

Final Report

WP3B – Framework on multi-media fate modelling within persistence assessment

Cefic-LRI ECO52 project

Sponsor

European Chemicals Industry Council (Cefic)

Authors

Dr. Stefan Hahn

Fraunhofer Institute for Toxicology and
Experimental Medicine (ITEM)

Nikolai-Fuchs-Straße 1, 30625 Hannover,
Germany

stefan.hahn@item.fraunhofer.de

Dr. Michael Klein, Dr. Judith Klein

Fraunhofer Institute for Molecular Biology
and Applied Ecology (IME)

Auf dem Aberg 1, 57392 Schmallenberg,
Germany

Judith.klein@ime.fraunhofer.de

Date: June 2022

Content

Acronyms and Abbreviations	4
1 Introduction and objectives	5
2 Guiding principles for multi-media fate modelling in P assessment.....	6
2.1 Terminology of Fate, Degradation and Persistence	6
2.2 Degradation rates and lifetime	8
2.3 Multi-media models	9
2.3.1 Range of available multi-media models	10
2.3.2 Input parameters for different models	12
2.3.3 Output from multi-media models	13
2.3.4 Applicability domain of existing multi-media models.....	14
2.4 Current status of multi-media fate modelling within PBT guidance	15
3 Considerations for multi-media fate modelling in P assessment.....	18
3.1 Conceptual and sensitivity analysis.....	18
3.2 Endpoints.....	19
3.3 Overall persistence concept.....	20
3.4 Dynamic multi-media fate modelling.....	22
3.5 Difficult test substances, UVCB and polymers	26
4 Multi-media fate modelling in P assessment	29
4.1 Testing strategy and compartment of concern.....	29
4.2 Remaining concern in untested compartment	31
4.3 Contradictory results from single compartments	34
5 Strategy for multi-media fate modelling in P assessment	36
5.1 Workflow	36
5.2 Uncertainty.....	37
5.3 Multi-constituent and UVCB	38
5.4 Weight of Evidence.....	39
6 Conclusion	40
7 Acknowledgements	43
8 References.....	44
Annex: Comparison of degradation rate, DegT50, lifetime and DegT90	46
Annex: Case studies.....	47

Acronyms and Abbreviations

DegT50	Degradation time 50
DT50	Disappearance time 50
ITS	Integrated Testing Strategy
L RTP	Long range transport potential
MMFM	Multi-media fate modelling
OECD	Organization for Economic Co-operation and Development
P	persistent
PBT	persistent, bioaccumulative, toxic
POP	Persistent Organic Pollutant
Pov	Overall persistence
UVCB	Substances of unknown or variable composition, complex reaction products or biological materials
vP	very persistent
vPvB	very persistent, very bioaccumulative

1 Introduction and objectives

Chemical persistence plays a key role in the determination of environmental exposure making it an important component in risk assessment and regulation. However, existing frameworks under which persistence is assessed have shown some limitations. Chemical degradation rates are prone to wide variability depending on environmental conditions, which is difficult to address in a weight of evidence approach. In addition, many substances are problematic, or fall outside the applicability domain of existing frameworks due to their specific characteristics.

Persistence assessment is usually based on compartment specific half-lives (EC, 2011). These compartment specific half-lives depend on environmental conditions, and thus will have a range for the same substance depending for example on soil type. Remaining concern exist if compartments have been untested, for example if the study is technically not feasible. Moreover, evaluating degradation half-lives using a compartment-by-compartment approach is overly simplistic, and neglects dynamic multimedia exchanges and degradation processes that may have an important bearing on the overall persistence of a substance in the environment. Based on information on adsorption or volatilisation, the influence of an individual specific half-life on overall persistence may indicate if information for all compartments is justified.

Overall persistence is the result of multi-media fate modelling. According to the current REACH guidance R.11, results from multi-media fate modelling could be explored in order to evaluate the environmental exposure and compartment(s) of specific concern. These distribution modelling results should only be regarded as qualitative or semi-quantitative and a case-by-case evaluation is needed (ECHA, 2017). Finally, challenges exist how multi-media fate modelling can assist in the persistence assessment of difficult substances, UVCB or polymers. Overall, guidance is needed to harmonize the use of such multi-media fate modelling in persistence assessment methodologies, to facilitate the use of all available supporting information, and to increase the transparency of any decision.

In this document, based on the outcome of the literature review (WP1) and the modelling exercises (WP3A), a methodology will be prepared how to integrate the multi-media fate modelling and overall persistence concept into the persistence assessment framework to improve the robustness of current persistence assessment methodologies. Under consideration of the applicability domain of the models, the approach will describe in a clear and simple way how to use the models to get information on sensitive and critical parameters. It will demonstrate how the overall persistence can be used to derive evidence on the compartment of concern as well as to decide on remaining concern in untested compartments, and how multi-media fate modelling can help to interpret contradictory results from single compartments. This approach will be supplemented with examples from the exercises, and possibilities will be discussed how it can be used to support the persistence assessment of difficult test substances, UVCBs and polymers.

This document is part of a series of reports produced as part of the Cefic-LRI ECO52 project: 'Expanding the conceptual principles and applicability domain of persistence screening and prioritization frameworks, including single constituents, polymers, and UVCBs.'

2 Guiding principles for multi-media fate modelling in P assessment

2.1 Terminology of Fate, Degradation and Persistence

In Table 1 key-definitions for terms given in the REACH guidance R.7b (Table R.7.9—1 Glossary of terms associated with degradation) are summarised.

Table 1: *Glossary of terms according to REACH guidance R.7b*

Term	Definition
Persistence	A substance that resists degradation processes and is present in the environment for a long time. Specific criteria have been established in Persistent Organic Pollutant (POP) protocols, in the TGD and in REACH (PBT/vPvB; see sections 1.1.1 and 1.2.1 of Annex XIII to REACH). In the latter persistent (P) and very persistent (vP) refers to substances that have degradation half-lives above certain trigger values in surface water, sediment or soil.
Fate	Distribution of a substance in various environmental compartments (e.g. soil or sediment, water, air, biota) as a result of transport, partitioning, transformation, and degradation.
Biodegradation	The biologically mediated degradation or transformation of substances usually carried out by microorganisms.
Abiotic degradation	Degradation mediated through processes other than biodegradation such as hydrolysis, photolysis and interactions with other substances (e.g. oxidation). Abiotic degradation studies typically provide a measure of primary degradation.
Hydrolysis	Decomposition or degradation of a substance by reaction with water
Photolysis	Chemical decomposition or degradation induced by light or other radiant energy. Direct photolysis in natural water involves the transformation of a substance resulting from the direct absorption of a solar photon. Indirect photolysis in natural water sometimes involves the transformation of a substance due to energy transfer from naturally occurring photosensitizers in electronically excited triplet states. However, indirect photolysis more often involves the transformation of a substance due to reactions with transient oxidants such as hydroxyl radicals, molecular oxygen in a singlet electronic state, and peroxy radicals. Indirect photolysis is an important transformation process for substances in the gaseous state in air.
Oxidation	A substance may undergo oxidation/reduction or other transformation reactions (under storage, use etc.). These reactions may be slow and initiated for instance by the atmospheric oxygen or the presence of other oxidising agents.
Half-life, $t_{1/2}$	Term used to characterise the rate of a first or pseudo-first order reaction. It is the time interval that corresponds to a concentration decrease by a factor 2. The half-life and the degradation rate constant are related by the equation $t_{1/2} = -\ln 2/k$. Half-lives are usually expressed in hours or days and can be assigned to either primary degradation or ultimate biodegradation (mineralisation).
DT50	(Disappearance Time 50) is the empirically measured time within which the initial concentration of the test substance is reduced by 50%. It should be stated whether the DT50 refers to primary degradation or mineralisation (ultimate biodegradation)
DT90	(Disappearance Time 90) is the time within which the initial concentration of the test substance is reduced by 90%. In the case of a first-order reaction, this time would be slightly longer than 3 half-lives

Over the past years more terms than listed in Table 1 have been commonly used to describe persistency. Some of them are summarised in **Fehler! Verweisquelle konnte nicht gefunden werden..**

Table 2: Further terms often used to describe persistence

Term	Definition
DegT50	(Degradation Time 50) is the time within which the initial concentration of the test substance is degraded by 50%. It is not mentioned in the REACH guidance but it was invented by FOCUS (2006) and the term is meanwhile quite often used in risk assessment. In contrast to the Half-life, $t_{1/2}$ it is not limited to first order kinetics
Multi-media fate model	Multimedia models describe the total environment by a set of spatially homogeneous boxes; one box for each environmental compartment in which the chemical is assumed to be evenly distributed. The number, size, properties etc of boxes can vary (OECD 36, van Leeuwen and Hermens, 1995)
Overall residence time or overall persistence	The overall residence time is the mean time that a molecule resides in the system, taking into account all intra-media and transfer processes. It is calculated using a multimedia model. In addition an advective residence time can be calculated in which the only losses are by advection, i.e. no reactions and other processes. Finally a reaction residence time can be calculated in which there are no advective and no other losses: this is the definition of overall environmental persistence which is most relevant in this context. The model used can be level II or level III. The level III requires mode of entry information. The level II does not (OECD 36, Scheringer 1996, Webster et al. 1998, Guoin et al. 2000)

In the glossary above reference is given to the Annex XIII to REACH. REACH regulation 253/2011 (Annex XIII; see sections 1.1.1 and 1.2.1) specifies the criteria for the identification of persistent substances (EC, 2011).

A substance fulfils the persistence criterion (P) in any of the following situations:

- a) the degradation half-life in marine water is higher than 60 days;
- b) the degradation half-life in fresh or estuarine water is higher than 40 days;
- c) the degradation half-life in marine sediment is higher than 180 days;
- d) the degradation half-life in fresh or estuarine water sediment is higher than 120 days;
- e) the degradation half-life in soil is higher than 120 days;

A substance fulfils the “very persistent” criterion (vP) in any of the following situations:

- a) the degradation half-life in marine, fresh or estuarine water is higher than 60 days;
- b) the degradation half-life in marine, fresh or estuarine water sediment is higher than 180 days;
- c) the degradation half-life in soil is higher than 180 days.

In summary, the persistence criteria are based on compartment specific half-lives. Moreover as mentioned in the PBT guidance (REACH 2017), “*The P/vP assessment should cover all three (five) environmental compartments (water, marine water, sediment, marine sediment, soil). However, a substance can already be concluded as P or vP if the criteria are fulfilled for one compartment only.*”

In addition similar trigger values are applied within the POP criteria as outlined in the Annex D of the Stockholm convention (SSC 2020). Screening criteria for evidence of persistence are half-life of the chemical in water greater than two months, or that half-life in soil greater than six months, or that half-life in sediment greater than six months. For long-range transport, upon other terms, the half-life in air should be greater than two days for chemical that migrates significantly through the air.

In persistence assessment advection is not considered as a possible removal process. That means reduction of concentrations must be based on degradation or transformation rather than volatilisation

or transportation/advection by the water phase. Typical processes considered for the persistence assessment are:

- Biodegradation
- Hydrolysis
- Photo degradation in air

Principally, photo degradation could also occur in water and soil, but it would be relevant only close to the surface. However, when considering data derived from these abiotic studies it must be considered that they cannot be used on their own within persistence assessment, but may be used as part of a Weight-of-Evidence approach. Furthermore, due to the large variation in the light available in different environmental compartments, the use of photolysis data is not generally recognised for persistence assessment. This is discussed in more details in the Chapter R.7b of the Guidance on IR&CSA.

In this situation the overall persistence seems to be most suitable to assess persistence dependent on environmental conditions. At least, it could decide on the compartment of concern where most effort should be put in to analyse the behaviour of a compound further.

2.2 Degradation rates and lifetime

In the persistence assessment of substances it has to be differentiated between substances which are only removed by transport processes from a compartment (disappearance) and substances which are subject to a true (irreversible) degradation. Degradation of substances is usually by abiotic processes (hydrolysis, photolysis) or biological processes (aerobic and anaerobic biodegradation, mineralization).

Generally (pseudo) first order kinetics is assumed for the calculation of degradation according to following equation:

$$N(t) = N_0 e^{-kt}$$

k = degradation rate constant (1/d)

t = time (d)

This is the only kinetic with a constant half-life independent on the actual concentration. N(t) is the number of molecules. For this reason the substance concentration c could be used instead of the number N. Based on this definition, the half-life (DegT50) of the compound can be easily calculated using the following equation:

$$\text{DegT50} = \ln(2)/k$$

DegT50: Half-life of the compound (d)

However, compounds often don't degrade according to 1st order kinetics and half-lives are not independent on the concentration (FOCUS 2014). Therefore it is recommended by FOCUS (2014) to base degradation on the experimental DegT90. This covers a broader interval for the assessment in case the degradation delays or stops after reaching 50%.

It can be calculated according to the following equation:

$$\text{DegT90} = \ln(10)/k$$

DegT90: Time for 90% degradation of the compound (d)

To compare these DegT90 values with the trigger from Annex XIII (EC, 2011) which are solely half-lives, these values have to be converted. According to the FOCUS guidance (FOCUS, 2014), half-lives can be estimated by dividing the DegT90 values by a factor of 3.32. This approach is not described in the REACH guidance R.11 (ECHA, 2017).

In addition to k or DegT50 or DegT90 the mean lifetime τ is alternatively used to describe the degradation and removal of compounds. It is the time at which the concentration is reduced to $1/e = 36.8\%$ of its initial value and can be calculated according to the following equation:

$$\tau = 1/k$$

For example, the overall persistence (Pov) as a residence time in a system represents usually a lifetime.

However, whereas the DegT50 was defined by FOCUS (2014) purely based on degradation (e.g., biodegradation, hydrolysis, photolysis),

$$k = k_{deg}$$

often the lifetime is used including other processes (e.g., volatilisation, advection or partitioning).

$$k = k_{deg} + k_{vol} + k_{leach}$$

In so far according to FOCUS (2014) the lifetime (disappearance to 63%) corresponds to the DT50 (disappearance time to 50%) rather than the DegT50 (degradation time to 50%).

In contrast, as overall persistence is defined in a closed system, i.e. there are no advective and no other losses out of the system (no export), but only advection and partitioning between the compartments is allowed, the lifetime represents in this case a true degradation in the system.

The degradation rate, DegT50, lifetime such as overall persistence, and DegT90 can be easily converted into each other. A comparison for the criteria as given in Annex XIII (EC, 2011) is summarized in the Annex.

2.3 Multi-media models

Multimedia models describe the total environment by a set of spatially homogeneous boxes; one box for each environmental compartment in which the chemical is assumed to be evenly distributed. The number, size, properties etc. of boxes can vary (van Leeuwen and Hermens, 1995). As presented above persistence criteria are based on compartment specific half-lives. If the criteria are fulfilled for a single compartment a substance can already be concluded as P or vP. However, likelihood of long presence in the environment depends not only on compartment specific DegT50 values but also on the distribution and partitioning/transportation between compartments.

When analysing the equations in multi-media models the overall persistence can be understood also as the average of compartmental half-lives weighted by the mass in the respective compartment of the environment (system), the overall presence in the environment is not influenced by possible long half-lives in single compartments where the substance is absent due to its inherent properties and the resulting distribution to other compartments. For this reason, substances could be persistent in a specific compartment according to the criteria mentioned above without any influence on the overall time of presence in the environment.

As a consequence, the distribution and partitioning/transportation between compartments as calculated by multi-media modelling is essential for the parameter overall persistence, and thus these modelling is a key process in the weight-of-evidence for P assessment.

Multi-media models describe the environment using a set of compartments that are homogeneous subsystems exchanging gas, water, solids, and chemical contaminants with other adjacent compartments (OECD 45). The model could either describe the global environment (e.g., the unit world as described by Mackay and Paterson (1981, 1982) or there are only used to calculate a local, regional, or continental situation (e.g., the model EUSES in the EU). These multimedia models can be used for “benchmarking” known pollutants (OECD 45). Benchmarking is a relative approach for ranking

chemicals by comparing model estimates for LRTP and Pov to a suite of chemicals with known LRTP/Pov values.

Multi-media models can be classified in four levels of complexity (Parnis and Mackay, 2020):

- a) Level I: System at Equilibrium (initial substance loading, but no emissions over time)
- b) Level II: System at Equilibrium (including permanent substance load and degradation)
- c) Level III: Open System at Steady State and Non-equilibrium (constant compartment specific release pattern)
- d) Level IV: Dynamic Open System (variable compartment specific release pattern)

In this framework it is referred to level III and level IV as most suitable for information on weight-of-evidence for P assessment. Though global half-lives can be estimated based already at level II the assumption of equilibrium conditions for the environment is often not adequate. Only at levels III and IV the distribution is calculated dependent on the initial emission into the environment because non-equilibrium conditions are assumed.

The steady state solution (level III) describes the distribution of substance between the considered compartments assuming constant emission at steady state and non-equilibrium conditions. Steady state distribution is calculated for each compartment separately.

Steady state concentrations are usually calculated based on following processes

- emission into the system,
- transport out of the system,
- distribution between environmental compartments
- degradation in the different compartments

“Transport out of the system” is mentioned in the list above because regularly open systems are used to calculate the environmental distribution (e.g., EUSES in the EU). Basically, all local, regional, or continental scenarios are open systems including import or/and export of substances.

In addition to level III (constant emissions over time) level IV describes a dynamic situation. It allows the variation of emission rates. Therefore, it is possible to simulate the accumulation of chemicals in the environment after the start of the emission but also the prediction of the reduction of the chemical in all environmental compartments after the release of the substance was reduced or completely stopped. Finally, only based on level IV simulation it can be estimated how long it will take to reach the (level III) steady state conditions.

2.3.1 Range of available multi-media models

In the following some multi-media models will be described shortly. There are surely more models available appropriate for the P assessment.

Epiwin modelling (Level III) / EQC model / RAIDAR

Originally Epiwin (Estimation Programs Interface running on Windows®) is a collection of physical/chemical property and environmental fate estimation programs developed by EPA's and Syracuse Research Corp. (SRC). However, Epiwin also contains a level III multimedia fugacity model and predicts partitioning of chemicals among air, soil, sediment, and water under steady state conditions for a default model "environment". Some (but not all) system default values can be changed by the user.

Similar model is implemented in the EAS-E-Suite including RAIDAR and the F-Pest model¹. The environmental fate model is similar in many aspects to the EQUilibrium Criterion (EQC) model², but with significant updates outlined in the RAIDAR publications. The release pattern can be selected. Different regional-scale environments and more user-options for parameterizing the environment for fate simulations and other updates are planned for phase 2. These models give as output the %mass distribution, the media concentrations and fugacities. Three different lifetimes will be calculated: (i) reaction residence time, also referred to as Overall Persistence (POV), (ii) advection residence time, and (iii) overall residence time. Please note that the reciprocal overall residence time equals the sum of reciprocal reaction residence time and advection residence time.

The Tool (Level III):

The OECD P_{ov} and LRTP Screening Tool is a closed system three compartment (air, water, soil) level III multimedia fate model. The Tool is a Microsoft Excel file based on VBA (Visual Basic for Applications). The user has to activate the use of macros. The Tool was a result of an OECD/UNEP Workshop on The Use of Multimedia Models for Estimating Overall Environmental Persistence and Long-Range Transport in the Context of PBT/POPs Assessment that was held in Ottawa, Canada, in October 2001 (OECD 2002).

SimpleBox (Level III and/or IV)

SimpleBox is a multimedia mass balance model that simulates environmental fate of chemicals as fluxes (mass flows) between a series of well-mixed boxes of air, water, sediment and soil on regional, continental and global spatial scales. A special feature of this model is that the regional and continental scales are connected - so called nested multimedia model. SimpleBox is operated as Microsoft Excel spreadsheet, supported by numerical computations in R, which are linked to the spreadsheet via RExcel. Documentation has been published for model versions 1-4 in various technical RIVM National Institute for Public Health and the Environment documents. The SimpleBox spreadsheet model, the supporting R-tools and its documentation files are freely available for non-commercial use. A SimpleBox version capable of handling nanomaterials (SimpleBox4.0-nano) is also available. Default scenario sets are available which describe the regional and continental scale as given in the ECHA guidance on environmental exposure assessment (R.16; ECHA, 2016).

MUST (Level III and/or IV)

Multimedia stock pollution tool (MUST)³ is a user-friendly implementation calculating the stock pollution in the environment for the assessment of long term behaviour of chemicals. The basic fugacity model is based on Mackay III and Mackay IV (Mackay and Paterson 1982). Scenario parameters can be freely changed by the user. Default scenario sets are available which describe the regional and continental scale as given in the ECHA guidance on environmental exposure assessment (R.16, ECHA, 2016). Additionally emission entries can be modified using a sewage treatment plant (STP, SimpleTreat).

Focus models

FOCUS models are special multimedia models to estimate concentrations in ground and surface water. They were originally developed for the registration of pesticides. However, they are meanwhile used also in the registration of other active substances (e.g., biocides, veterinary compounds) in the EU. FOCUS models are dynamic numerical models which do not use the concept of fugacity. According to the above definitions for multi-media models they could be best classified as level IV models. As they

¹ [EAS-E-Suite - ARC Arnot Research & Consulting](#)

² <https://www.trentu.ca/cemc/resources-and-models/eqc-equilibrium-criterion-model>

³ https://www.ime.fraunhofer.de/en/Research_Divisions/Division_AE/Software_E/MUST.html

only reflect part of the environment (e.g., surface water) they cannot be used to estimate the overall persistence of substances.

2.3.2 Input parameters for different models

Substance related important input parameters for level III and IV multi-media fate models are:

- Degradation rate constants or half-lives in the environmental compartments (water, sediment, soil, air); sum of biodegradation and hydrolysis (and photolysis) in the different compartments.
- Partition coefficients between the compartments (K_{oc} , K_{aw})

In order to reduce the complexity multi-media fate models calculate partition coefficients for water-soil or water-sediment based on the K_{oc} (sorption constant in soil related to the organic carbon content) and the organic carbon content in soil or sediment. Though this is an acceptable methodology for the majority of organic compounds it limits the applicability of the model to these type of substances. Instead of using K_{oc} , compartment specific sorption constants (K_p) can be used directly for each compartment type (soil, sediment suspended matter) without using equations to estimate K_p values via the organic carbon-content normalized K_{oc} . No way which way will be chosen, the model itself uses at the end compartment specific sorption constants. There are substances classes (e.g., weak acids, pK_a about 3 to 5) which sorption constant show a significant pH dependency rather than correlation with organic carbon in soil. When these substances are simulated the model have to be improved by estimating sorption constants based on organic matter and pH in soil. The theory for this dependency is well established and already considered in the FOCUS models (FOCUS 2009). In order to simulate sorption in soil correctly dependent on pH following additional input parameters are needed

- Sorption constant K_{oc} at minimum pH
- Sorption constant K_{oc} at maximum pH
- pK_a -value of the substance

Apart from the K_{oc} (in the model responsible for the distribution between water and soil) also Henry's law constant plays an important role as it drives the distribution between air and water. For many compound this constant can be easily calculated based on vapour pressure, water solubility and molar mass. However, in exceptional cases (e.g., no water solubility, formation of hydrogen bonds) the respective equation doesn't work and Henry's law constant must be obtained differently. Again, multi-media models have to be improved in case they simply use water solubility and vapour pressure for calculating Henry's law constant. The simplest way here would be the acceptance of this constant as an additional input parameters instead of estimating it.

In addition, use specific information are important input parameters for Level III and IV simulations as well:

- Initial emission rates into the compartments (release pattern (mode of entry))
- Connection to sewage treatment plant can change the initial emission rate

Results from Level III and Level IV simulations are dependent on the release pattern of the substance. Sewage treatment plants (STP) will probably change the mode of entry to the compartments, and thus will be an important input parameter for the overall presence in the environment of a chemical as well. For example industrial substances are often emitted into water. If the chemical will be distributed in the STP into air due to volatility, the altered release pattern should be considered within the multi-media fate models. For this the fraction emitted to air and water could be adjusted based on the K_{aw} . In addition, in some countries sewage sludge will be

applied to agricultural soil. In this case, for adsorbing substances the mode of entry will be shifted in the direction of soil instead of water.

Apart from these input parameters the calculated distribution and the overall persistence is sensitive to, but cannot be changed in all models:

- Definition of the environment (e.g. relative size of compartments)

Especially, the compartmental dimensions (volumes, depths) or better the relative size of compartments and environmental “quality parameters” like organic carbon content in soil and sediment will also influence the distribution considerably.

Open systems (i.e., calculations including transport parameters out of the system like residence times in air or water) should not be used to calculate the overall persistence since these parameters dominate the distribution between compartments.

Compared to the above mentioned parameters additional small compartments (e.g., suspended solids or biota in water) do not significantly change the calculated distribution because their volumes are relatively small. Therefore, results with OECD ‘the tool’ (only three compartments: water, soil, air) are well comparable with more complicated environmental models (e.g., MUST: air water, soil, sediment, biota, suspended sediment) if the major volumes of the major compartments and the fluxes are defined comparably (i.e., no transport out of the system in both models).

2.3.3 Output from multi-media models

Multi-media models calculate several output parameters which can be important for the persistence assessment:

- **Steady state distribution**
The steady state distribution is an important output of a level III simulation. It shows the distribution of the substance in the system after an infinite number of years. It is dependent on substance specific input parameter (partitioning, degradation), the release pattern and the definition of the environmental scenario (number of compartments and sizes). The steady state distribution can be calculated for **closed systems** (e.g., global scale) as well as for **open systems** (regional, continental scale).
- **Overall persistence**
The overall persistence can be expressed as the residence time of the chemical in the system, which is the mass of chemical in the box divided by the total rate of output (or input when steady-state applies). It is calculated using a multimedia model and does usually not include any transportation (losses) outside the system borders. As a residence time it represents the lifetime in a **closed system**. However, it can also be easily converted into half-life. In this case the overall persistence is basically the mean of half-lives for the single compartments weighted by its distribution between compartments using level III simulation (which assumes steady state conditions). Under unsteady-state, or dynamic conditions, principally a “dynamic” overall persistency could also be calculated during a level IV simulation.
- **Regional/continental lifetime (convertible to Regional/continental DT50)**
The regional and continental lifetime give suitable information about the actual disappearance of a substance in the environmental compartments based on a level III calculation. They are also output of a level III calculation. As regional and continental scenarios are defined as **open systems** (including outflow via the air or water compartment) they also include transportation outside the system (e.g., outside Europe). The regional and continental lifetime give an estimation for the overall concentration decline in an open environmental system when the emissions would stop.

- **Compartmental clearance time or lifetime**
The compartment specific lifetime is a parameter obtained by level III modelling. According to the definition of this parameter (i.e., the ratio of the total mass at steady-state for the compartment divided by the emission mass flux entering the compartment (see Wegmann et al. (2009)). It can be calculated only to environmental compartments which receive direct emissions (e.g. soil). Similar to the regional/continental half-lives it delivers information about the decline after emissions stopped.
- **Area under curve**
The area under the curve is a level IV parameter and describes the distribution of a substance under non-steady state conditions. It describes in principle a similar situation as the steady state concentrations but it gives also information about the variation of distribution with time. If the steady state concentration (level III) differs significantly from the area under the curve, the level III steady state concentrations are questionable.
- **Reduction (%) (maximum value divided by end value)**
This is a level IV parameter which is comparable to the “Clearance time in compartment”. However, here in contrast to the time for a fix reduction (69.3% for lifetime or 50% for DT50) the actual reduction to a certain percentage after a fix time period (e.g., 10 years) without emission is calculated. This parameter elucidates how fast clearance would be if the decline were dynamic.

2.3.4 Applicability domain of existing multi-media models

For many years multi-media models are used in the exposure assessment of chemicals. In the European Union the model EUSES, a fugacity (Mackay) level III model, is recommended to calculate environmental concentrations to be used in the risk assessment of general chemicals (ECHA, 2016). Mackay level III models are also given as supporting information for the persistence assessment in REACH guidance R.11 (ECHA, 2017). Discussion and information on applicability of multi-media models for P assessment is additionally given in OECD 36 (OECD, 2002).

Due to the small number of environmental compartments in combination with high scales (continent, region) models like EUSES are only suitable for calculating generic concentration. The result represent average concentrations and distribution which are perfectly suitable for calculating endpoints like the overall persistence or residence times.

Especially the assumption of instantaneous mixing within a phase (e.g., water) makes it difficult to compare the results with measured concentration (e.g., monitoring data). Instead the FOCUS models are suitable for direct comparison with measured concentrations.

In addition, the multimedia fate models are difficult to use for inorganic and organometallic material. The reason is that often different distribution processes are relevant for such chemicals. Moreover, if adsorption processes are based on ionic interactions, these have to be considered by using for example compartment specific K_p values instead of the organic carbon normalized value K_{oc} . In this case the pH dependency has to be considered as well.

2.4 Current status of multi-media fate modelling within PBT guidance

An Integrated Assessment and Testing Strategy (ITS, Figure 1) for persistence assessment is given in Figure R.11-3 of the PBT guidance R.11 (ECHA 2017), and the associated explanatory notes: “The testing strategy should aim to conclude on persistence with the least possible efforts in testing and at the same time cover the assessment of persistence in all environmental compartments (marine water, fresh or estuarine water, marine sediment, fresh or estuarine sediment and soil).” The R.11 guidance further points out that in order to reduce the amount of testing, the studies should be selected in such a way that they describe worst case conditions for analysing the persistence potential. This would also ideally be the environmental compartment with the best possibility to use the results for concluding the P/vP-assessment (as being “worst case”).

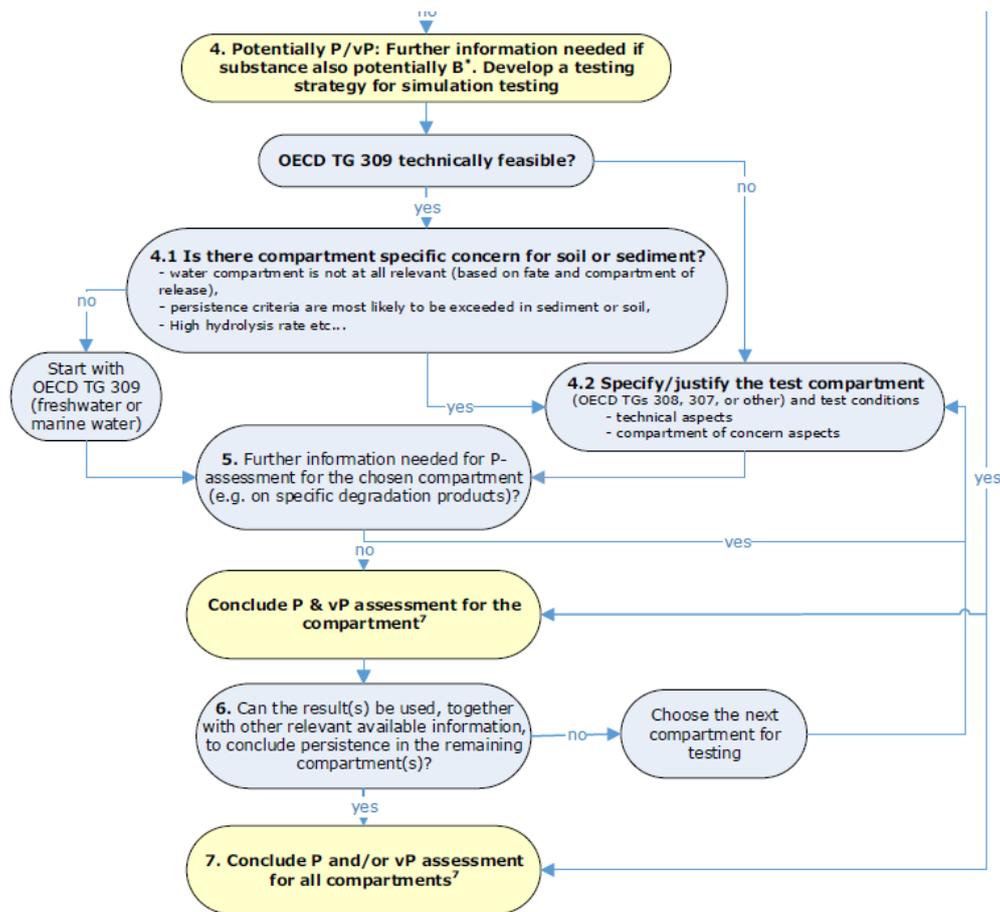


Figure 1: Second part of the Integrated Testing Strategy (ITS) for persistence assessment of REACH guidance R.11 (ECHA, 2017)

Multi-media modelling are useful for and partly specifically mentioned in different parts of this ITS.

ECHA (2017), explanatory notes to figure R.11-3: Section 4.1: “Information on degradation and from environmental monitoring data, emissions estimated in the CSR, distribution modelling data (e.g. Mackay Level III) and physico-chemical information should be assessed to determine whether there is an environmental compartment (pelagic surface water, pelagic marine, sediment, marine sediment or soil) of specific concern for persistence [...] Consideration of the environmental compartment(s) of most relevant exposure may also play a role in the identification of the specific environmental compartment for testing. Absence of exposure in a specific environmental compartment may, in exceptional cases, be acceptable to exclude certain compartments from the P/vP assessment. The following pieces of evidences may help in the identification of the potential environmental compartment of specific concern: [...] The life-cycle is well characterised and the environmental emission and exposure

assessment (including environmental fate, modelling and/or monitoring data) show that a specific environmental compartment is exposed.”

ECHA (2017), explanatory notes to figure R.11-3: Section 4.2, Specify/justify the test compartment: “[...] OECD TG 309 is the preferred test. If another test is selected for further testing, this should be justified. Possible reasons are [...]”

- Indications from available data (e.g. literature) suggest that persistence is likely to occur in a different environmental compartment (i.e. in soil or sediment), including evidence of direct or indirect exposure.
- The substance is a multi-constituent / UVCB which affects the test substance concentration at which the test can be performed (i.e. due to different multiple water solubilities of the individual constituents). “

ECHA (2017, explanatory notes to figure R.11-3: Section 6: “Exclusion of (a) certain environmental compartment(s) from the P/vP assessment based on absence of exposure may be acceptable only in very exceptional cases and upon justification. A justification of absence of exposure in (a) certain environmental compartment(s) is different from a justification for the purpose of normal quantitative risk assessment, because for (potential) PBT/vPvB substances, and hence for the PBT/vPvB assessment, distribution over a very long timespan would need to be considered as well.”

In addition, information on multi-media fate modelling is given in a separate chapter of the PBT guidance R.11 (ECHA, 2017) in chapter R.11.4.1.1.4.:

“Results from multi-media modelling (e.g. Mackay level III model as this is included in the EPIWIN QSAR package) could also be explored in order to evaluate the environmental exposure and compartment(s) of specific concern. Typically, the results used from such models are the relative (%) mass of the substance (in a steady state situation with continuous environmental release) in each environmental compartment, in a simple “Unit world” consisting of air, surface water, sediment and soil. Typically, the default situation is assumption of an environmental release pattern with equal release to air, surface water and soil (see the default settings in the Mackay level III part of the EPIWIN). It should be noted that the results of such models should be regarded as qualitative or at most semi-quantitative as they strongly depend on the relative size of the environmental compartments, the emission pattern and partitioning and transformation parameters employed in the modelling. Contrary to the result of Mackay fugacity level I modelling, Mackay level III modelling is also dependent on the release pattern (fraction of emission between air, water, soil) and thus also on the use of the substance.”

Further information is available in the outdated version of the PBT guidance from 2014 (ECHA, 2014):

[...] „ Nevertheless a case-by-case evaluation of the results of such models may be useful and may even indicate whether or not pristine environmental compartments (e.g. open sea) may be exposed to a significant extent (i.e. indicate a potential for long range environmental transport via the atmosphere).” “A number of multimedia models are available as well as a number of studies on comparison of these different models. One of the most relevant studies in the current context is the study performed by an OECD expert group which describes a comprehensive comparison of 9 multimedia models (Fenner et al., 2005).” [...] “When significant atmospheric transport can be ruled out as a distribution process on the basis of multimedia modelling or due to a short degradation half-life in air, then the relevant compartment to be investigated is that exposed via the water phase, i.e. receiving waters such as rivers, lakes, estuaries, the coastal zone, and/or their respective sediments.”

In conclusion, the persistence criteria are based on compartment specific half-lives. The persistence assessment should cover all three (five) environmental compartments (water, marine water, sediment, marine sediment, soil), and if the criteria are fulfilled for one compartment, a substance can already be concluded as P or vP. An Integrated Assessment and Testing Strategy (ITS, Figure 1) is given for persistence assessment. By considering this ITS (and its explanatory notes), multi-media fate modelling may be helpful

- (a) to decide on the compartment(s) of specific concern (tier 4.1 and 4.2), as well as
- (b) to support a weight-of evidence to decide on remaining concern in untested compartments (tier 6).

However, although explanatory notes discusses use of multi-media fate modelling to decide on testing strategy, it is unclear how this can support in practice fulfilling the aim to conclude on persistence with the least possible efforts in testing. In addition, it is not apparent that multi-media fate modelling can be used to exclude assessment of a compartment (absence of exposure or limited relevance on overall presence in the environment). Moreover, several endpoints are available from multi-media fate modelling such as relative (%) mass of the substance in a steady state situation or the overall persistence with different value for persistence assessment. Finally, the usefulness of multi-media modelling is limited by its uncertainty due to model parameters, relative size of the environmental compartments, and the release pattern.

In practice,

- lack of informative value of multi-media fate modelling results in developing a testing strategy and remaining concern
- lack of guidance on selection of models and suitable scenarios (e.g. relative size of the environmental compartments, and the release pattern, etc.)
- lack of technical guidance exist when preparing consistently and transparently justifications using multi-media fate modelling results such as overall persistence in a weight-of-evidence approach for persistence assessment. No specific threshold/criteria are given.

Overall, all these points limit the suitability of multi-media fate modelling in persistence assessment in Europe although mentioned in the ECHA guidance to persistence assessment. Usually, often all compartments still have to be assessed without using the information from multi-media fate modelling.

3 Considerations for multi-media fate modelling in P assessment

As mentioned above the persistence assessment of chemicals is based on the evaluation of the degradation half-lives for single compartments (water, sediment, soil) in comparison to specific trigger values. However, depending on the substance properties (and use pattern) some compartments might be more relevant than others, i.e. are compartments of specific concern. Multi-media modelling enables the possibility to consider the distribution and the partitioning/transportation between the compartments in the persistence assessment. Thereby, Level III multi-media models give information about the level and the distribution of contaminations at the steady-state and estimate the overall persistency of compounds. In addition level IV multi-media models give information about the time at which steady state (the plateau) will be reached, but also the clearance time after emission has been stopped. More information how multi-media models could be used in P assessment is summarised in OECD 36 (OECD, 2002).

3.1 Conceptual and sensitivity analysis

The calculation of overall persistence or other endpoints using multimedia fate models is a complex process. The result is primarily dependent on substance specific input parameters and the release pattern (mode of entry), but also on environmental specific parameters such as definition of the environmental compartments, i.e. relative size of compartments.

An evaluation of different multi-media fate models from Fenner et al (2005) using correlation coefficients indicate that often the overall persistence is in general agreement. This has been confirmed by Wegmann et al. (2009) with the correlation coefficients between P_{OV} and LRTP calculated by The Tool and other models for emissions to air.

With regard to scenario definitions these evaluations indicate that the number of compartments and especially the absence of model compartments (e.g., sediment) and the differences in compartment dimensions (e.g., depth of the water compartment, land-to-water surface ratio, open/closed scenarios) lead to significant differences of the overall persistency.

In addition, use specific information such as the release pattern (mode of entry) has a significant impact on the steady state distribution and thus the overall persistence. For this reason, the mode of entry and the alteration should be soundly selected and justified in using the multi-media fate models as supporting data (evidence) in P assessment. However, the starting point according to the PBT guidance R.11 (ECHA 2017) is a release pattern with equal release to air, surface water and soil. If a more relevant /realistic release pattern can be assumed based on knowledge about use of the substance, the model should be run with an appropriately changed release pattern. Typically, but depending on the use profile of the substance, it is relevant to run such models assuming the default environmental risk assessment emission pattern, e.g. release to water only (ECHA 2017). The mode of entry could be altered by the connection to a sewage treatment plant (STP). In this case volatilisation to air will change the emission into surface water, and adsorbing to sludge may result in an indirect emission to soil.

With regard to substance input parameter most relevant for the overall persistency is the degradation rate in the compartment where the substance is expected to accumulate. For substances with high P_{ow} these compartments are usually sediment and soil, whereas for substances with low P_{ow} the degradation in water is most relevant. Volatile substances often don't accumulate in any of these environmental phases but will partition to the air. Dependent on the scenario definition (open/closed system) they will either be transported out of the system or/and degraded by the sun light.

A sensitivity analysis using the model MUST (level III and level IV) where all kind of input parameters were included (Klein 2021) showed that the most sensitive parameters were dependent on the type

of substance and their properties. The conclusion was that for substances with high Koc (e.g., HBCDD) the degradation in soil was most relevant as long as the release pattern was not extreme (e.g., emission 100% to air). The overall persistence is then relatively stable against changes of the environmental scenario and always dominated by the degradation in soil. Other compounds (e.g., bisphenol A) stay mainly in the environmental compartment to which they were emitted. The overall persistence of these type of compounds is dominated by the degradation rate in the initial compartment. In contrast, the overall persistence of compounds, which are distributing to all environmental compartments (e.g., D4), is dominated by the scenario definition (e.g., soil depth, connection percentage to waste water treatment plants).

With regard to the question should the calculation be based on level III or level IV models the same author suggested level III simulations for most of the compounds because as shown by level IV simulations steady state is reached fast within a couple of months (e.g., for HBCDD, D4, Bisphenol A). After this period the results of level III and level IV wouldn't differ assumed the same (constant) release pattern is used. However, steady state will not be reached within a manageable number of time (e.g. 10 years) if the half-lives of the compound are extremely long. Klein demonstrated that a level IV simulation over 10 years significantly differs from respective level III results for Dechlorane plus with assumed DegT50 of 10^6 days in water and sediment and 350 000 days in soil, respectively (Klein 2021).

In conclusion, the variability and reliability of following parameters should be addressed in performing and interpretation of results from multi-media fate models within P assessment such as steady-state distribution and overall persistence:

- Substance specific parameters such as degradation rate constants or half-lives in the environmental compartments (water, sediment, soil, air); Partition coefficients between the compartments (Koc (or better specific K_a values), K_{aw})
- Environmental specific parameters such as relative size and number of compartments
- Use specific parameters such as release pattern (mode of entry)

The impact of substance specific parameters is beneficial to understand and interpret the expected overall time of presence of chemicals in the environment. These parameters will determine the expected time of presence in the environment and the accumulation potential, and thus the classification as P or not P. However, several other parameters are influencing the results as well, and thus should be considered in the uncertainty analysis, or better should be harmonized for comparable persistence assessment.

3.2 Endpoints

Different endpoints from multi-media fate modelling are available such as steady-state distribution, and overall persistence. Further alternative endpoints are the regional/continental lifetime or the compartmental clearance time as well as the Level IV endpoints area under curve, and reduction potential (reduction in percentage for a given time period). With regard to the assessment of persistence these endpoints are of different importance.

According to the R.11 REACH guidance *“Typically, the results used from multi-media fate models are the **relative (%) mass of the substance** (in a steady state situation with continuous environmental release) in each environmental compartment, in a simple “Unit world” consisting of air, surface water, sediment and soil.”* However, whereas it is clear that the compartment with the highest % distribution is a relevant compartment (compartment of concern?), it is often not clear if a compartment with 10% distribution or lower is still be of specific concern. For this reason, the endpoint “steady-state distribution” is of lower value to justify on the testing strategy or decide on persistence.

Another option is the **overall persistence**. Putting it simply, overall persistence is the mean of half-lives for the single compartments weighted by its distribution between compartments. A relatively low overall persistence is calculated when according to the distribution parameters the substance is partitioned into compartments where the substance is fast degrading. In contrast, high overall persistence can be expected when the compounds partitions into compartments with low degradation. The overall persistence does by definition usually not include any transportation (losses) outside the system borders. For this reason, the overall persistence cannot be compared with the actual decline observed in an open system in the environment after emission have stopped (i.e. as represented by lifetime or clearance time). That means the overall presence in the considered system could be completely different between open and closed systems even if the degradation half-lives in the environmental compartments are exactly the same.

As the **regional/continental lifetime** is based on an open system it may be primarily caused by transportation outside the system rather than degradation. In addition, concentrations outside the system could even accumulate. For this reason, lifetime or clearance time are probably not appropriate for persistence assessment, or only in cases where the transport outside of the system is not likely. It can only be used case by case as supporting information.

The situation is also dependent on substance properties. Substances which quickly reach steady state conditions (e.g., moderate degradation and sorption, see also the modelling report WP3A) can be sufficiently assessed based on Mackay level III modelling. For those substances the parameter “overall persistence” is most important. If compounds do not reach steady state conditions fast evaluation based on Mackay level IV models may be more appropriate because the distribution of the substance after a manageable number of years may be very different from its final distribution. For this type of compounds models which calculate a **dynamic overall persistence** may be more suitable in the persistence assessment. Furthermore, the **area under curve or the reduction (%) after a fix time period** (e.g., 10 years) without emission, i.e. after emissions stopped, may be useful to illustrate and rate the expected decline in the system instead of the total life time.

3.3 Overall persistence concept

Instead of evaluating compartment by compartment as suggested by Annex XIII (EC, 2011), the overall persistence can be used directly to get information about the long-term presence in the environment. As a result of multimedia fate and transport models it can be applied to support more realistic, and relevant P assessments than single compartment P models (Redman et al, 2021).

Overall persistence sets individual degradation rates for sediment, soil and water into context by considering the distribution of the substance at steady state conditions. Especially if the air compartment has a significant influence the single compartment approach is not sufficient, as it considers only water, sediment and soil. Volatile substances which are persistent in air could be false negative in the single compartment approach, or false positive if they are degradable in air. For example, McLachlan (2018) argued that persistence in any surface medium, is not sufficient for Octamethylcyclotetrasiloxane (D4). Although it has a half-life in sediment of 242 – 365 d, and an initial assessment indicates that D4 meets the POP criteria, model simulations clearly demonstrate that the initial assessment is at least debatable. This indicate that additional to single compartment half-lives case by case further information might be needed to better understand the behaviour of the substance and to come to an adequate conclusion.

Information on overall persistence can be used to justify on the testing strategy, and the remaining concern in untested compartments. Moreover, it may be helpful to understand and interpret single compartment results. If contradictory results on persistence exist for different compartments, it can solely be used to judge on the actual likeliness of the long-term presence in the environment.

Chemicals that are classified as P because of a high half-life in one compartment might be not regarded as persistent in the case where this half-life has no significant influence on overall persistence due to degradability in the other compartments where they transported in or mainly appear. However, in these cases the time for the transport will be relevant as well. For example a complete dataset is available for a substance, which is persistent in water (slightly above the trigger), and the same substance is not persistent in soil or sediment. Depending on the partitioning properties of the substance, the persistence in water may only have a marginal effect on the overall persistence and the long-term presence in the environment, and thus in this case the half-life in water should not be overvalued. Another example would be very volatile substances, so that concentrations in water (or soil) are negligible, especially if the substance is rapidly degraded in air. However, several model scenarios (e.g. release pattern (mode of entry), relative size of compartments) should be performed to cover different reasonable situations and to justify that the water (or soil) compartment has a negligible influence. In addition, the transport rate between the compartments has to be considered.

Besides using overall persistence as an additional evidence in the interpretation of single compartment results, it can also be used as an own metric. However, it is difficult to directly compare the overall persistence with the trigger value given in Annex XIII (EC, 2011). Is the degradation < 40 days more relevant than < 120 days? Is a value between both values most appropriate, e.g. 90 days (as suggested by Scheringer and Matthies (2006))? Please note the 90 days is a lifetime corresponding to about DT50 = 60 days.

The sensitivity analysis has shown, that the overall persistence is often dominated by degradation in soil, which suggest that 120 d (or 180 d) will be the most appropriate trigger. However, other substances will be dominated by the degradation rate in the initial compartment where the substance is emitted (mode of entry), and finally some substances which are distributing in significant amounts to all compartments are dominated by the environmental specific parameters (e.g. number of compartments, relative size of compartments, considering waste water treatment plants).

A meaningful trigger for the overall persistence could be based on the dominant compartment instead of using one for all. This dominant compartment is defined as the compartment with maximum distribution in steady state and strong correlation of overall persistence with the respective half-life in this compartment.

Table 3 presents the recommended trigger for the overall persistence. These are the trigger from Annex XIII with the adaptation that for the overall persistence concept only the dominant compartment, which has to be clearly justified, is deciding. The trigger values are given as DegT50 values to be directly comparable to the single compartment trigger. However, it can easily be converted into lifetime values (see chapter2.2).

Table 3: Recommended triggers for the overall persistence (expressed as DegT50, Pov or DegT90) dependent on the dominant compartment

Dominant compartment ^o	Trigger for persistent compounds (d)			Trigger for very persistent compounds (d)		
	DegT50	Pov	DegT90	DegT50	Pov	DegT90
Water	40	60	133	60	90	200
Sediment	120	175	400	180	260	600
Soil	120	175	400	180	260	600
Air		?			?	

^o Compartment with the maximum distribution in the multi-media calculation and strong correlation of overall persistence with the respective half-life in this compartment

As mentioned above, compounds often don't degrade according to 1st order kinetics and half-lives are not independent on the concentration (FOCUS 2014). Therefore it is recommended to base the degradation rate on the measured experimental DegT90. This covers a broader interval for the assessment in case the degradation delays or stops after reaching 50%. However, independent on considering DegT50, lifetime or DegT90 values for the assessment, for persistence assessment it is important that always only true degradation is considered.

Advantages of overall persistence concept

- Sets individual degradation rates for sediment, soil and water into context by considering the distribution of the substance at steady state conditions.
- Considers not only water, sediment and soil, but also impact of fate in air compartment.
- Will help in the interpretation of contradictory results between compartments and the influence on the expected time of presence in the environment.

Further advantages have already been described by Scheringer and Matthies (2006).

Disadvantages and uncertainties

- Overall persistence is not directly comparable to the Annex XIII trigger values. The approach for selection of the dominant compartment should be verified.
- Distribution may be influenced by the multi-media fate model and the scenario definition (e.g. release pattern, number of compartments, relative size of compartments). Several different scenarios have to be performed covering different reasonable scenarios.

Nevertheless, we believe that the overall persistence concept based on level III modelling is the perfect parameter to describe the persistence of compounds. It does meet the criteria for an appropriate parameter for the expected long-term presence in the environment. Multimedia fate and transport models represent powerful tools that should be used to evaluate P in chemical regulation and environmental risk assessment (Redman et al, 2021). However, it is necessary to give guidance which scenarios (e.g. release pattern, relative size of compartments) are most reliable, and to give guidance how to select the most dominant compartment. The selection must be sufficiently justified.

3.4 Dynamic multi-media fate modelling

In addition to level III (constant emissions over time) level IV describes a dynamic situation. It gives an indication of whether environmental concentrations of a substance are expected to stabilize, or continue to rise (leading to ever greater accumulation and exposure). Only based on level IV simulation it can be estimated how long it will take to reach the (level III) steady state conditions. In addition, level IV modelling allows the variation of emission rates. Therefore, it is possible to simulate the accumulation of chemicals in the environment after the start of the emission but also the prediction of the reduction of the chemical in all environmental compartments after the release of the substance was reduced or completely stopped.

Only a level IV analysis can answer the questions

- How long does it take to reach steady state (and if the level III results are valid)?
- How long does it take to reach a certain decline after emissions reduced to some extent or totally?

Level IV multi-media fate modelling result additionally in the endpoints area under curve, and reduction potential (reduction in percentage for a given time period).

The overall persistence is usually based on steady state concentrations. However, this steady state is far in the future if in specific compartments the degradation is significantly slower than the persistence

criteria, and it is unclear if the corresponding overall persistence reflects also the situation in the near or mid future. In these cases the dynamic multi-media fate modelling provides additional information which may be useful for the weight-of-evidence in the persistence assessment. Level IV modelling can provide the alteration of the overall persistence over time, i.e. a time-dependent overall persistence $Pov(t)$. This is illustrated for two example substances in Figure 3: Time-dependent overall persistence $Pov(t)$ for the example substance D4 (regional scale – closed system – no STP) Figure 3 (Dechlorane plus) and Figure 2 (D4) using constant emission. For further input parameters please consult the report on the modelling exercises.

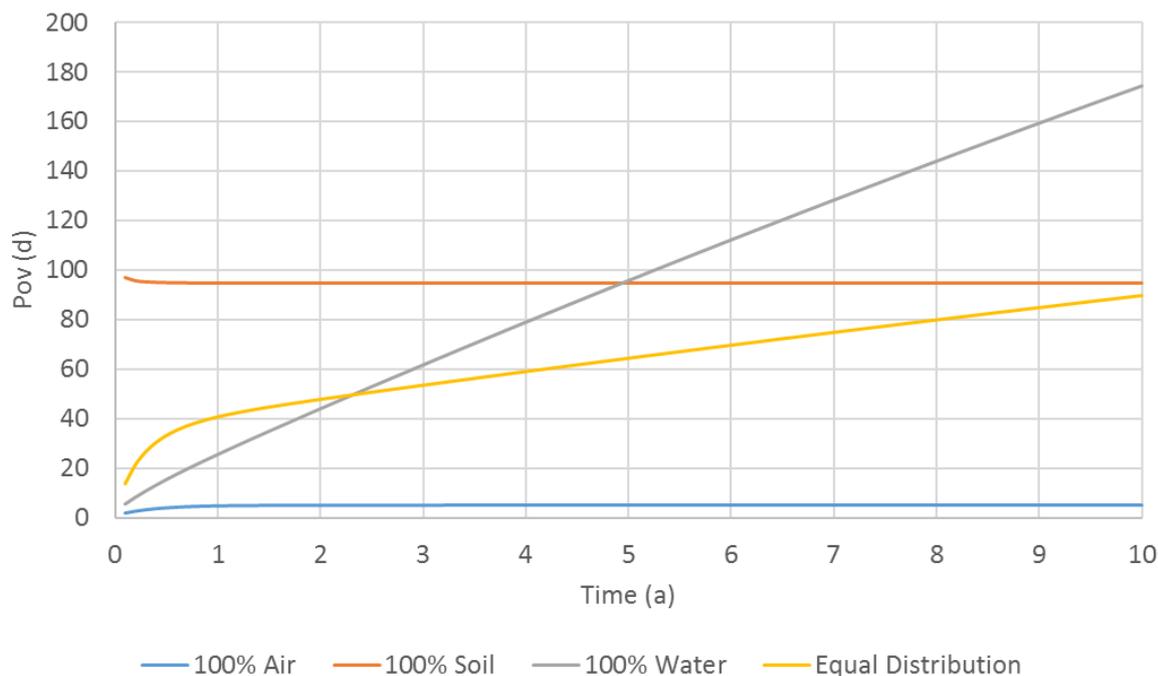


Figure 2: Time-dependent overall persistence $Pov(t)$ for the example substance Dechlorane plus (regional scale – closed system – no STP)

For Dechlorane plus the $Pov(t)$ graph shows that the overall persistence (Pov expressed as half-life) depends on the mode of entry. For the mode of entry 100% to soil the value is stable within the first 10 years and equal to the Pov at steady state (95 days). However, it is increasing over time, if the mode of entry is equally distributed or 100% to water. For comparison, the overall persistence (expressed as half-life) at steady state (Level III) is 4322 days. For this reason, the steady state Pov does not represent the overall presence after short-time exposure very well.

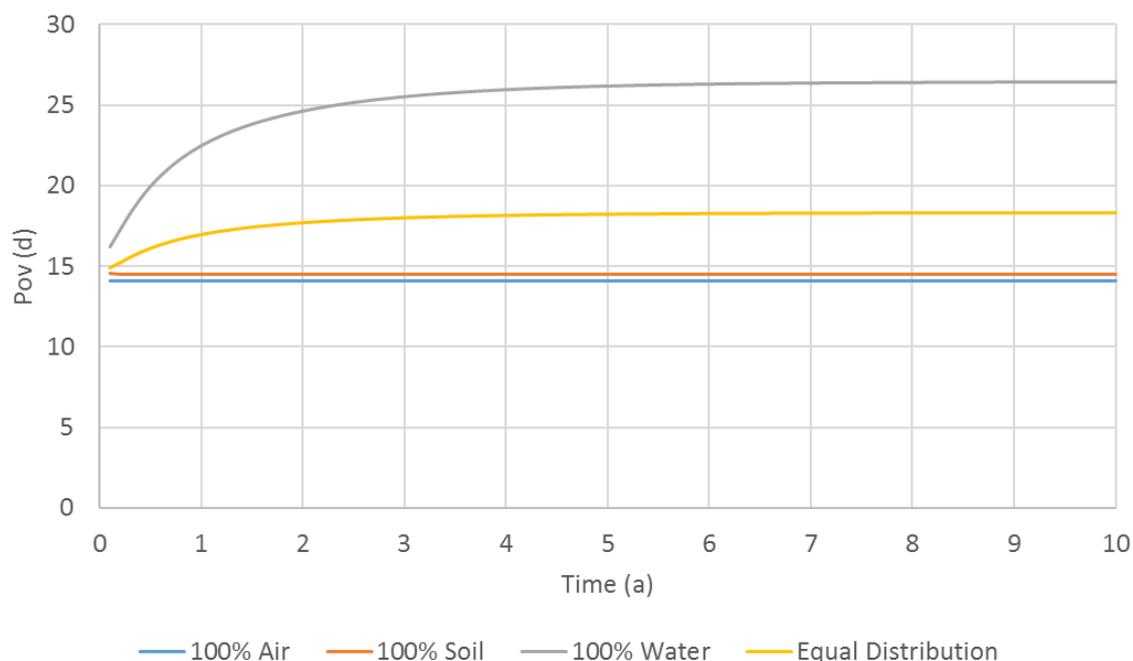


Figure 3: Time-dependent overall persistence $Pov(t)$ for the example substance D4 (regional scale – closed system – no STP)

For D4 the $Pov(t)$ graph shows that the overall persistence (Pov expressed as half-life) depends on the mode of entry as well. However, for this substance the Pov reached a nearly constant value already after a relatively short time of emission (< 5 years). Thus, overall persistence at steady state (using Level III) is representative also for near and mid future. However, in this graph it is not yet diagrammed what happened after emission stopped.

The differences in decline of a chemicals was addressed by Cousins et al. (2019) who simulated the concentrations of two chemicals both with Log Kow of 8 and half-lives of 2 d and 2000 d, respectively. Furthermore, the same half-lives in all compartments were used. Finally, the same dynamic emission with equal amounts into soil, water and air was simulated for both chemicals: start in year 0, increase by 10 mol h^{-1} every year, peak in year 10 at a value of 100 mol h^{-1} . Then the emissions decreased by 10 mol h^{-1} every year. The modelling resulted in typical graphs of expected accumulation and decline of the substance in the environment. Cousins et al (2019) demonstrate that the decline after emissions stopped depends very much on the half-life:

- Fast degrading compound : The concentrations during use are low, the decline is fast
- Slow degrading compound : The concentrations are significantly higher and it takes about 30 years (i.e., 5 half-lives) to reduce the plateau by about 2 orders of magnitude)

In this example the same degradation rate has been used for all compartments for simplifying the results. If this is the case, also the overall persistence has this degradation rate. However, what is the impact on such graphs if the degradation rates are not the same, and in specific case if contradictory results are available for different compartments with regard to persistence, i.e. not persistent in one compartment but persistent in another compartment.

This is illustrated by simulations using MUST (Figure 4). In this example the equal emissions into soil, water and air was simulated over 10 years, followed by a complete stop of emissions. The decline in the environment after the emission stopped is slow due to the long half-life in sediment of 315 d. The level IV also shows that half-life in the environmental compartment are different and in some phases clearance is reached fast (e.g., water).

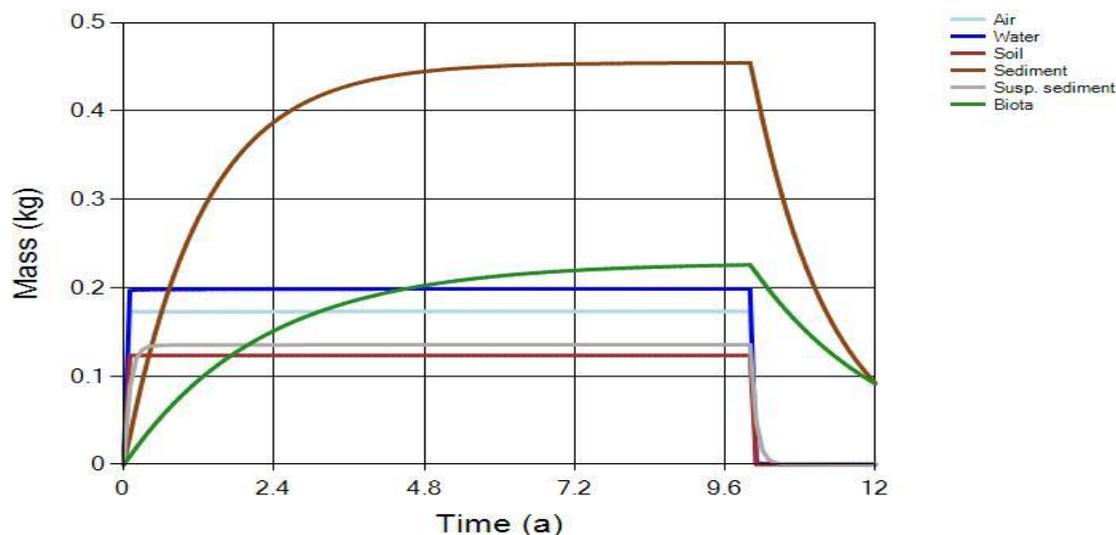


Figure 4: Dynamic masses in the environment for D4 as example substance ($\text{LogKow}=6.5$, $\text{logKaw}=-3.6$) with sediment half-life of 315 days based on dynamic exposure (10 years with constant emission then total stop) using the MUST model

Finally, Kim et al. (2017) made a direct comparison of a level III with a level IV model. The level III steady state distribution was the initial concentration for three different future emission scenarios: stepwise, exponential, and linear reduction of emission. For the exercise they considered three different water bodies (Lake Ontario and Oslofjord and Lake Pepin) and two substances (D5 and PCB-180). For the comparison the response times of D5 and PCB-180 concentrations in water and sediment were considered. Though the dynamic model provides a closer simulation of actual conditions the authors concluded that for many purposes a simple level III model would be adequate for many regulatory purposes.

However, this is not in contradiction to the previous examples since the residence times in the environmental compartment analysed by Kim et al. (2017) were relatively short so that the benefit from a complex level IV simulation compared to the steady state solution was indeed limited.

Overall, steady state will not be reached within a manageable number of time (e.g. 10 years) if the half-lives of the compound are extremely long. However, this seems to be not relevant for persistence assessment as this is not the case if the half-lives of the compound are lower or near the trigger values of persistence (40 d, 120 d, 180 d). In this case, steady state is reached fast within 1-2 years. After this period the results of level III and level IV wouldn't differ assumed the same (constant) release pattern is used, and the benefit of level IV simulation for persistence assessment is limited. However, dynamic modelling can give a better understanding of the processes to be considered in the persistence assessment. Especially if a relatively slow decline is observed in one specific compartment, it shows that this single compartment may be relevant even if the overall persistence is low.

3.5 Difficult test substances, UVCB and polymers

Difficult test substances:

Multi-media fate models can be used to support the justification on testing strategy and remaining concern of untested compartments for difficult to test substances. Substances difficult to test for persistence are for example poorly soluble, sorbing, volatile, toxic to microorganisms, ionisable, complexing, unstable, or chiral compounds. Not all of these properties can be addressed by multi-media fate modelling.

If a substance has a very low water solubility (typically below 1 µg/L), the measurement of the degradation in water may be challenging using OECD TG 309. However, this is probably not necessary, as these substances are hardly found in the water compartment, i.e. the solubility in water can have an impact on the compartment of concern or absence of exposure. In this case, multi-media fate modelling may be used to justify that the water compartment has no influence on the overall persistence, and measurement of degradation in soil, sediment or air will be more appropriate.

The same is valid for volatile substances. It is expected that multi-media fate modelling can be used to justify that water or soil compartment is not of interest, especially if it can be shown that mode of entry is the air compartment as well.

An additional property which result in difficulties to test is the sorbing behaviour. This result often in difficulties to interpret the results, e.g. for OECD 308. Multi-media fate models give insight in the understanding of the influence of the adsorption and the fate and transport between the compartments. As already mentioned above use directly K_a and not K_{oc} for sorbing substances where you have no correlation with OC .

UVCB:

When UVCB substances are released into the environment the different components in the mixture may partition differently in the compartments due to different partitioning properties. As the components could also degrade differently the composition will change with time even though the partitioning properties may be quite similar. Overall, the behaviour of the single components is different.

When simulating the fate of UVCBs with multi-media fate models it is important to realise that the fugacity concept was originally developed for single substances with clearly defined physico-chemical properties (e.g., water solubility, vapour pressure). This situation is the reason why UVCBs are called “difficult” substances.

A possible procedure was to test (and also to simulate) all single constituents separately. However, this is somewhat an extreme view especially when the constituents behave similarly with regard to partitioning and degradation. To evaluate PBT properties of substances containing multiple constituents, impurities and/or additives, specific assessment approaches have been described in the REACH guidance R.11, chapter R.11.4.2.2.2. This includes

- Known constituent approach
- Fraction profiling (or Block profiling) approach
- Whole substance approach

The simplest option is the known constituent approach. In this case each constituent will be evaluated separately, and the multi-media fate modelling will be done with the properties of each known constituent. If the fraction profiling approach will be expected to be most appropriate, the range of properties per fraction has to be specified. In this case several combinations of the input parameters are possible per fraction (min value of each property is used with min and max values of the other

substance properties). This can result in a high number of modelling results representing the expected range of overall persistence. Alternatively, in the block method one or more representative constituent(s) is/are chosen for each of the fractions for which testing and assessment is carried out. This key constituent per fraction represents the behavior of the respective fraction. Multi-media fate modelling can help to justify the selection of representative key constituents by comparing the steady-state distribution and overall persistence of different constituents per fraction. The last option would be the whole substance approach, which is only possible if all the constituents therein can be justified to be very similar. It is a specific case where the whole substance can be seen as one fraction/block with constituents of similar properties and one or more representative constituent(s) is/are chosen for which modelling is carried out. Multi-media fate modelling can help to decide if the whole substance approach is applicable or if the whole substance is better divided in different fractions.

In conclusion, multi-media fate modelling can help to select the most appropriate approach. For example, by modelling the ranges (of Koc and Kaw) for specific fractions it can help to identify if the specification of the fraction is accurate, or a refinement of the specification of the fraction and the assignment of key constituents to these fractions is necessary. Multi-media fate modelling may also be helpful to decide if the whole substance approach is sufficient (impact of distribution of a value in comparison to a specific value).

Modelling could also be used to support testing one or more constituents of a UVCB in the same biodegradation test. Normally simulation tests are conducted on single substances or constituents and concerns have been raised about studies where more than one substance has been tested in the same vessel, as it is suspected that this can promote the degradation of substances via co-metabolism (ECHA, 2017). However, for UVCBs data are generally needed on a large number of constituents and being able to test multiple constituents at once would greatly increase efficiency. Multi-media fate modelling could support justification for this. For example, if constituents are shown to have similar equilibrium or steady state distributions this can support the notion that they are likely to remain in the presence of each other once emitted to the environment as part of a UVCB. An evaluation has been performed in the modelling report (Klein, 2021) to analyse which input parameters are the driving factor that causes different overall persistence based on equal emission into the compartments air, water and soil. The authors used five hypothetical components which covered a significant range with regard to their environmental distribution (range log Pow: 3.5 to 6.1, log Kaw -7.8 to -1.2, Koc 1800 to 22350 L/kg). The degradation in water, soil and sediment varied between 4 and 71 days, 25 and 3000 days and 10 and 2300 days, respectively. The substances were simulated separately using MUST and its regional scenario. Similar as in the sensitivity analysis the dominant compartment was found mostly to be soil for all constituents making the half-life in soil the most important parameter for the overall persistence. The simulations showed that the degradation in water hardly influences these results. Even though that may have been caused by the selection of compound properties, especially the high sorption constant for all constituents it points out that the soil compartment would be of greater importance for the overall persistence than water. Based on these results it was recommended for the chosen mixture to estimate the range of DegT50 in soil of the constituents and to calculate the overall persistence for mass weighted average and worst case situations (e.g., 90th percentile DegT50 in soil). With regard to the other parameters (e.g., Koc-value, DegT50 in water) average values could be considered because they hardly influence the overall persistence. Furthermore, Klein (2021) showed that volatile constituents in UVCBs wouldn't show high overall persistence. That was found because half-life in air is often rather short compared to the other environmental compartments.

Polymers (and microplastic)

The situation for modelling the distribution in the environment for polymers is somewhat similar to UVCB because polymer do have often complex, variable and unknown composition. In addition, they have large molecular sizes, and are often water insoluble and thus exist in particulate physical form.

Insofar the concept of multi-media fate modelling does not hold for these special substances without additional assumptions and adaptations. Furthermore, this class is heterogeneous since there are soluble polymers available which behave differently compared to polymers which do not mix homogeneously with the environmental compartments air, water or soil.

- Water soluble polymers can be simulated in a similar way as UVCB. This includes also simplifications such as modeling only the most representative or the average fraction of molecules, but also the block method as described previously.
- In contrast, following the whole substance approach doesn't seem reasonable for polymers since their composition is often not defined with regard to exact molecular formulas.
- Polymers which do not solve in water but remain small particles can be simulated with specific models (e.g., simpleBox4Nano, MendNano, nanoDUFLOW, iStream, NanoFASE). However, these models are only able to simulate the environmental distribution after these polymer particles have been released into the environment.

As often it is difficult to determine experimentally the classical degradation rates in the environmental compartments, it is currently not possible to estimate the overall persistence for these compounds. At the most existing simulation results could be used to determine the compartment of concern (similar as for classical substances) and develop methodologies to analyse the half-life of these compounds in the dominant compartment further.

4 Multi-media fate modelling in P assessment

In the following different cases will be discussed, to illustrate how multi-media fate modelling can support the persistence assessment, i.e. selection of an adequate testing strategy, obtain information about remaining concern in untested compartments, and how to interpret contradictory results from single compartments. By including multi-media fate modelling the distribution and the partitioning/transportation between the compartments will be considered in persistence assessment.

4.1 Testing strategy and compartment of concern

Usually information from up to five compartments (freshwater and marine water, freshwater and marine sediment, soil) are required based on Annex XIII (EC, 2011). However, depending on the substance properties (and use pattern) some compartments might be more relevant than others. According to the REACH guidance R.11 (ECHA, 2017), *“specific concern for persistence is normally present for the environmental compartment for which the P/vP criteria are most likely to be exceeded or where the degradation half-life is the closest to the criteria (if the criteria are not exceeded)”*. In the sense of the protection goal every compartment which have a significant influence on long-term presence in the environment can be regarded as compartment of specific concern for persistence.

Multi-media fate modelling can give evidence on the compartment of concern. Thereby compartment of concern depends on substance inherent properties such as K_{oc} and K_{ow}, but also on use pattern. However, as mentioned above scenario definition (e.g., absence of model compartments, differences in compartment dimensions) may have significant impact as well.

In addition, multi-media fate modelling can be used as supporting data to justify if a substance is not likely to be expected in a specific compartment (= absence of exposure). As mentioned in the R.11 guidance (ECHA, 2017) *“Absence of exposure in a specific environmental compartment may, in exceptional cases, be acceptable to exclude certain compartments from the P/vP assessment.”* However, a definition is necessary about “absence of exposure”. In the guidance for exposure based adaptation (R.5, ECHA) following information is available:

- Absence of exposure is defined as ‘relevant exposure can be excluded’ or ‘no exposure’). It has to be differentiated to exposure being unlikely (i.e. not ‘absent’ or ‘excluded’), or not significant (‘limited exposure’, ‘no significant exposure’).
- “Likelihood of exposure” to man and environment is “negligible” (= absence of exposure).
- No-release should not mean zero in the scientific sense, but is to be interpreted as ‘practically no release’. Thus, no release should be demonstrated case-by-case based on:
 - ...
 - Resulting exposure concentrations are in the range of the natural background concentrations.
 - The release is so low that exposure of man and the environment can be excluded (= absence of exposure/negligible likelihood of exposure).

Indeed this information is more driven by the risk assessment and the question in which case additional information will result in an improvement (reduction of uncertainty) for the risk assessment. In the sense of persistence assessment, absence of exposure may need a different definition. Some important information is already available in the R.11 guidance (ECHA, 2017) within the explanatory notes about further information needed to conclude on P/vP – Testing strategy (tier 4).

Water is expected to be a relevant compartment *“unless based on the fate and release(s) of the substance, it is considered that the water compartment is not a relevant environmental compartment*

at all.” This is interesting with regard to multi-media fate modelling, as it results in supporting information to justify the relevance of the compartment.

For example a very volatile substance (high K_{aw} , low K_{oc}) may not be able to partition to water or soil, or if it will be after direct emission in water or soil it will evaporate in short time. An evaluation of persistence in single compartments such as water and soil will not give adequate information on the long-term presence in the environment. In contrast, multi-media modelling can be used to show that the degradation in soil or water will not have any impact on the overall persistence.

The second example would be, if a substance has a very low water solubility (typically below 1 $\mu\text{g/L}$). In this case the measurement of the degradation in water may be challenging using OECD TG 309. Due to the low water solubility emission to soil or air is more likely unless solubilizer are present. Emission to water results in partitioning to sediment or air depending on density, K_{oc} or K_{aw} . Multi-media modelling can be used to show that the degradation in water will not have any impact on the overall persistence.

The final case would be if the substance is not adsorbing and it has a high water solubility. In this case soil or sediment compartment is probably not affected.

In a first step, multi-media fate modelling can be used to get steady-state distribution values. This distribution considers the different properties such as K_{oc} and K_{aw} , but also the use pattern can be considered by varying the mode of entry. In addition, initial degradation values for each compartment can be based on QSAR and the influence can be investigated by varying the input parameters. Usually the highest distribution will indicate the compartment of concern at steady state, and the most influencing compartment on the overall persistence. The distribution can also indicate which compartment may not be affected (absence of exposure). However, this may be challenging and acceptable only in exceptional cases.

As examples for such calculation, different case studies are summarised in the annex. In these examples the emission scenario was equal distribution for case studies 1 to 3 and emission to water only (100%) for case study 4. In order to keep the simulation simple schematic half-lives were assumed for soil (not P: DegT50 100 d, P: DegT50 180 d), water (not P: DegT50: 30 d, P: DegT50 60 d) and sediment (not P: DegT50 100 d, P: DegT50 180 d). Furthermore, it was assumed that non persistent compounds in water are also not persistent in sediment and vice versa. Finally, no extreme results considering very persistent compounds are presented (e.g., DegT50 = 100 000 d or K_{oc} = 100 000 L/kg). These case studies are not exhaustive, and different scenarios and mode of entries may be necessary to get an appropriate picture for each case. Nevertheless, case study 4 shows for example that depending on the properties of the substance of interest both water as well as soil could be the compartment of concern and should be tested first.

Overall, multi-media fate modelling are suitable to give evidence on the influence of specific parameters (e.g. degradation rates, partitioning coefficients such as K_{oc} and K_{aw} , mode of entry), and thus on the development of an appropriate testing strategy (ITS tier 4), e.g. the identification of the compartment of specific concern, i.e. the main compartment which has to be tested first, or on absence of exposure, i.e. the compartment where a testing may not be relevant.

4.2 Remaining concern in untested compartment

Overall persistence sets individual degradation rates for sediment, soil and water into context by considering the distribution of the substance at steady state conditions. For this reason, it is possible to find out by variation of the parameter of concern if a compartment may have a significant impact on the overall persistence, and thus the long-term presence in the environment.

It will additionally help to clarify and justify the remaining concern of an untested compartment (point 6 of the ITS), i.e. impact on the uncertainty about the long-time presence of the substance in the environment, if an additional study will not be performed.

If a significant impact is observed, especially if the P/vP criteria are exceeded or where the degradation half-life is close to the criteria (if the criteria are not exceeded), the missing compartment can be regarded as compartment of concern, and thus a verification if the substance is persistent in this compartment based on testing is essential.

This is illustrated with the case studies “water” and “soil”. The first case addresses the question in which situations an additional DegT50 in soil doesn’t seem necessary when the substance is not persistent in water. In the second case it is reverse: When an additional test in water doesn’t result in more information when it is known that the substance is not persistent in soil. The simulations were performed using the model MUST considering the environmental scenario “EU continental”. The continental scenarios was used as open system but calculating the overall persistence without including export parameters. Furthermore equal emission into air/water/soil was assumed.

Case study “water”

In this example the substance is not volatile, and information on degradation in water (OECD 309) is available in accordance with the starting of the ITS. It was found that the substance is not persistent in water. However, degradation data in soil and sediment is not available. Following questions should be addressed:

- Is soil and/or sediment a compartment of concern?
- When is an additional DegT50 for soil and/or sediment essential?

The substance data considered for case “water” is given in Table 4. This case consists of 4 variations all with Log Kaw of -7 and an assumed half-life in sediment of 100 days. Two parameters were modified. Variations a/b are fast degrading in water (DegT50 = 2 days), whereas variation c/d are slower degrading but still not persistent (DegT50 = 30 days). With regard to the sorption constant Koc case scenarios a/c are hardly sorbing to soil (Koc = 10 L/kg) whereas scenarios b/d are strongly sorbing (Koc = 5000 L/kg). That means the four variations cover all possible combinations for these two properties. Finally, the soil DegT50 was varied in the range of 10 to 10000 days. We focussed on the necessity of soil degradation study. If sediment study will be of interest, the soil degradation has to be fixed, and the sediment degradation rate to be varied.

Table 4: Substance data considered for case “water”

	Case_water_a	Case_water_b	Case_water_c	Case_water_d
DegT50 water (d)	2	2	30	30
DegT50 sediment (d)	100	100	100	100
Log Kaw (-)	-7	-7	-7	-7
Koc (L/kg)	10	5000	10	5000
DegT50 soil (d)	10 ... 10000	10 ... 10000	10 ... 10000	10 ... 10000

The results for the case study “water” are presented in Figure 5.

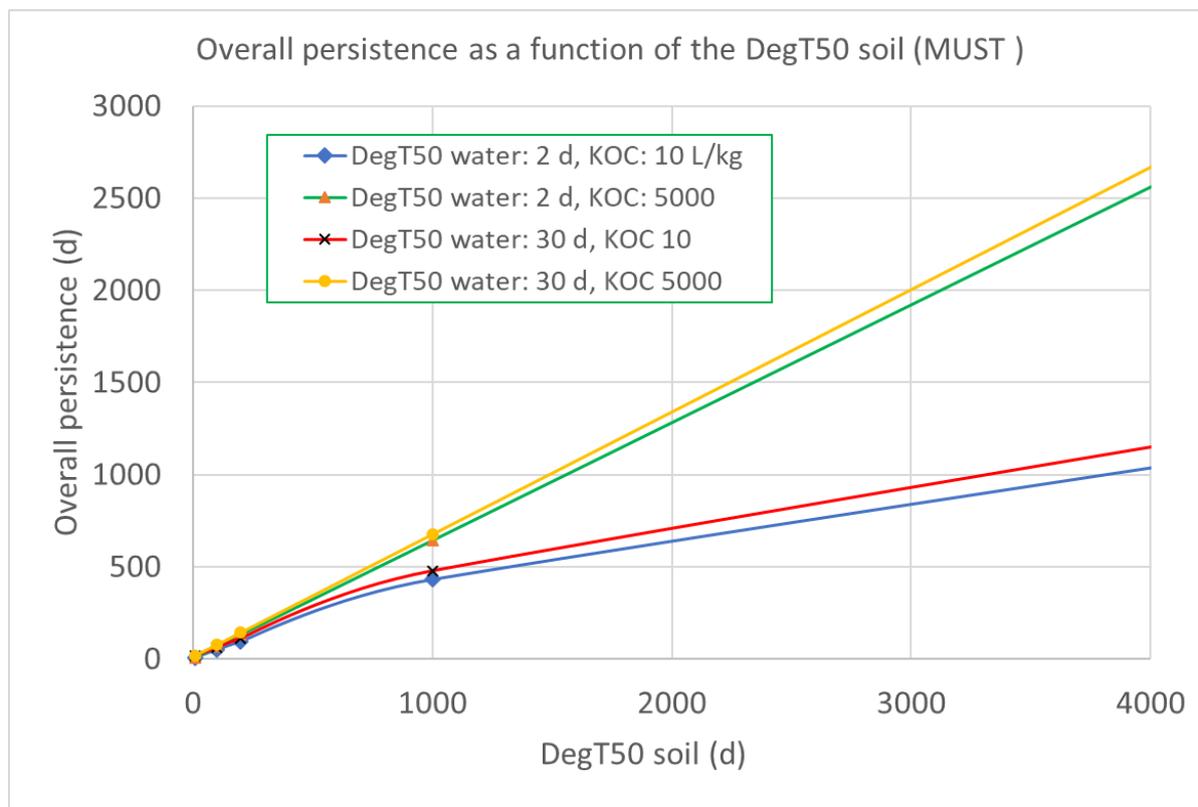


Figure 5: Results of case study “water”; overall persistence expressed as DT50; model MUST considering the environmental scenario “EU continental”; open system; equal emission into air/water/soil

The results can be interpreted as follows:

- If the persistence in soil is extremely high (DegT50 > 1000 d) the overall persistence is dominated by the Koc, i.e. lower overall persistence if Koc is low, and increasing with Koc.
- The half-life in water is not very sensitive to the overall persistence, i.e. the green and the yellow curve express different half-lives in water but a similar overall persistence.
- As long as the DegT50 in soil is moderate (DegT50 < 150 d) the overall persistence is similar for all cases; it remains below 120 d and even below 180 d if the soil DegT50 is 200 d.

The case demonstrates that the potential uncertainty of the water degradation value has no or only a marginal impact on overall persistence, since independent on how fast the degradation in water is, the overall persistence remains similar. The strong correlation between soil half-life and overall persistence indicates that soil should be considered as compartment of concern, and thus additionally to the degradation in water information on degradation rate in soil is necessary. After verification of a value for degradation in soil, in a similar approach the impact of variation of degradation in sediment should be evaluated before starting additionally a water/sediment study.

Case study “soil”

In this second example, the substance is again not volatile, and information on degradation (OECD 309) is not available, for example due to very low water solubility, or the substance is hydrolysable, or the study is technically not feasible. As a starting point degradation in soil (OECD 307) has been performed. It was found that the substance is not persistent in soil with a very fast degradation time (DegT50 = 10d). Following questions should be addressed:

- Is water a compartment of concern?
- When is an additional DegT50 for water/sediment essential?

The substance data considered for case study “soil” is given in Table 5. This case consists of only 2 variations all with Log Kaw of -7 and a half-life in soil of 10 days, and an assumed half-life in sediment of 30 days. For the parameter Koc two variations were considered: variation “a” is hardly sorbing to soil (Koc = 10 L/kg) whereas variation “b” is a strongly sorbing compound (Koc = 5000 L/kg). Finally, the DegT50 in water was varied in the range of 10 to 10000 days.

Table 5: Substance data considered for case “soil”

	Case_soil_a	Case_soil_b
DegT50 soil (d)	10	10
DegT50 sediment (d)	30	30
Log Kaw (-)	-7	-7
Koc (L/kg)	10	5000
DegT50 water (d)	2 ... 10000	2 ... 10000

The results for the case study “soil” are presented in Figure 6.

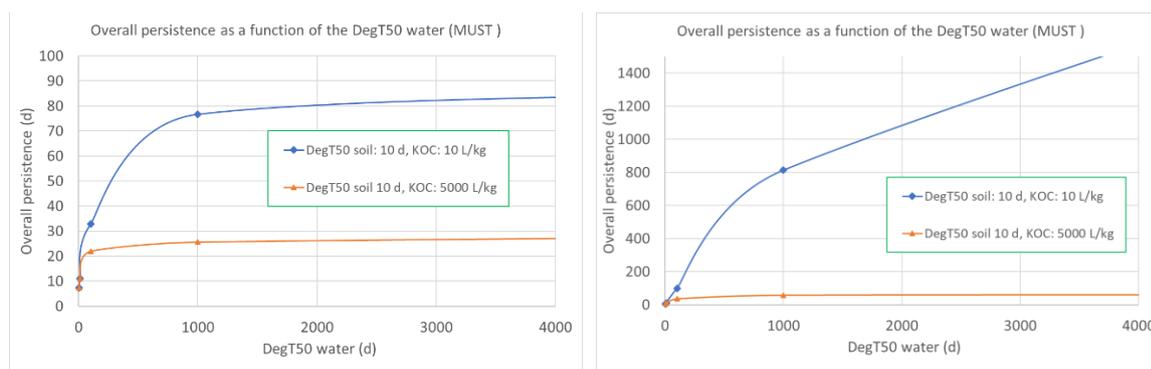


Figure 6: Results of case study “soil”; overall persistence expressed as DT50; model MUST considering the environmental scenario “EU continental”; open system; equal emission into air/water/soil (left), emission 100% to water (right)

The results can be interpreted as follows:

- The overall persistence depends on the mode of entry as expected. If the emission is solely to water and the substance has a low sorbing potential, the unknown water degradation rate has more influence on the overall persistence.
- For equal distribution, the overall persistence is very much driven by the short half-life in soil and the sorption constant, but hardly dependent on the DegT50 in water. The short half-life in soil guarantees that the overall persistence remains relatively low especially for highly sorbing compounds (Koc > 5000 L/kg). If the substance has a low Koc the overall persistence will be higher but remains below 90 d independent on the DegT50 in water.
- For 100% to water, the overall persistence remains below 90 days for highly sorbing compounds. For these compounds the impact of untested water on overall persistence is low. In contrast for low sorbing compounds, the impact is higher.

The case demonstrates that due to the fast degradation in soil, water may be excluded as compartment of concern for high sorbing compounds, since the overall persistence remains below 90 days independent of the degradation rate in water and the mode of entry. An additional half-life in water has no influence on the overall persistence and wouldn't add relevant information for the persistence

assessment. In contrast for low sorbing compounds, the remaining concern is higher, and water degradation may probably be tested.

Summary

As shown by the case studies multi-media fate modelling and the overall persistence approach are suitable in the evaluation of the remaining concern of untested compartment (ITS tier 6). Multi-media fate and transport models can also be applied to characterize the influence of different environmental factors, use and/or release patterns, and the uncertainty in available input data (Redman et al, 2021).

Especially case study "soil" shows clearly that for some cases testing of degradation rate in water is scientifically not justified if we have equal distribution as release pattern. For the mode of entry 100% to water, testing in water is in our example not justified for substances with high K_{oc}. This seems helpful especially if the substance has a low water solubility or testing is technically not feasible.

However, as mentioned above the scenario definition (e.g., release pattern, number of model compartments, compartment dimensions) may have significant impact on the results. For this reason this has to be considered in the evaluation of the uncertainty and the level of confidence, probably using different reasonable models and scenarios. For Europe, the generally accepted number of compartments or compartment dimensions used in models such as SimpleBox or MUST (e.g.) seems to be most appropriate.

4.3 Contradictory results from single compartments

There are cases where it makes sense to assess additionally the overall persistence and not only compartment by compartment. If contradictory results on persistence exist for different compartments, multi-media fate modelling are a helpful tool to understand and to judge on the actual likeliness of the long-term presence in the environment. For this reason, information on overall persistence from multi-media fate modelling may be helpful to identify situations where chemicals are classified as P because of a high half-life in one compartment but which has no significant influence on overall persistence due to degradability in the other compartments where they transported in or mainly appear. However, in these cases the time for the transport will be relevant as well.

For example a complete dataset is available for a substance, which is persistent in water (slightly above the trigger), and the same substance is not persistent in soil or sediment. In this case, depending on the partitioning properties of the substance, the persistence in water may only have a marginal effect on the overall persistence and the long-term presence in the environment (see case study "soil" above). In this case the half-life in water should not be overvalued. However, several model scenarios should be performed to cover different reasonable situations and to justify that the water (or soil) compartment has a negligible influence. Another example would be very volatile substances, so that concentrations in water (or soil) are negligible, especially if the substance is rapidly degraded in air.

Besides using overall persistence as an additional evidence in the interpretation of single compartment results, it can also be used as an own metric for the presence in the environment and to solve the issue of contradictory results. However, overall persistence is not directly comparable to the Annex XIII trigger values. The approach for selection of the dominant compartment should be verified (see chapter 3.3). In addition, again it has to be noted that distribution may be influenced by the multi-media fate model and the scenario definition (e.g. release pattern, number of compartments, relative size of compartments). Several different scenarios have to be performed covering different reasonable scenarios. In addition, the transport rate between the compartments has to be considered, and to understand if presence in single compartments are still important even though overall persistence is low.

Finally, overall persistence using Level III modelling represents the overall degradation potential at steady state, which could be different to the near or mid future. Dynamic multi-media fate modelling can give a better understanding of the processes to be considered in the persistence assessment as shown in chapter 3.4. Especially if a relatively slow decline is observed in one specific compartment, it shows that this single compartment may be relevant even if the overall persistence is low.

5 Strategy for multi-media fate modelling in P assessment

The examples, considerations and discussion in this report together with the literature review (WP1) and modelling exercises (WP3A; Klein, 2021) present several methodologies how multi-media fate modelling (MMFM) can be used to get information about sensitive and critical parameters, and to get evidence to decide on testing strategy and came to the conclusion on persistence. In the following it will be summarized how these different multi-media modelling methodologies can be used, interpreted and implemented in a weight-of-evidence approach to improve the robustness of current persistence assessment.

Multi-media fate modelling results in values for steady state distribution and on overall persistence, which could give evidence on compartment of concern, i.e. which compartment is most likely affected and should be primarily tested, and which compartment could probably be neglected from the persistence assessment as the influence on overall persistence is negligible. In addition the overall persistence can be used to conclude on remaining concern in untested compartments as illustrated by case studies. If the outcome of the single compartments are conflicting, the overall persistence concept can be used to judge about the relevance of the single compartment on overall presence of the substance in the environment. Finally, dynamic Level IV modelling gives the opportunity to include area under curve, as well as the recovery time or reduction potential (reduction in percentage for a given time period) to resolve challenges with substances which reach steady-state only far in the future. Thereby also a time-dependent overall persistence ($P_{ov}(t)$) is a promising tool to understand the impact.

However, scenario definition (e.g., release pattern, number of model compartments, compartment dimensions) may have significant impact on the results. For this reason this has to be considered in the evaluation of the uncertainties and the level of confidence.

5.1 Workflow

The methodology to use multi-media fate modelling in the persistence assessment framework should include several building blocks and follow a stepwise approach:

- Step 1. Collect and assess information
 - a. Specification (“Profiling”) of the substance
 - b. Existing information on (bio)degradation and partitioning properties
- Step 2. Problem formulation and select approach
- Step 3. Perform modelling exercise and assess level of confidence by considering uncertainties
- Step 4. Conclusion

At the beginning, the substance identity should be defined as far as possible. It is clear that multi-media fate modelling can only be done for specific substances, i.e. specific partitioning coefficient and degradation rates, and it has to make sure that the modelling represent the substance. In addition, the already existing information on the (bio)degradation and partitioning (K_{oc} , K_{aw}) has to be summarized, and the uncertainties already in the input parameters have to be documented.

In the next step, the problem to be solved has to be clearly formulated. This may be different if the modelling will be used to develop a testing strategy, or to evaluate the remaining concern of untested environment, or if it will be used to justify that a compartment result has no impact on the overall persistence.

To solve this question, the most suitable approach should be selected based on:

- (a) Level III steady-state concentration and overall persistence will be used to get evidence on compartment of concern or information on specific compartment is negligible
- (b) Level III steady-state concentration and overall persistence will be used to get evidence on remaining concern of untested compartment
- (c) Level III overall persistence concept is used for interpretation of the data to get evidence on impacts of specific compartments, and if contradictory results exist
- (d) Level IV dynamic modelling (Pov(t)) is considered if steady state is expected to exist in far temporal distance, or if the decline after emission stop is of interest.

After performing the modelling exercise, the uncertainties and the level of confidence has to be evaluated (see below).

Based on the outcome, a conclusion for the problem formulation has to be prepared. All used input parameters, models and scenarios should be documented according to Good Modelling Practice.

The workflow is illustrated in Figure 7.

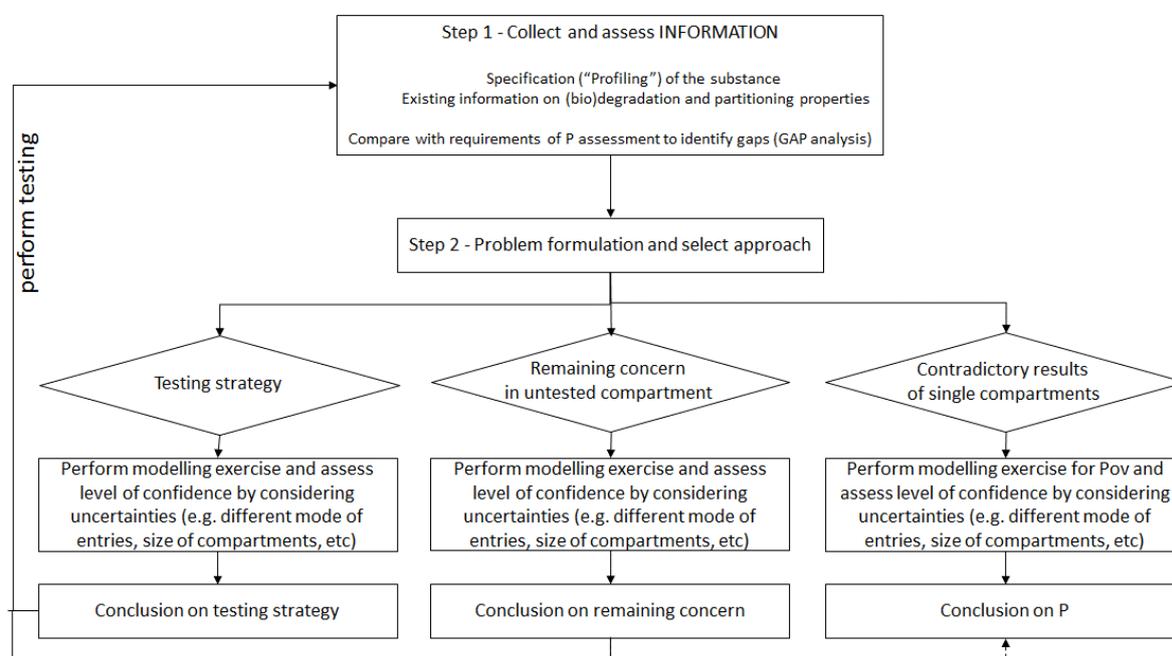


Figure 7: Workflow on integrating multi-media modelling in the decisions under the ITS.

Overall, this methodology can result in further problem formulation with regard to the persistence assessment of the substance. For example in a first step the modelling is only used to decide on the testing strategy, and after performance of the test new modelling exercises may be needed, refining the outcome of the preliminary modelling. For this reason, the workflow have to be run through several time until a conclusion on persistence assessment is sufficiently justified.

5.2 Uncertainty

Scenario definition (e.g., release pattern, number of model compartments, compartment dimensions) may have significant impact on the results. For Europe, the generally accepted number of compartments or compartment dimensions used in models such as SimpleBox or MUST (e.g.) seems to be most appropriate.

After performing the modelling exercise, the level of confidence has to be evaluated. For multi-media fate modelling it is important to consider uncertainties coming from

- input parameters (degradation rates, K_{oc} , K_{ow}) as well as
- mode of entry
- the selection of model and scenario

This can be estimated qualitative and quantitative, if possible, using a set of different reasonable models, scenarios (compartment dimensions, release pattern) and input parameter.

For the mode of entry, a tiered approach is promising:

Tier 1: In a first step, equilibrium distribution, and different emission scenarios will be compared. The result give evidence about the level of confidence of the available modelling. However, this is usually a worst-case assumption, and further information can be used to reduce the uncertainty in tier 2 and 3.

Tier 2: If the substance is release via wastewater, substance inherent properties (K_{ow} , K_{oc}) can be used to refine the mode of entry. For example a volatile substance will be release into air via STP. The K_{ow} can be used to refine the 100% water emission scenario.

Tier 3: In this step, a further refinement of the release pattern can be done, if specific information is available about the use pattern.

Overall, this uncertainty analysis can result in further problem formulation with regard to the persistence assessment of the substance. For this reason, if the uncertainty is not acceptable, further testing might be necessary.

5.3 Multi-constituent and UVCB

The steps in the workflow mentioned above (step 1 collect and assess information, step 2 problem formulation and approach selection (testing strategy, remaining concern or impact on overall persistence) are also applicable to multi-constituent or UVCB substances.

However, as mentioned above, multi-media fate modelling can only be done for specific substances, i.e. specific partitioning coefficient and degradation rates, so that it has to make sure that the modelling represent the substance. This substance profiling is specifically important for multi-constituent or UVCB substances.

To evaluate PBT properties of substances containing multiple constituents, impurities and/or additives, specific assessment approaches have been described in the REACH guidance R.11, chapter R.11.4.2.2.2. This includes

- Known constituent approach
- Fraction profiling (or Block profiling) approach
- Whole substance approach

Based on the profiling of the substance and the distribution properties, it has to be decided which approach seems to be most appropriate for evaluation the persistence (and B and T) of the substance. Depending on the approach, multi-media modelling will be done for known constituent, or for representative key constituents. Thereby, multi-media modelling will help to justify the selection of representative key constituents by comparing the steady-state distribution and overall persistence of different constituents per fraction or for the whole substance.

5.4 Weight of Evidence

Finally, prepare the building blocks for the multi-media fate modelling as part of the Weight-of-Evidence (WoE) for persistence assessment of the substance. Use the guiding principles published by OECD (OECD 2019), and the **ECHA template**⁴ for weight-of evidence to structure the information, and for documentation and communication of the persistence assessment:

- Problem formulation
- Summarize information on degradation
- Level of confidence and uncertainty

Especially the tables of the template are helpful to illustrate the available data, as well as the confidence and uncertainty of a justified and not justified conclusion on persistence. Important is that all aspects above will be used to create the WoE. Examples of previous WoE approaches for persistence assessment are given in Redman et al (2021).

⁴ <https://echa.europa.eu/de/support/guidance-on-reach-and-clp-implementation/formats>

6 Conclusion

Chemical persistence plays a key role in the determination of environmental exposure making it an important component in risk assessment and regulation. Persistence potential of substances can be assigned based on compartment specific degradation rates or half-lives. However, this approach neglects dynamic multimedia exchanges and degradation processes that may have an important bearing on the overall presence of a substance in the environment.

Differences between persistent and non-persistent substances are beside the degradation rate (overall persistence), the expected level of contamination (steady-state concentration) or area under curve, as well as the recovery time or reduction potential (reduction in percentage for a given time period). These endpoints are available by multi-media fate modelling (MMFM).

In this report it has been discussed how multi-media fate modelling can be used to get information about sensitive and critical parameters, to get evidence to decide on testing strategy as well as the remaining concern of untested compartments, and came to the conclusion on persistence. Finally, it has been summarized how the different multi-media modelling methodologies can be used, interpreted and implemented in a weight-of-evidence approach to improve the robustness of current persistence assessment.

Overall, as shown by the examples and case studies multi-media fate modelling and the overall persistence approach are suitable tools to improve persistence assessment. Overall persistence sets individual degradation rates for sediment, soil and water into context by considering the distribution of the substance at steady state conditions. For this reason, it is possible to find out by variation of the parameter of interest if a compartment may have a significant impact on the overall persistence, and thus the long-term presence in the environment. This guides to the identification of the compartment of specific concern and development of an appropriate testing strategy (ITS tier 4). In addition, it is helpful especially in the evaluation of the remaining concern of untested compartment (ITS tier 6), i.e. impact on the uncertainty about the long-time presence of the substance in the environment, if an additional study will not be performed. If contradictory results exist for different single compartment, multi-media modelling give evidence how to interpret the data. Dynamic multi-media fate modelling can give a better understanding of the processes to be considered in the persistence assessment, the alteration of the overall persistence over time, and the period of decline of the presence in the environment after emission reduction.

Multi-media fate and transport models can also be applied to characterize the influence of different environmental factors, use and/or release patterns, and the uncertainty in available input data (Redman et al, 2021). By including multi-media fate modelling the distribution and the partitioning/transportation between the compartments will be considered. Using this methodology the available compartment specific degradation rates will still be compared with the trigger values for P or vP. However, there are cases where it makes sense to assess additionally the overall persistence and not only compartment by compartment.

Scenario definition (e.g., release pattern, number of model compartments, compartment dimensions) may have significant impact on the results. For this reason this has to be considered in the evaluation of the uncertainty and the level of confidence, probably using different reasonable models and scenarios. For Europe, the generally accepted number of compartments or compartment dimensions used in models such as SimpleBox or MUST (e.g.) seems to be most appropriate.

Further research needs

Several further research needs have been already touched on during the development of the modelling framework. In detail these are:

- Decision is necessary to stick to the Annex XIII criteria or that a new concept is necessary due to shortcomings of the “old” persistence concept (Redman et al, 2021).
- Definition of absence of exposure with regard to persistence assessment
- Generally accepted trigger value for the overall persistence concept
 - Same as for the single compartment
 - Approach for selection of the dominant compartment should be verified
 - Alternative trigger values
- Generally accepted scenario definition with regard to persistence assessment. Unit world was suggested at the literature. For Europe, the model SimpleBox or MUST (e.g. number of compartments, compartment dimensions) seems to be most appropriate. According to Scheringer and Matthies (2006) a consensus model for calculating Pov is available (OECD Pov and LRTP Estimation Tool) and also an approach that makes Pov results independent of the release compartment (the temporal remote state as described by Stroebe et al. (2004)).
- Should a multimedia modelling approach include a WWTP and application of sludge to soil? This is quite specific and removal of this would make a more generic assessment (if considering the four different emission scenarios).
- Level IV will result in area under curve, and time-dependent Pov(t), as well as recovery time, and reduction potential (reduction in percentage for a given time period).
 - how to derive trigger, does it need to be comparable to Annex XIII

In addition, multi-media fate modelling can give a better understanding on how the different parameters will have an impact on the long-term presence of substances in the environment. This can be compared with the protection goal. For example, as illustrated in the dynamic multi-media fate modelling part, the result give a picture how fast the substance will reach steady state concentrations and how fast the substance is removed from the system after emission stops. If the half-life of the compound is lower or near the trigger values of persistence (40 d, 120 d, 180 d), the steady state is reached fast within 1-2 years. The same time period is necessary for the clearance time.

For this reason the persistence criteria, the time-frame for recovery and the negligible exposure approaches should be discussed in view of how the persistence assessment framework can contribute to the protection goal as well as the zero pollution ambition considering following aspects:

- Persistence as hazard criteria? Persistence is a synonym for presence in the environment and thus more an exposure endpoint. However, long-term presence in the environment is also an indication that (unknown) effects may occur more likely, thus P is regarded as indication of (substance-inherent) hazard.
- Persistence as substance inherent property, or is it emission dependent, thus use dependent? If we define P as exceeding specific single compartment half-lives, it is not emission dependent. If we define P as not being present in environment for long-time, it depends on definition of “being present”. If we define P as potential for increased or poorly-reversible exposure of the whole environment, it depends rather on overall persistence, than on single compartment half-lives.
- P should be a criteria so that long presence in the environment is not likely, i.e. sufficient short clearance time after emission has been stopped.

- What is the difference between non-persistent and persistent substances? Even non-persistent substances could have measurable (and relevant) steady state concentration. However, the level of steady state concentration depends on emission rate. For same emission rate, the level of the steady state concentration will be different between persistent and non-persistent substances. In addition, the lifetime/clearance time/recovery time, i.e. how long does it take to remove the substance from the environment, is different after emission stops.
- What is the target for zero pollution/negligible exposure? 10% of steady state after ceasing emission or fixed value such as the TTC, e.g. $< 0.1 \mu\text{g/l}$ in water or $100 \mu\text{g/kg}$ in soil, or...?

This document is part of a series of reports produced as part of the Cefic-LRI ECO52 project: 'Expanding the conceptual principles and applicability domain of persistence screening and prioritization frameworks, including single constituents, polymers, and UVCBs.'

7 Acknowledgements

We would like to thank members of the project research team Graham Whale (Whale Environmental Consultancy Ltd), Dieter Hennecke (Fraunhofer IME), Chris Hughes (Ricardo Energy & Environment) for their valuable contributions to this work. We would also like to thank the monitoring team for their oversight and helpful input to the project.

8 References

- Cousins, I.T., Ng, C.A., Wang, Z., Scheringer, M., 2019. Why is high persistence alone a major cause of concern? *Environ Sci Process Impacts* 21, 781-792.
- EC, 2011. COMMISSION REGULATION (EU) No 253/2011 of 15 March 2011 amending Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards Annex XIII.
- ECHA, 2014. Guidance on Information Requirements and Chemical Safety Assessment Chapter R.11: PBT/vPvB Assessment. Version 2.0 November 2014.
- ECHA, 2016. Guidance on information requirements and Chemical Safety Assessment Chapter R.16: Environmental exposure assessment Version 3.0 February 2016.
- ECHA, 2017. Guidance on Information Requirements and Chemical Safety Assessment Chapter R.11: PBT/vPvB assessment. Version 3.0 June 2017.
- Fenner, K., Scheringer, M., MacLeod, M., Matthies, M., McKone, T., Stroebe, M., Beyer, A., Bonnell, M., Le Gall, A.C., Klasmeier, J., Mackay, D., Van De Meent, D., Pennington, D., Scharenberg, B., Suzuki, N., Wania, F., 2005. Comparing estimates of persistence and long-range transport potential among multimedia models. *Environmental science & technology* 39, 1932-1942.
- Gouin, T., Mackay, D., Webster, E., Wania, F., 2000. Screening chemicals for persistence in the environment. *Environmental Science & Technology* 34, 881-884.
- Klein, J., 2021. Modelling exercises. Report for WP3A, CEFIC LRI Eco 52.
- Leeuwen, C.J.v., Hermens, J.L.M., 1995. *Risk Assessment of Chemicals - An introduction*. Springer, Dordrecht.
- Mackay, D., Paterson, S., 1981. Calculating fugacity. *Environmental Science & Technology* 15, 1006-1014.
- Mackay, D., Paterson, S., 1982. Fugacity revisited. *Environmental Science & Technology* 16, 654A-660A.
- McLachlan, M.S., 2018. Can the Stockholm convention address the spectrum of chemicals currently under regulatory scrutiny? Advocating a more prominent role for modeling in POP screening assessment. *Environ Sci Process Impacts* 20, 32-37.
- OECD, 2002. Report of the oecd/unep workshop on the use of multimedia models for estimating overall environmental persistence and long-range transport in the context of pbts/pops assessment. OECD series on testing and assessment No 36.
- OECD, 2004. Guidance document on the use of multimedia models for estimating overall environmental persistence and long-range transport. OECD series on testing and assessment No 45.
- OECD, 2019. Guiding Principles and Key Elements for Establishing a Weight of Evidence for Chemical Assessment. Series on Testing and Assessment No 311.
- Parnis, J.M., & Mackay, D., 2020. *Multimedia Environmental Models: The Fugacity Approach* (3rd ed.). CRC Press. <https://doi.org/10.1201/9780367809829>
- Redman, A.D., Bietz, J., Davis, J.W., Lyon, D., Maloney, E., Ott, A., Otte, J.C., Palais, F., Parsons, J.R., Wang, N., 2021. Moving persistence assessments into the 21(st) Century: A role for weight-of-evidence (WoE) and overall persistence (Pov). *Integr Environ Assess Manag*.
- Scheringer M, 1996. Persistence and spatial range as endpoints of an exposure-based assessment of organic chemicals. *Environ. Sci. Technol.* 30:1652-1659.

Scheringer, M., Matthies, M., 2006. Persistence Criteria in the REACH Legislation: Critical Evaluation and Recommendations. Final Report, 21.12.2006.

Stroebe, M., Scheringer, M., Hungerbühler, K., 2004. Measures of Overall Persistence and the Temporal Remote State, Environ. Sci. Technol. 38, 5665–5673.

SSC 2020. Stockholm Convention on Persistent Organic Pollutants (POPs). Text and Annexes, revised in 2019. Secretariat of the Stockholm Convention (SSC), September 2020.

Webster E., D. Mackay, F. Wania., 1998. Evaluating environmental persistence. Environ. Toxicol. Chem. 17:2148-2158.

Wegmann, F., Cavin, L., MacLeod, M., Scheringer, M., Hungerbühler, K., 2009. The OECD Software Tool for Screening Chemicals for Persistence and Long-Range Transport Potential. Environmental Modelling & Software 24, 228-237.

Annex: Comparison of degradation rate, DegT50, lifetime and DegT90

	k Degradation rate days⁻¹	DegT50 Half-life ln(2)/k days	Pov overall persistence (lifetime, residence time) 1/k days	DegT90 ln(10)/k days
P in Fresh or estuarine water	0.0173	40	60	133
P in marine water vP in marine, fresh or estuarine water	0.0116	60	90	200
P in soil P in fresh or estuarine water sediment	0.00578	120	175	400
P in marine sediment vP in soil vP in marine, fresh or estuarine water sediment	0.00385	180	260	600

Annex: Case studies

In these examples the emission scenario was equal distribution for case studies 1 to 3 and emission to water only (100%) for case study 4. In order to keep the simulation simple schematic half-lives were assumed for soil (not P: DegT50 100 d, P: DegT50 180 d), water (not P: DegT50: 30 d, P: DegT50 60 d) and sediment (not P: DegT50 100 d, P: DegT50 180 d). Furthermore, it was assumed that non persistent compounds in water are also not persistent in sediment and vice versa. Finally, no extreme results considering very persistent compounds are presented (e.g., DegT50 = 100 000 d or Koc = 100 000 L/kg).

Case study 1 – Substance with low volatility, and not P in water

Substance with low volatility has been tested for deg in water (OECD 309, DegT50 30 d, substance is not P). Open questions addressed by modelling:

- Is the compartment of concern water or soil?
- Should in any case an additional DegT50 test be performed for soil?

The results of the simulation are presented in the following table for four combinations of Koc and Soil-DegT50 to address the open questions.

Case 1: level III simulation with MUST for 4 different combinations of a substance which is not persistent in water/sediment)

Name	Case_1_a	Case_1_b	Case_1_c	Case_1_d
DegT50 water (d)	30	30	30	30
DegT50 sediment (d)	100	100	180	180
Log Kaw (-)	-7	-7	-7	-7
Koc (L/kg)	10	5000	10	5000
Soil DegT50 (d)	60	60	180	180
WW treatment plant in sludge (%)	0.21	51.73	0.21	51.73
Level 3 Air(%)	2.08	1.58	1.3	0.94
Level 3 Water(%)	16.87	6.45	10.36	3.82
Level 3 Soil(%)	80.92	86.05	88.26	91.73
Level 3 Sediment(%)	0.13	5.75	0.08	3.4
Level 3 Susp.sediment(%)	0	0.08	0	0.05
Level 3 Biota(%)	0	0.09	0	0.05
Overall persistency (d)	62.05	76.65	102.2	131.4

The results demonstrate that it is likely that soil will be the compartment of concern for the compound. More than 80% of the amount released will be distributed to soil even if the Koc of the compound is only 10 L/kg and the substance is not persistent in soil (variation a). If the compound is persistent in soil about 90% in soil is expected for the steady state distribution independent on the sorption behaviour (variations c and d). But also strongly sorbing compounds which are not persistent will be found in the soil compartment at steady state conditions at similar percentages as persistent compounds (variation b). It can be concluded that an additional DegT50 test in the soil compartment is essential for the assessment of the compound, because the overall persistence will be very much correlated with the half-life in soil. However, the test will not change the distribution in the environment very much.

Case study 2 – Substance with low volatility, and persistent in water/sediment

Substance with low volatility has been tested for deg in water (OECD 309, DegT50 100 d, substance is P. Open questions addressed by modelling:

- Is the compartment of concern water or soil
- Should in any case an additional DegT50 test be performed for soil?

The results of the simulation are presented in the following table for four combinations of Koc and Soil-DegT50 to address the open questions

Case 2: level III simulation with MUST for 4 different combinations of a substance which is persistent in water/sediment

Name	Case_2_a	Case_2_b	Case_2_c	Case_2_d
DegT50 water (d)	100	100	100	100
DegT50 sediment (d)	180	180	180	180
Log Kaw (-)	-7	-7	-7	-7
Koc (L/kg)	10	5000	10	5000
Soil DegT50 (d)	60	60	180	180
WW treatment plant in sludge (%)	0.21	51.73	0.21	51.73
Level 3 Air(%)	1.87	1.42	1.22	0.88
Level 3 Water(%)	25.23	8.95	16.12	5.53
Level 3 Soil(%)	72.7	77.1	82.53	85.84
Level 3 Sediment(%)	0.2	12.29	0.13	7.6
Level 3 Susp.sediment(%)	0	0.11	0	0.07
Level 3 Biota(%)	0	0.13	0	0.08
Overall persistency (d)	76.65	87.6	116.8	142.35

The results demonstrate that also in this situation (P in water) it is likely that soil will be the compartment of concern for the compound. However, compared to case 1 the percentages in soil are always below respective results of case 1. Nevertheless, more than 70% of the released emission will be distributed to soil even if the Koc of the compound is only 10 L/kg and the substance is not persistent in soil (variation a). If the compound is also persistent in soil more about 80% in soil is expected for the steady state distribution (variations c and d). But also strongly sorbing compound which are not persistent will be found in the soil compartment at steady state conditions (variation b). Similar conclusion can be drawn as in case 1: An additional DegT50 test in the soil compartment is essential for the assessment of the compound, because the overall persistence will be very much correlated with the half-life in soil. However, the test will not change the distribution in the environment very much. Compared to case 1 the overall persistency is always longer in this situation because of the contribution of the water/sediment half-lives to this parameter.

Case study 3 – Substance with low volatility and not P in soil

Substance with low volatility has been tested for deg in soil but not in water. Open questions addressed by modelling:

- Is the compartment of concern water or soil
- Should in any case an additional DegT50 test be performed for water?

The results of the simulation are presented in the following table for four combinations of Koc and DegT50 in water/sediment to address the open questions.

Case 3: level III simulation with MUST for 4 different combinations of a substance which is not persistent in soil

Name	Case_3_a	Case_3_b	Case_3_c	Case_3_d
Soil DegT50 (d)	60	60	60	60
Log Kaw (-)	-7	-7	-7	-7
Koc (L/kg)	10	5000	10	5000
Soil DegT50 water (d)	30	30	100	100
Soil DegT50 sediment (d)	100	100	180	180
WW treatment plant in sludge (%)	0.21	51.73	0.21	51.73
Level 3 Air(%)	2.08	1.58	1.87	1.42
Level 3 Water(%)	16.87	6.45	25.23	8.95
Level 3 Soil(%)	80.92	86.05	72.7	77.1
Level 3 Sediment(%)	0.13	5.75	0.2	12.29
Level 3 Susp.sediment(%)	0	0.08	0	0.11
Level 3 Biota(%)	0	0.09	0	0.13
Overall persistency (d)	62.05	76.65	76.65	87.6

The results demonstrate that soil remains the most relevant environmental compartment for this situation. It is not likely that the water compartment will become the compartment of concern even if the substance is moderately persistent. That may change if the compound is extremely persistent in water but, at the same time, non-persistent in soil. Again, the overall persistence is dominated by the half-life in soil. Even if the half-life in water/sediment is changed by a factor of 3 the overall persistence remains still close to the half-life in soil. If the substance is found to be persistent in soil the situation wouldn't change but only intensify the result (soil as the compartment of concern)

It can be concluded that an additional DegT50 test in water is neither not essential for the assessment of the distribution in the environment nor for the calculation of the overall persistence.

Case study 4 – same compound as case 3 (not persistent in soil) but use pattern indicate emission to water only

Substance with low volatility has been tested for deg in soil (not persistent) but not in water. Open questions addressed by modelling:

- Is the compartment of concern water or soil when the emission are to water only

The results of the simulation are presented in the following table for four combinations of Koc and DegT50 in water/sediment to address the open questions.

Case 4: level III simulation with MUST for 4 different combinations of a substance which is not persistent in soil but use pattern indicate emission to water only

Name	Case_4_a	Case_4_b	Case_4_c	Case_4_d
Soil DegT50 (d)	60	60	60	60
Log Kaw (-)	-7	-7	-7	-7
Koc (L/kg)	10	5000	10	5000
Soil DegT50 water (d)	30	30	100	100
Soil DegT50 sediment (d)	100	100	180	180
WW treatment plant in sludge (%)	0.21	51.73	0.21	51.73
Level 3 Air(%)	0	0	0	0
Level 3 Water(%)	98.52	18.11	98.76	21.15
Level 3 Soil(%)	0.7	65.26	0.43	49.22
Level 3 Sediment(%)	0.77	16.14	0.8	29.05
Level 3 Susp.sediment(%)	0	0.23	0	0.27
Level 3 Biota(%)	0	0.26	0	0.31
Overall persistency (d)	29.2	69.35	62.05	98.55

The results are completely different from the previous cases and demonstrate how much the level III simulations responds to the initial emission into the environment. Now the most relevant parameter is the sorption constant which is overruling the results of the degradation in water and sediment. Substances with low sorption will be primarily found in the water compartment, the overall persistence is driven by the half-life in this compartment (variation a and c). However, significant amounts of strongly sorbing compounds will finally end up in the soil even when they are initially released only to water (variation b and d). Background is the assumption of waste water treatment plants connected to water in the model. This leads to significant amount of residues in soil (via sludge). It can be concluded that a degradation test in water/sediment is essential for the risk assessment (distribution in the environment as well as overall persistence), especially for low sorbing compounds.

Summary case study 1-4

Looking at all results of the 4 case studies following conclusions can be drawn:

- Due to the scenario definition (e.g., volumes of air, water and soil, export via water/air compartment) there is normally a preferred compartment in a multi-media model. When basing the multi-media simulation on an equal distribution with regard to the initial emissions (i.e., 33% in air, water, and soil) the simulation will focus on this special scenario. If using MUST and the continental scenario this compartment will be soil for with substances of low volatility. It is likely that also other models result in similar estimates assumed the environmental scenario is defined in a similar way.
- The overall persistence is driven by the half-life in the dominant compartment (i.e., soil in the case studies using MUST)
- Also the distribution is driven by the dominant compartment, additional tests on persistence in other compartment (e.g., water and sediment) wouldn't change that.
- For volatile substance it has to be checked in how far air will replace soil as the dominant compartment and consequently the degradation in air will influence the overall persistence significantly.

The above conclusions are valid for non-persistent and persistent compounds as long as degradation rates in soil are not extremely short (i.e. < 40 d). If so, the dominant compartment would shift to water (low Koc) or sediment (high Koc).

EC, 2011. COMMISSION REGULATION (EU) No 253/2011 of 15 March 2011 amending Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards Annex XIII.

ECHA, 2017. Guidance on Information Requirements and Chemical Safety Assessment Chapter R.11: PBT/vPvB assessment Version 3.0 June 2017.

Wegmann, F., Cavin, L., MacLeod, M., Scheringer, M., Hungerbühler, K., 2009. The OECD Software Tool for Screening Chemicals for Persistence and Long-Range Transport Potential. Environmental Modelling & Software 24, 228-237.