipation DT_{50} value derived in this manner could include contributions from both true degradation and loss via re-partitioning back into the water phase. Since the re-partitioning process is not currently simulated in MAMPEC (see Figures 1 and 2) any error that would be introduced due to double counting this process can be ignored. Note that if there were insufficient data points from the time of peak sediment residues onwards it would not be possible to derive a reliable sediment DT_{50} and therefore the use of a default value of 1000 d as per the

simple first tier would be fully justified. An example of this approach is also included in Appendix I. If further refinement of the sediment phase behaviour is required, reference should also be made to the TGD (see Section 2.3.6.5 page 56), which describes the upper 3cm of a typical EU marine sediment as being composed of 3mm of top sediment which is aerobic, with the remaining 27mm being anaerobic. Where information is available from both aerobic and anaerobic water sediment systems, it may be appropriate to consider deriving a millimetre averaged DT_{50} value to reflect the changing redox potential across typical upper sediment layers if this is not adequately accounted for in the aerobic study.

A further possible refinement at the higher tier could be to include consideration of aqueous phototransformation. Whilst this guidance recommends that this process is excluded from first tier assessments, it is recognised that on a case by case basis, aqueous phototransformation could be a significant process for some substances in some environments. However due to the uncertainty in determining the significance of this process, it is recommended that this option is only considered in cases where sufficient data is available to run the advanced photolytic degradation routine in MAMPEC (e.g. data on absorption and quantum yield for wavelengths between 290[9] and 850nm). Where such data is available phototransformation could be considered for all three in-service scenarios. However due to the uncertainty with how the steady state model MAMPEC handles diurnal and seasonal variations in sunlight levels, it is recommended that multiple simulations are performed with the advanced photolysis routine both enabled and disabled in order that the sensitivity to the model output can be assessed. The acceptance of the exposure levels derived with the photolysis routine enabled should be made on a case by case basis, taking into account all relevant information from laboratory or field data, including monitoring studies.

Additional refinement options are possible where these are adequately supported by underlying data and are clearly reported in regulatory submissions. Where a number of refinement options are being applied, it is recommended that exposure assessments are performed in a step wise manner in order that the impact of each separate refinement step on the exposure levels can be clearly determined.

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[9] the MAMPEC guidance suggests a minimum wavelength of 280 nm. However this is inconsistent with OECD 316 which recommends a wavelength of 290 nm for direct photolysis. For consistency with the OECD guideline a revised lower limit value is proposed.

Appendix I: Worked example

To illustrate the above options a worked example is provided below. The following dummy data set has been generated for a PT 21 active substance.

Summary of fate endpoints:-

Hydrolysis DT_{50} values

pH	DT50 at 12°C
5	>100 d
7	2.5 d
Sterile seawater (pH 8)	1.9 d
9	14 hours

OECD 308 Water/sediment simulation study DT_{50} values

Residue data from aerobic marine water sediment study at pH 8 and 20°C

| % AR as parent	0	1	3	7	14	30	60	90	120
Water	98	70	35	8.5	0.5	<0.1	<0.1	<0.1	<0.1
Sediment	1	7.5	17.5	20.3	18.6	12.7	6.1	2.8	0.9
Total system	99	77.5	52.5	28.8	19.1	12.7	6.1	2.8	0.9

First tier approach

Summary: Set abiotic and photolytic rate constants to zero for water and sediment; derive a single first order whole system DT_{50} from the water-sediment studies (e.g. OECD 308) as the input parameter for the biological degradation rate of the main degrading compartment (water or sediment) and set biological degradation rate to 1000 d (0.000693 1/day) in the other compartment.

The following kinetic fits were derived using the FOCUS DEGKINv2.xls spreadsheet using the total water sediment system residues as reported in the table above. Although the SFO fit was acceptable based on a chi^2 value of 14.7% (and less than the suggested 15% level recommended by FOCUS) the SFO fit did not necessarily provide an acceptable visual fit. In cases such as this where the fit to SFO kinetics does not fully meet all of the statistical and visual indicators of goodness of fit recommended by FOCUS kinetics, further consideration of non-SFO fits may be warranted. Therefore in this case the fit using FOMC kinetics was also explored (FOMC considered appropriate over hockey stick or DFOP kinetics since 10% of initial concentration was reached within the experimental period, again in line with FOCUS kinetics).

SFO kinetics (see Chapter 5 of FOCUS Kinetics for guidance on different kinetic models)
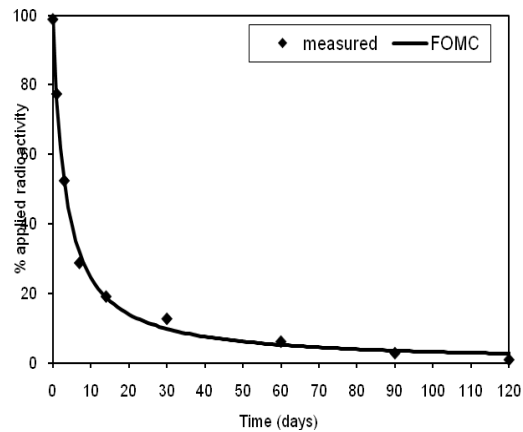[$M = M0*e^{-kt}$, where M0 is total present at $t = 0$, M is total present at time t]

M0 = 93.9
$k = 0.160$ d^{-1}
$DT_{50} = 4.3$ d
$DT_{90} = 14.4$ d
Chi^2 error level = 14.7%
t test P<0.05
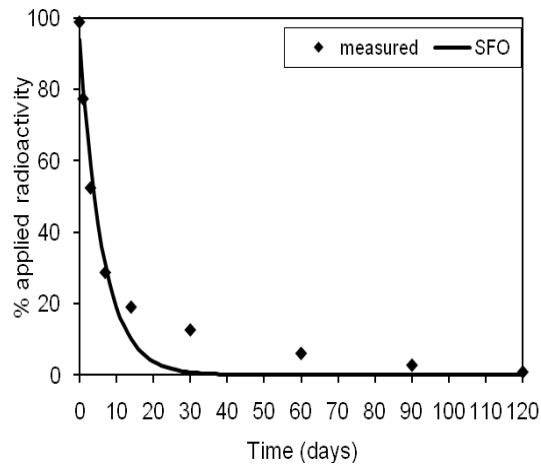
FOMC kinetics
[$M = M0 / (t/beta +1)^{\wedge}alpha$]

M0 = 99.6
alpha = 0.996 (CI = 0.729 – 1.26)
beta = 3.245 (CI = 1.68 – 4.82)
$DT_{50} = 3.3$ d
$DT_{90} = 29.5$ d
SFO DT_{50} back calculated from FOMC $DT_{90}/3.322$ to be inputted into MAMPEC = 8.9 d
Chi^2 error level = 4.1%

Visually and statistically the fit using FOMC kinetics is improved over the SFO fit, which is not unusual since the FOMC kinetic includes an additional parameter compared with the SFO kinetic. Since the MAMPEC model requires an SFO input parameter, further consideration is needed over whether the SFO fit is acceptable for the purposes of the exposure assessment, or whether the FOMC fit must be used. This further consideration should make use of all data available and an example is provided below.

One simple approach that could be used is to consider whether the SFO fit is adequate to describe at least 90% of the degradation of the active substance in the whole system (i.e. whether the SFO fit is acceptable up to the time when residues drop below 10% of initial applied material). For the example above, this would involve considering data up to an including the 60 d time point (where residues are first measured below 10% AR). However as can be seen from the SFO plot above, even limiting the consideration of the goodness of fit for 90% of the degradation would not support the selection of the SFO fit since the visual fit is still relatively poor using this reduced data set. Further consideration is therefore required.

In this case the tendency toward a biphasic fit for the whole system degradation rate is partially a result of the fact that over time, the slower sediment phase degradation rate has a greater influence on the whole system behaviour compared with the early period of the study, where whole system behaviour is dominated by behaviour in the water phase.

Data is also available from the abiotic hydrolysis studies, which support a DT_{50} via hydrolysis alone of 1.9 d at 12°C in sterile seawater at a pH comparable to the marine water sediment study. This information may support the use of the whole system value as an input parameter for the biodegradation rate constant in water, since the water phase can be considered to be the main degrading compartment in this case (a simple 1000 d default DT_{50} can be assigned to sediment to reflect the slower degradation in this compartment at the first tier).

The information that the substance degrades rapidly via abiotic hydrolysis may also be used to support the use of the SFO whole system kinetic fit (i.e. DT_{50} of 4.3 d) in this case since the SFO fit is close to that expected by hydrolysis alone. Note that if the use of the SFO fit could not be appropriately justified, the FOMC kinetic would be used, and since it would be incorrect to directly input the FOMC DT_{50} into an SFO exposure model, the FOCUS kinetic work around of dividing the FOMC DT_{90} by 3.322 would be needed (i.e. FOMC work around of DT_{90} of 29.5/3.322 = DT_{50} of 8.9 d).
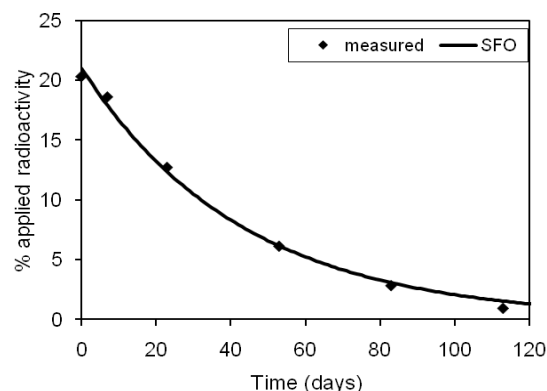
<u>Higher tier refinement options</u>

Refining the 1000 d default value for the sediment compartment from the simple first tier above can be achieved by calculating a sediment dissipation DT_{50} from the time point of peak sediment residues onwards.

The following kinetic fits were derived using the FOCUS DEGKINv2.xls spreadsheet using data for sediment phase from the peak of 20.3% from day 7 onwards. Day 7 residues were taken to be time 0, and all later time points corrected accordingly as shown below (corrected time points in brackets):-

% AR as parent	7 (0)	14 (7)	30 (23)	60 (53)	90 (83)	120 (113)
Sediment	20.3	18.6	12.7	6.1	2.8	0.9

SFO fit

M0 = 21.03
k = 0.023
DT_{50} = 29.9 d
DT_{90} = 99.3 d
Chi^2 error level = 4.1%
t test P<0.05

The SFO fit for the sediment dissipation DT50 is acceptable based on the visual and statistical criteria.

A further refinement option would be to conduct an assessment in accordance with level PII as recommended by FOCUS kinetics. Applicants are advised to consult the detailed FOCUS kinetic guidance for further information on this specific method and associated indicators of goodness of fit. However an example of the kind of kinetic fitting procedure that would need to be applied with this refinement is shown below.

The following multi-compartment model and associated optimised parameters were derived using ModelMaker 4.0 software and data for parent residues in both the water phase and sediment phase as reported above and are shown in Figure 1 and 2 below.
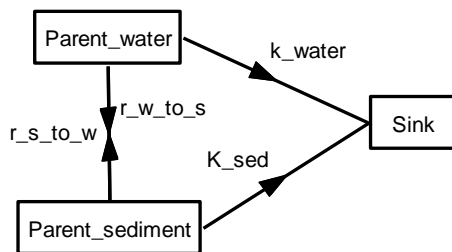

Name	Optimize result	Optimize error
Main		
K_s	0.026254	0.00560914
K_w	0.257428	0.00473129
Parent_initial	99.1476	0.511019
r_sw	0.000314472	0.00733932
r_ws	0.0914262	0.00206147

Figure 1: ModelMaker Scheme   Figure 2: Parameters optimised
                                                          during the kinetic fitting

Where the following parameter definitions apply:-

K_s = rate constant for true degradation in sediment
*K_w = rate constant for true degradation in water*
Parent_initial = mass of parent in water phase at 0 d
r_sw = rate constant for transfer from sediment to water
r_ws = rate constant for transfer from water to sediment

Note that in the context of kinetic analyses, a sink compartment is any compartment without an outflow, regardless of which components it represents. The sink compartment often represents CO_2, bound residues and minor unidentified residues, as well as any metabolite, identified or not, that is not included in the fit.

The optimised parameters resulted in the following visual fits against the measured data:-
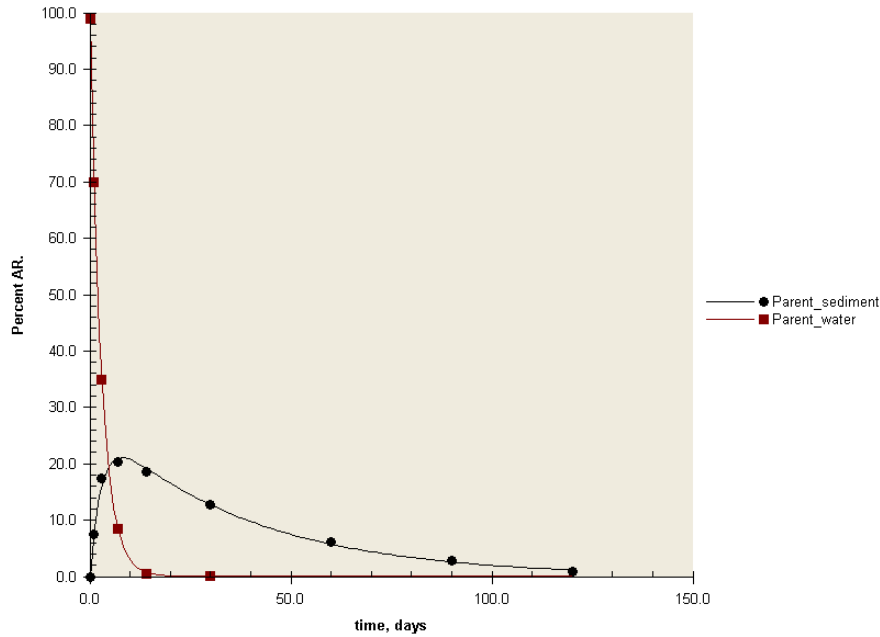
Based on the optimised model fits, the following degradation rates were derived:-
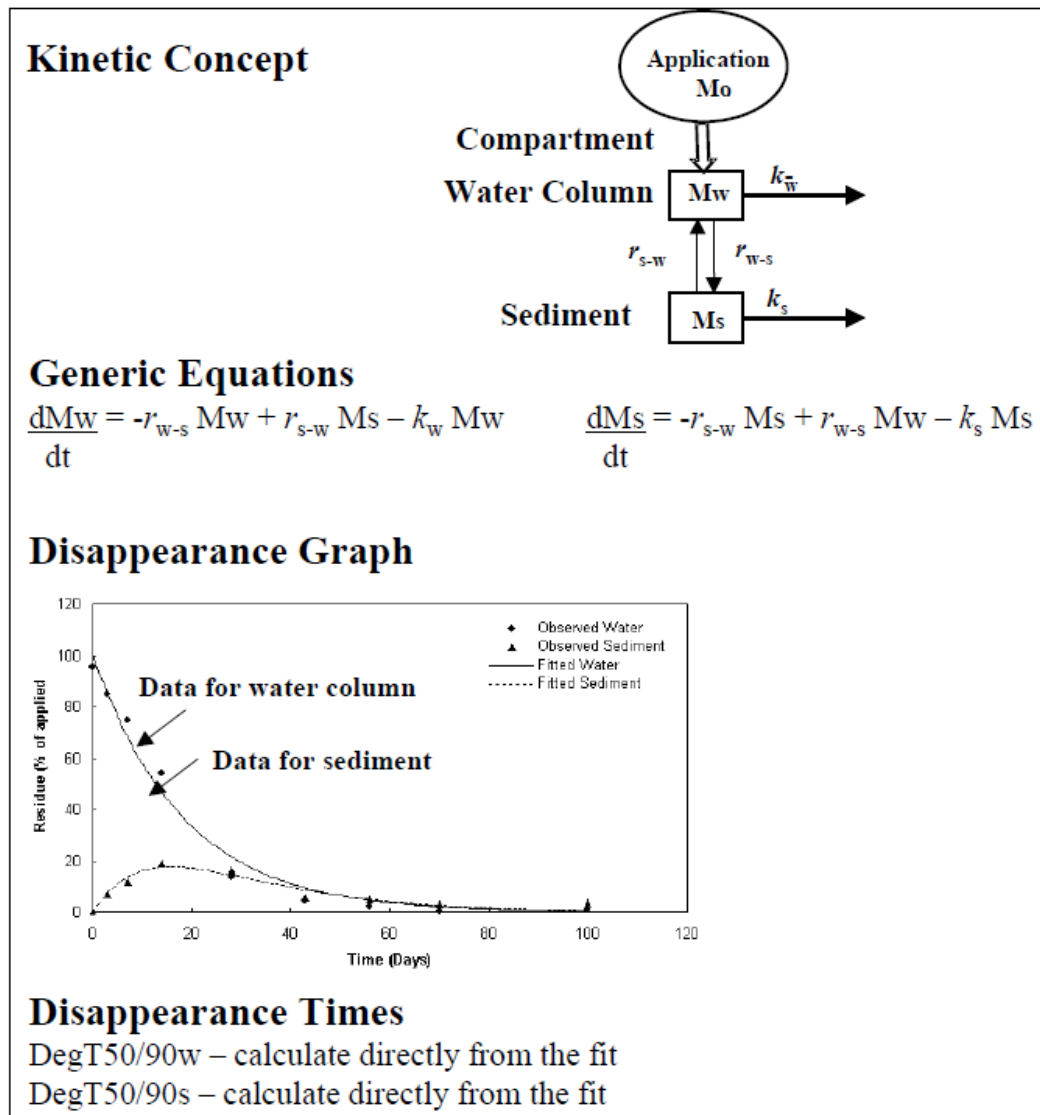
degDT$_{50water}$ = 2.7 d (chi^2 = 0.6%; derived from the K_w parameter)
degDT$_{50sediment}$ = 26.4 d (chi^2 = 5.8%; derived from the K_s parameter)

Visually the fits were considered acceptable. In addition the results were consistent with the available fate data (i.e. the relatively rapid degradation rate in water was broadly consistent with the results of the abiotic hydrolysis studies). The degradation rates in both water and sediment compartments were greater than zero (t-test on both K_w and K_s parameters indicated they were significantly different from zero at a significant level of P= 0.05). However, the specific Fsed test failed because the back transfer rate from sediment to water was not significantly greater than zero (this can be seen with the relatively large optimise error for r_sw, with P = 0.483 and therefore not significantly different from zero). Therefore this refinement option would not be appropriately supported for this data set since not all goodness of fit criteria have been met.

Appendix II: Details of the Level P-II assessment of water sediment studies

10.3.3 Level P-II

At Level P-II, both persistence and modelling endpoints are estimated using a two-compartmental approach, comprising water column and sediment compartments. As shown in Box 10-2, after an application is made to the water column, first-order kinetics are used to describe degradation in these compartments (rate constants k_w and k_s) as well as reversible transfer between these compartments (rate constants r_{w-s} and r_{s-w}). Only first-order kinetics were used for degradation due to the complexities of implementing biphasic kinetics, which is a limitation when degradation rate slows down over time.

Kinetic Concept

Generic Equations

$$\frac{dMw}{dt} = -r_{w-s}\,Mw + r_{s-w}\,Ms - k_w\,Mw \qquad \frac{dMs}{dt} = -r_{s-w}\,Ms + r_{w-s}\,Mw - k_s\,Ms$$

Disappearance Graph

Disappearance Times

DegT50/90w – calculate directly from the fit
DegT50/90s – calculate directly from the fit

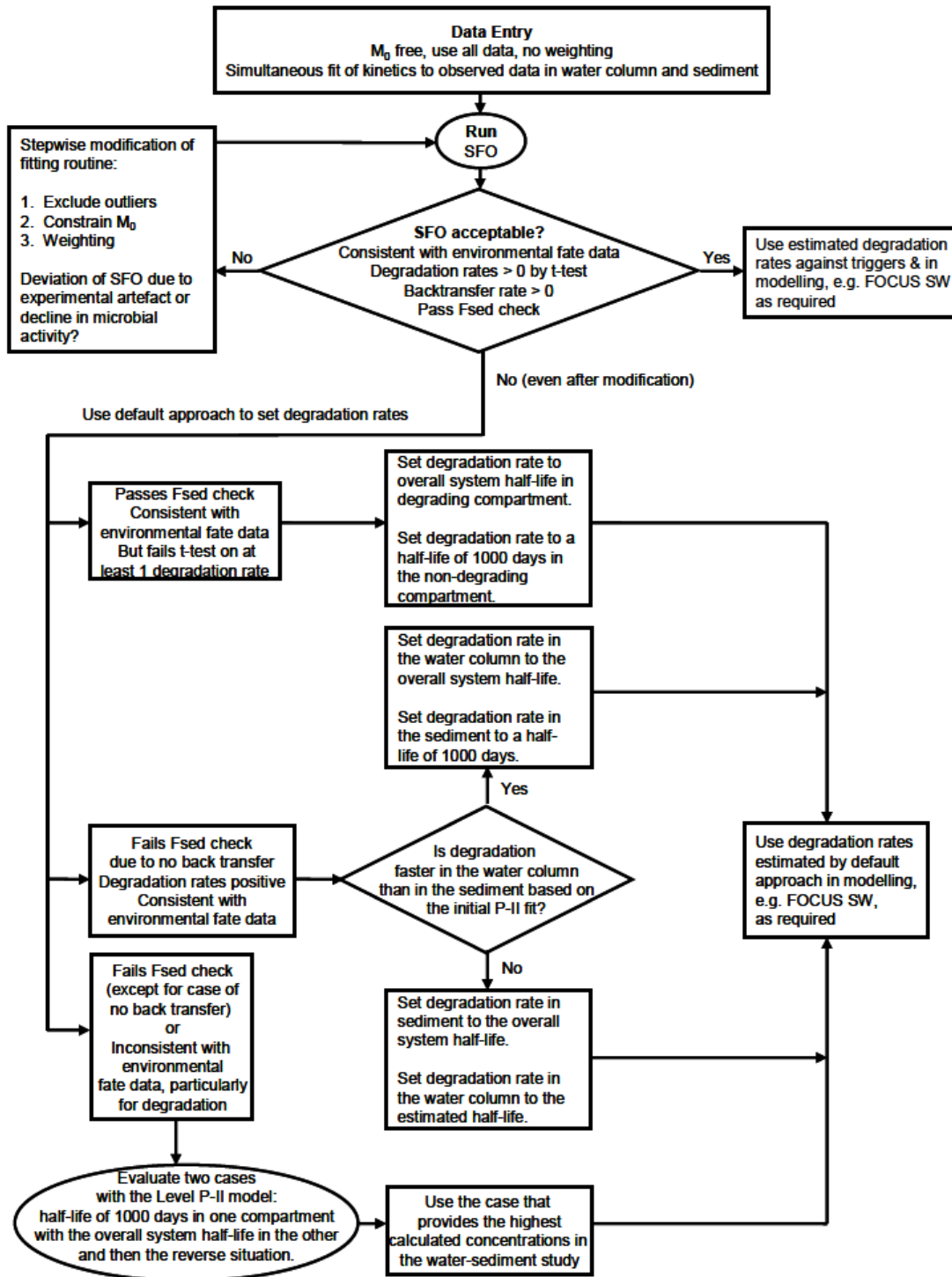**Box 10-2. Kinetics at Level P-II**

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Figure 10-3. Recommended procedure at level P-II to estimate both persistence and modelling endpoints.

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For full details of the Level PII approach please refer to Section 10.3.3 of the FOCUS degradation kinetics guidance (available at http://viso.ei.jrc.it/focus/dk/doc.html).

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Appendix III: Comparison of modelling and monitoring data

Wherever it is technically feasible to do so, the outputs from the different tiers of the MAMPEC exposure assessments should be compared, quantitatively or at least qualitatively, with data from the real environment (e.g. monitoring data which is of sufficient quality and quantity to allow a comparison to be undertaken).

A number of possibilities exist for this qualitative comparison:-

- comparing modelled and monitored water concentrations
- comparing bottom sediment concentration
- comparing concentrations in suspended matter
- comparing observations of K_d based on field data and Kd predicted by MAMPEC (C_{susp}/C_{diss}).

Care should be taken when performing such comparisions to ensure concentration endpoints are consistent. For example sediment or suspended matter concentrations may be expressed on a wet or dry weight basis. Sediment concentrations may be derived from different sampling depths. Different analytical methods may also be used if the monitoring data comes from a variety of sources. Significant differences in the environments that are modelled or monitored may also mean concentrations are not directly comparable. For example modelled concentrations are available within commercial harbour and pleasure craft marina environments. Modelled concentrations are also simulated for the wider environment outside of these scenarios. Detailed reporting of the monitoring sites will aid the comparison process, especially when supported by reliable usage data.

Where significant differences do occur the reasons for such differences should be explored. In particular the key assumptions behind the MAMPEC predictions (e.g. scenario dimensions and environmental conditions, emission rates, degradation, exchange with surrounding areas etc) compared with conditions in the monitored environments should be considered. With regard to degradation rates selected for the MAMPEC modelling, MS agreed at TMII2013 that for the specific purpose of a qualitative assessment of monitoring versus modelling data it may be acceptable to relax the strict criteria of Level P-II approach. In this specific situation only, it is proposed that the F_sed test and positive back transfer rate checks could be dropped to improve the chances of deriving DT50 values from these PII assessments. The qualitative comparison should ideally be performed in a stepwise manner with first tier and refined input parameters.

In most cases it is unlikely that monitoring data can be used directly as a higher tier refinement over modelled concentrations for the purposes of decision making at Annex I level. This is because in most cases it may be difficult to conclude that the monitoring data provides the same level of protection as the standard EU scenarios without very detailed reporting and analysis.

Glossary

Chi2 test: The χ^2-test considers the deviations between observed and calculated values (numerator) for each separate model relative to the uncertainty of the measurements (denominator). The latter term describes the measurement error with a common error model. *Err* is a term of proportionality scaled with the mean observed which describes the dependence on the measured values. The overall measurement error term is thus constant throughout the measurement period.

$$\chi^2 = \sum \frac{(C-O)^2}{(err/100 \times \overline{O})^2}$$

where
C = calculated value
O = observed value
$\overline{O}$ = mean of all observed values (element of scale in error model (denominator))
err = measurement error percentage(element of proportionality in error model (denominator))
The calculated $\chi2$ for a specific fit may be compared to tabulated $\chi^2 m,\alpha$
where
m = degrees of freedom = number of measurements minus number of model parameters
α = probability that one may obtain the given or higher $\chi2$ value by chance.

Degradation: Degradation processes, such as microbial degradation, hydrolysis and photolysis, break down substances in different environmental compartments by transforming them into degradation products. Degradation also includes processes such as oxidation and transformation into microbial biosynthetates or polymerization products, which may result in larger molecules than the parent substance.

Dissipation: Overall process leading to the eventual disappearance of substances from the environment,or an environmental compartment. Dissipation comprises two main types of processes: transfer processes, such as volatilisation, leaching, plant uptake, run-off or erosion that transfer substances to different environmental compartments; and degradation processes such as microbial degradation, hydrolysis and/or photolysis transforming substances into degradation products.

Single first order: Single first-order kinetics (SFO) is a simple exponential equation with only two parameters (M0 – the toal amount of chemical at time 0 and k- the rate constant). It assumes that the number of pesticide molecules is small relative to the number of degrading micro-organisms and their enzymes or number of water molecules in the case of hydrolysis. As a result, the rate of the change in pesticide concentration (dM/dt) is at any time directly proportional to the actual concentration remaining in the system. For SFO kinetics, the time for a decrease in the concentration by a certain percentage is constant throughout the experiment and independent of the initial concentration of the pesticide.

Equation (integrated form)   **Underlying differential equation**

$M = M_0\, e^{-k\,t}$ $\frac{dM}{dt} = -k\,M$

Sink: In the context of kinetic analyses, a sink compartment is any compartment without an outflow, regardless of which components it represents. The sink compartment often represents CO_2, bound residues and minor unidentified residues, as well as any metabolite, identified or not, that is not included in the fit.

References

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Generic guidance for FOCUS surface water Scenarios Version: 1.1
Date: March 2012

FOCUS guidance available from:-   http://viso.ei.jrc.it/focus/dk/