Persistence Criteria in the REACH Legislation: Critical Evaluation and Recommendations

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Table of contents

Zusammenfassung

Im vorliegenden Gutachten wird auf der Grundlage der Datenanforderungen gemäß REACH, Anhang VII bis IX, ein zweistufiger Vorschlag zur Identifizierung von Stoffen mit persistenten Eigenschaften erarbeitet. Im ersten Schritt (screening) werden die leichte biologische Abbaubarkeit und das Potential für photochemischen Abbau zur Klassifikation herangezogen. Anhand von 70 Beispielchemikalien wird die Eignung der leichten biologischen Abbaubarkeit als Screening-Kriterium untersucht. Im zweiten Schritt (PBT assessment) werden Abbauhalbwertszeiten zum Vergleich mit den Kriterien des Anhangs XIII aus quantitativen Struktur-Abbaubarkeits-Beziehungen (QSAR) für Stoffe, die in Mengen größer als 10 t/a produziert oder importiert werden, und aus Simulationstests für Stoffe über 100 t/a herangezogen. Es wird empfohlen, die Persistenzkriterien um eine Abbauhalbwertszeit in Luft von zwei Tagen zu erweitern. Die aus QSAR und Simulationstests resultierenden Unsicherheiten bei der Identifizierung persistenter Stoffe werden durch eine Bewertung weiterer verfügbarer Befunde (weight of evidence) abgeschätzt. Als Alternative zur PBT-Bewertung mittels Referenzchemikalien wird vorgeschlagen, die zeitliche Verweildauer in der Umwelt (Gesamtpersistenz) und die Ausdehnung der räumlichen Verteilung (Ferntransportpotenzial) zu begrenzen.

Introduction

Persistence (P) has long been recognized as a property of concern in the assessment of chemicals. This is particularly the case when high P occurs in combination with potential for bioaccumulation (B) and toxicity (T). Possible adverse impacts of substances that combine P, B and T are difficult to anticipate because they may result from chronic, low-level exposure and/or they may occur by mechanisms not identified in acute toxicity assessments. The current risk assessment approach of comparing exposure against effect levels therefore does not provide a complete picture of possible adverse impacts of persistent and bioaccumulative substances. Consequently, environmental legislation increasingly focuses special attention on persistent compounds, as in the Stockholm Convention, which limits or prohibits the production and use of certain persistent organic pollutants (UNEP, 2001). Moreover, persistent chemicals may be transported over long distances; in particular those substances that have appreciable vapour pressure and are slowly degraded in air.

The European chemicals legislation and several international conventions have issued criteria to regulate persistent chemicals. Persistence plays an essential role in the EU legislation proposal REACH (Registration, Evaluation and Authorisation of Chemicals) (European Council, 2006). A substance is considered persistent (or very persistent) if its degradation half-lives in water, sediment or soil exceed specific values given in Annex XIII of the draft REACH regulation. The approach of assessing substances by comparison to half-life criteria has already been used in other national and international assessment and prioritization schemes (Environment Canada, 1995; UNECE, 1998; US EPA, 1999; UNEP, 2001). Whereas the Stockholm Convention and other international conventions (OSPAR, 1992; UNECE, 1998) do not explicitly indicate how degradation half-lives should be determined, REACH has established the standard information required for substances manufactured or imported in quantities of more than 1 tonnes/year in Annex VII and additional standard information in Annexes VIII and IX for more than 10 and 100 t/a, respectively.

There are two main problems in connection with the persistence evaluation under REACH. First, registrants are not required to submit half-life data for chemicals below 100 t/a, which makes it impossible to apply the persistence criteria defined in Annex XIII to these chemicals (about 20 000 compounds). Second, the persistence criteria defined in Annex XIII of REACH are not comprehensive because there is no criterion for air, which means that there are persistent chemicals that will not be identified under REACH.

In the present report, we discuss these two problems and propose possible solutions. In Section 1, we describe the information requirements for the P assessment under REACH along with property estimation methods that may be used to fill data gaps. In Section 2, we explore screening criteria that can be used to identify possible P chemicals among the compounds below 100 t/a. In Section 3, we discuss the P evaluation criteria in REACH and propose a half-life criterion for air. We also discuss uncertainties of measured and estimated half-life data and explore in which way overall persistence (P_{ov}) and long-range transport potential (LRTP) can be used in the persistence assesment under REACH. Finally, we propose a testing strategy for persistent chemicals in Section 4.

1 Status description

1.1 Data requirements

Standard information requirements related to the P criterion are established in Annexes of REACH for substances manufactured or imported in quantities of more than:

- 1 t/a: vapour pressure $p°$, water solubility S_w, n-octanol-water partition coefficient, K_{ow}, and ready biodegradability test result (Annex VII).

  For substances between 1 and 10 t/a, information on persistence is only required if application of (Q)SARs or other evidence indicates that they are likely to meet the criteria in Annex XIII or the classification criteria for any human health or environmental effects endpoints under Directive 67/548/EEC (Annex III).
- 10 t/a: as above, plus hydrolysis as a function of pH and adsorption/desorption screening, i.e. K_d and K_{oc} values (Annex VIII).
- 100 t/a: same as above, plus dissociation constant pK_a, simulation testing on ultimate degradation in surface water, soil simulation testing if K_{oc} is high, sediment simulation testing if K_{oc} is high, and identification of degradation products (Annex IX).

No details are specified about the test conditions, e.g. which OECD or other test guidelines should be used.

1.2 Property estimation methods

For Annex-VII substances (below 10 t/a) no information that can be readily transformed into degradation half-lives is required; for Annex-VIII substances (below 100 t/a) only pH-dependent hydrolysis testing is required. Thus methods have to be used to calculate or estimate degradability of these substances from other available properties, screening test results, or from chemical structure. Howard (2000), Jaworska et al. (2003), and Arnot et al. (2005) give overviews on structure-biodegradability relationships (SBR) and quantitative structure-biodegradability relationships (QSBR) for primary and ultimate biodegradation under aerobic and anaerobic conditions. Six of these methods have been compiled as BIOWIN1_6, which are available online in EpiSuite (US EPA, 2006). Other QSBR methods are CATABOL (Jaworska et al., 2002) and the structure similarity approach through atom-centered fragments (ACF) (Kühne et al., in press). EpiSuite contains also estimation methods for photodegradation by OH-radicals (AOPWIN) and hydrolysis (HYDROWIN). AOPWIN has been shown to yield reliable results for volatile compounds (small compounds as in the training set of AOPWIN) (Müller, 2005). Biodegradation estimation, in contrast, is much more diverse and uncertain. Several authors have used empirical test data to correlate BIOWIN estimates with primary and ultimate biodegradation half-lives in water, soil and sediment (Howard, 2000; Aronson et al., 2006; Fenner et al., 2006). Most interesting are data from screening tests on ready biodegradability, because they will be available for most substances manufactured or imported in quantities greater than 1 t/a (see Section 1.1).

Partition coefficients are not explicitly required for P assessments but are helpful for taking into consideration the environmental distribution and identifying the most relevant degradability information for a substance. K_{ow} is available for all substances and K_{oc} can be estimated from K_{ow} or fragment methods (see PCKOCWIN in

EpiSuite). Henry's law constant, H, can be estimated as the quotient of vapour pressure and water solubility: $H = p°/S_w$, which is also available for all substances regulated under REACH.

1.3 PBT assessment methods

The PBT profiler developed by EPA (US EPA, 2003) contains QSARs to estimate environmental degradation half-lives and other related information from chemical structure. BIOWIN, AOPWIN, HYDROWIN and others have been adopted from EpiSuite (see Section 1.2) to support manufacturers, importers, risk assessors and the general public with a quick online PBT screening assessment. A steady-state non-equilibrium multimedia model is used to calculate the environmental distribution and the environmental compartments of concern. Half-lives used as model input are derived from AOPWIN (air) and BIOWIN (water, soil, sediment). It is assumed that the half-life for aerobic biodegradation obtained from BIOWIN is valid for water; for soil and sediment, half-lives two and nine times as long as in water are assumed. The main output of the PBT profiler is a comparison of the chemical's individual half-lives, BCF and toxicity to the corresponding PBT criteria used by the US EPA (US EPA, 1999). Overall persistence and long-range transport potential are also calculated by the PBT profiler and are reported on a background page called "P2 considerations and more information".

1.4 Weaknesses in P assessment under REACH

There are five problems associated with the P evaluation procedure as it will be implemented under the REACH legislation. First, insufficient data are required under REACH to apply the P criteria. This is especially the case for chemicals below 100 t/a, for which no information from simulation testing on biodegradation will be required (see Section 1.1). For chemicals over 100 t/a, results from simulation tests will be available. However, it is not clear whether these data actually represent degradation kinetics (and not degradation and other processes such as transfer to other media in combination, see Section 3.3 and Appendix 3). Second, the half-life criteria are not comprehensive because they do not include a criterion for persistence in air. Third, the selection of the numerical values of the half-life criteria in Annex XIII is not optimal because they are based on the half-lives of certain reference chemicals (chemicals similar to Persistent Organic Pollutants with highest half-lives in soil and lowest half-lives in air). This means that persistent chemicals with other half-life combinations (high persistence in air, lower persistence in soil and water) will not be identified by these criteria. Fourth, the criteria defined in Annex XIII require "available half-life data collected under adequate conditions" so that half-lives estimated from chemical structure are probably not sufficient for classifying a chemical as P. Finally, long-range transport, which is a problem occurring on a shorter time scale than local contamination by persistent chemicals, is not addressed at all. With the P criteria as they are defined in REACH, it is not ensured that long-range transport in air or water will not occur. Taking these problems together, it is clear that the possibility exists that some chemicals which are persistent in the environment will not be identified as persistent under REACH.

2 Evaluation of screening criteria for the identification of possible P chemicals

In the present European Technical Guidance Document (TGD) (European Commission, 2003), screening criteria are defined for P and B, which have the purpose to identify possible PBT chemicals which are then further evaluated in the actual PBT assessment. So far, similar screening criteria have not been defined under REACH. However, screening criteria will be needed under REACH to enable registrants to identify possible P chemicals. Application of the screening criteria will be an important element of the chemical safety assessment, particularly for chemicals below 100 t/a, for which no actual half-life data are available.

The present TGD mentions the following P screening criteria: test for ready biodegradability, test for inherent biodegradability, and estimated half-life data (p. 165/166 and Table 31 on p. 168 of part II of the present TGD). The objective of this part of our project is to evaluate whether the ready biodegradability test or half-life data estimated from chemical structure are more useful as screening criteria under REACH.

2.1 Compilation of a set of example chemicals

From the data set of OECD high production volume chemicals provided by UBA, 72 chemicals were selected as example chemicals, see Tables A1 and A2 (Appendix 1). 36 of the 72 chemicals are readily biodegradable, 36 are not. The chemicals selected cover several orders of magnitude of air/water and octanol/water partition coefficient, indicating that they represent a wide range of environmental partitioning behavior. The half-lives estimated from BIOWIN of the example chemicals cover a range from 0.7 d to 1230 d for water/soil and from 1 hr to 200 d for air.

Results (yes/no) for the ready biodegradability test ("rbt" in the following) were taken from the data file provided by UBA, half-life values were estimated with BIOWIN and AOPWIN and partition coefficients were mainly taken from the handbook by Howard and Meylan (1997). BIOWIN output was converted into half-lives with the relationships for primary biodegradation and ultimate biodegradation derived by Arnot et al. (2005). The distribution of the example chemicals in the chemical space defined by log K_{ow} and log K_{aw} is shown in Figure 1. Figure 2 shows distributions of the half-lives for aerobic biodegradation as derived with BIOWIN (Primary Survey Model) and for reaction with OH radicals as obtained with AOPWIN.

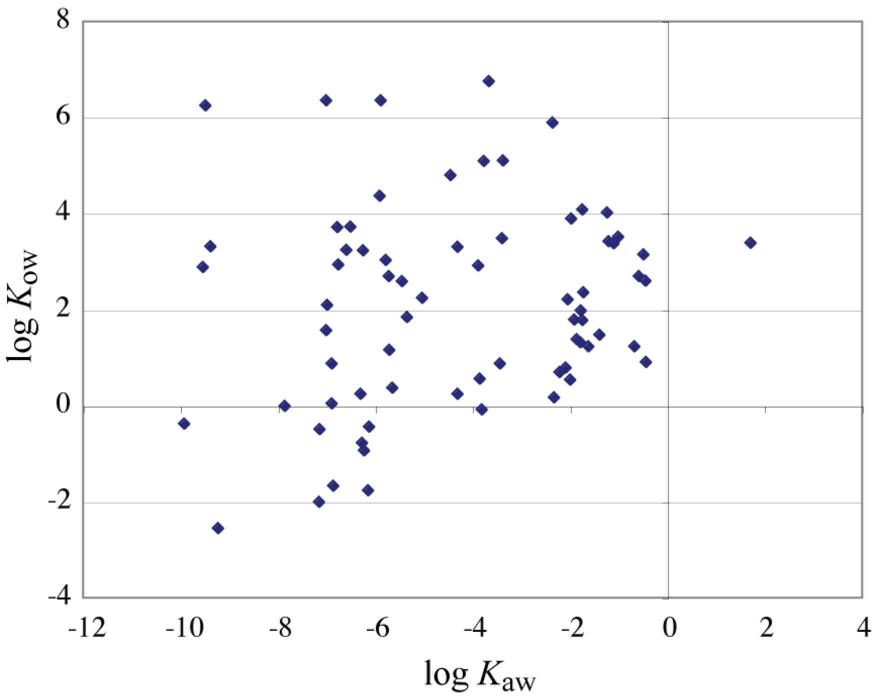

Figure 1: log K_{aw} and log K_{ow} values for the 72 example chemicals.

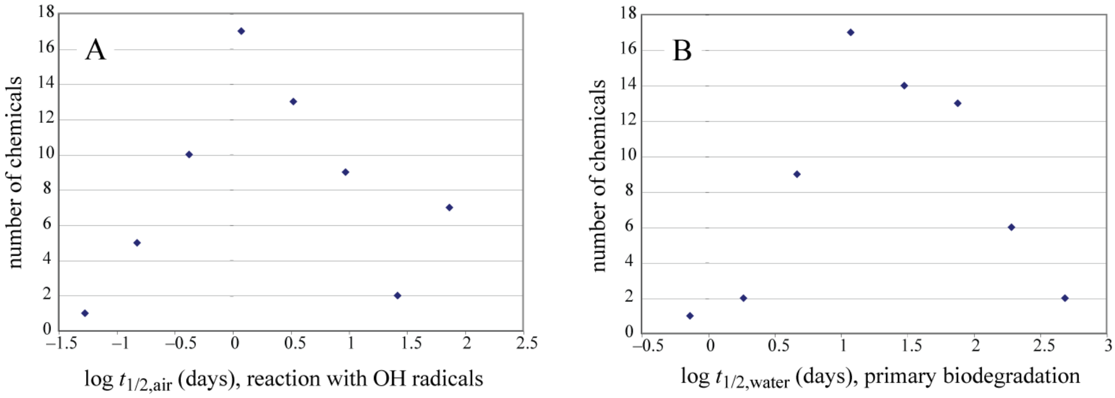

Figure 2: Histograms showing the distribution of half-life values of the 72 example chemicals. A: half-lives in air derived from AOPWIN. B: half-lives for biodegradation in water and soil, derived from BIOWIN-4 (Primary Survey Model) output and the corresponding regression equation in Arnot et al. (2005, p. 18). Distributions of biodegradation half-lives obtained with BIOWIN-3 (Ultimate Survey Model) output and the corresponding regression equation in Arnot et al. (2005, p. 17) and with the conversion scheme proposed by Aronson et al. (2006, p. 1957) are shown in Figure A1 in Appendix 1.

BIOWIN-3 and BIOWIN-4 results indicate the potential for aerobic biodegradation in general, i.e. without a reference to particular degradation processes in water or in soil. Boethling et al. (1995) found that degradation half-lives in soil can be shorter or longer than in water and that the ratio of half-lives in the two media is approximately log-normally distributed. Therefore, we did not introduce a constant factor to distinguish soil half-lives from water half-lives but use the BIOWIN output (after conversion into half-lives) for both water and soil. This is different from the approach used in the US EPA PBT profiler, where it is assumed that half-lives in soil are twice as long as half-lives in water (US EPA, 2003).

We performed the analysis presented in Section 2.2 below several times and with increasing numbers of example chemicals. This showed that with 50 or more chemicals the distribution of half-lives and their relationship to the ready test results as described below is approximately stable. In other words, it is unlikely that the results described below will significantly change if a higher number of example chemicals are used.

There is only one very persistent chemical in the set of example chemicals (pentabromodiphenylether). Persistent or very persistent chemicals (PCBs, organochlorine pesticides, additional brominated diphenylethers) are likely to be not degradable in the ready test. Therefore, most of them would increase the number of chemicals with consistent results (high half-lives and not readily biodegradable). In other words, our knowledge of cases in which ready-test results and estimated degradation half-lives are not consistent would not improve with a higher number of known persistent chemicals in the set of example chemicals. If the set of example chemicals is to be expanded, chemicals with half-lives between 10 and 60 days are of most interest because they would help to identify cases in which estimated half-life and result from the ready test are not consistent.

2.2 Evaluation of P screening criteria

The ideal screening criterion for P under REACH would have several defining characteristics. First, it must be possible to apply the screening criterion to all substances, regardless of the tonnage level produced or imported. Second, the screening criterion should produce very few, or ideally even zero, “false negatives”, where a false negative is a substance that is classified as “not P” by the screening criterion, but is in reality persistent. Third, to avoid excess work in the evaluation process, the screening criterion should produce as few “false positives” as possible, where a false positive is a substance that is classified as “P” by the screening criterion, but is in reality non-persistent.

With these ideal characteristics in mind, we compare two possible screening criteria for P under REACH; (i) results from the ready biodegradability test, and (ii) half-life threshold values in combination with half-lives estimated from chemical structure with the BIOWIN model. The ready-test results are compared with rankings of the 72 substances according to estimated half-lives in water or soil. Except for a few outliers (see below), the two types of degradation information are consistent, i.e. most of the chemicals ranked in the lower 50% according to half-lives also have a “yes” in the rbt and most of the chemicals ranked in the upper 50% according to half-lives have “no” in the rbt, see Figure 3. The upper and lower 50% of estimated half-lives are divided by a half-life of 13.7 days.

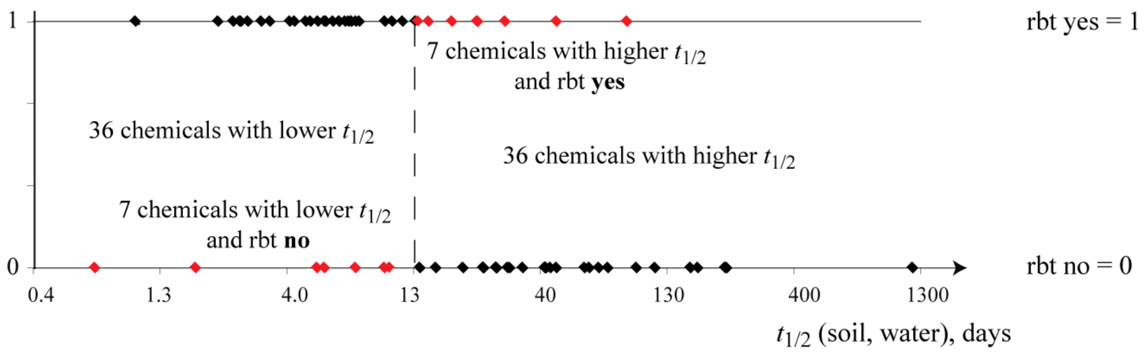

Figure 3: Ranking of the example chemicals according to estimated half-lives for aerobic biodegradation in comparison to yes/no classification from the ready biodegradability test.

There are seven chemicals with estimated half-lives below 13.7 days (0.73 to 10.6 days) that are not readily biodegradable. These chemicals would be screened into the "P" category by the ready-biodegradability criterion, but would be "not P" under a criterion of 13.7 days half life estimated by BIOWIN. These compounds are listed in Table 1; they include, among others, three long-chain substituted aromatic compounds, and two methacrylates. Correspondingly, there are also seven chemicals with half-lives above 13.7 days (15.1 to 91.5 days) which are readily biodegradable. They are also listed in Table 1.

Table 1: Chemicals with opposite classifications in rbt and half-life ranking. A half-life of 13.7 days separates the two main groups of chemicals with "yes" and "no" in the rbt.

no.	Chemical	CAS no.	rbt result	estimated half-life (days); from BIOWIN-4 primary biodegradation and regression by Arnot et al. (2005)
1	tris(ethylhexyl)benzene, 1,2,4-tricarboxylate	3319-31-1	no	0.73
2	di(ethyl-hexyl)-terephthalate	6422-86-2	no	1.82
3	methylacrylate	96-33-3	no	5.49
4	ethylacrylate	140-88-5	no	5.87
5	butylated hydroxytoluene	128-37-0	no	7.80
6	nonylphenol	25154-52-3	no	10.1
7	1,1-difluoroethylene	75-38-7	no	10.6
8	toluene	108-88-3	yes	15.1
9	theophylline	58-55-9	yes	18.7
10	1-diethylaminoethanol	100-37-8	yes	23.5
11	p-tert-butylphenol	98-54-4	yes	23.7
12	bisphenol A	80-05-7	yes	30.3
13	1,4-dichlorobenzene	106-46-7	yes	48.4
14	trichloromethylbenzene[a]	98-07-7	yes	91.6

a: trichloromethylbenzene is rapidly hydrolyzed (which is not reflected by the BIOWIN result) so that the "yes" from the ready test does not indicate a false negative.

The half-life scale in Figure 3 offers the possibility for P screening criteria other than the present rbt yes/no criterion, e.g. half-lives for aerobic biodegradation of 40 days and 10 days. When these two criteria are evaluated in comparison to the ready test, a first, straightforward observation is that the 40 days criterion divides the set of example chemicals (and also the entire universe of chemicals) in a way that there are fewer possible P chemicals (26% of the example chemicals) whereas the 10 days criterion generates even more possible P chemicals (60% of the example chemicals), see Figures 4 and 5. Does this mean that the 40-days criterion is preferable to both the ready test and the 10-days criterion?

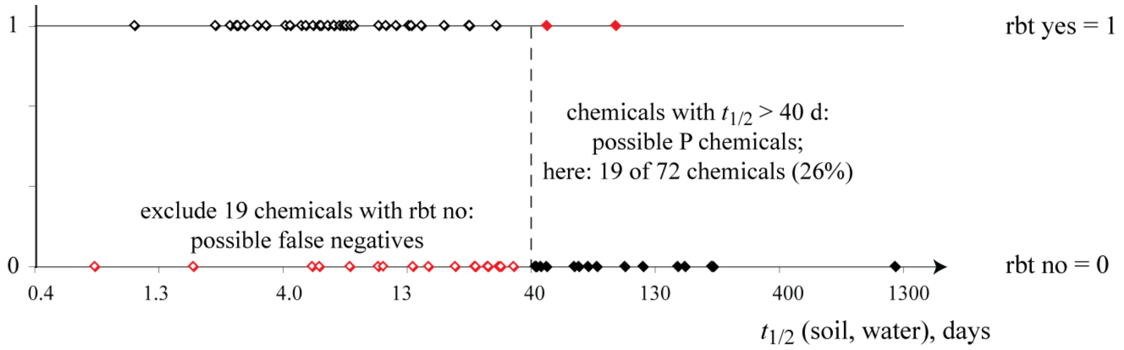

Figure 4: Classification of the 72 example chemicals according to estimated aerobic biodegradation half-lives with a criterion of 40 days.

This depends on the second of the above requirements for a screening criterion, the number of possible false negatives, i.e. persistent chemicals that are not identified by the screening criterion. Unfortunately, for the example chemicals there are no actual degradation half-lives to which we could compare the half-life estimates in order to determine the number of chemicals with erroneously low estimated half-life values. In general, half-life estimates from the BIOWIN-4 model are – at least – uncertain by a factor of 5 (Fenner et al., 2006).

It is this uncertainty in the half-life estimates creating the possibility of a considerable number of false negatives that makes a criterion defined in terms of half-lives unfavorable. Although the number of possible P chemicals can be reduced by setting a relatively high half-life criterion, this approach should not be chosen because it is likely to generate a high number of false negatives.

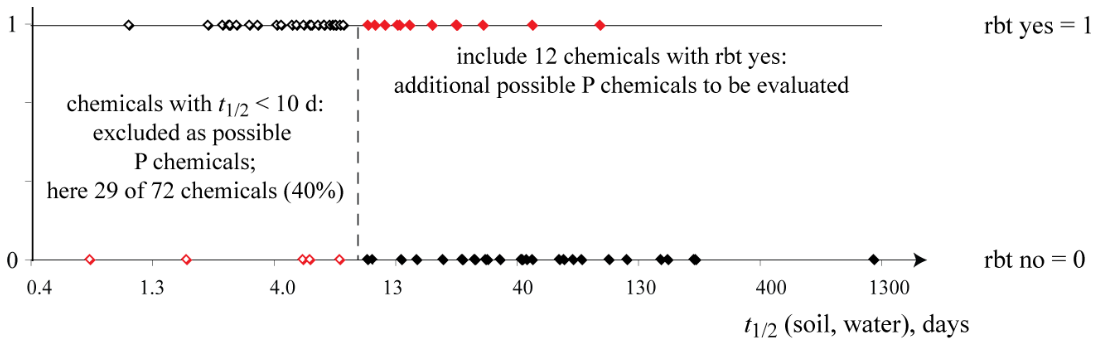

Figure 5: Classification of the 72 example chemicals according to estimated aerobic biodegradation half-lives with a criterion of 10 days.

The ready biodegradability test, in contrast, has according to Federle et al. (1997) and Aronson et al. (2006) the advantage that it generates only few false negatives. An example may be 1,4-dichlorobenzene, see Table 1, for which it is known that it is not rapidly degraded in the environment. Howard et al. (1991) report half-lives between one month and six months in water and soil for this compound.

In conclusion, we can state that it is difficult to reduce the number of false positives (which is in principle desired to reduce the number of chemicals undergoing P evaluation) without increasing the number of false negatives. It is very likely that the BIOWIN estimation method in combination with a half-life criterion of, for example, 40 days will create a considerable number of false negatives, which should be avoided. At the same time, it would be difficult to specify the kind and number of these false negatives because the uncertainties of the BIOWIN model are poorly characterized. Therefore, we recommend using the rbt yes/no result under REACH as the screening criterion for identification of possible P chemicals. This meets the requirement that rbt results are available for most chemicals over 1 t/a. In addition, we recommend that the kind of false negatives caused by the rbt (environmentally persistent chemicals showing ready biodegradability) be further investigated.

2.3 Screening criterion for persistence in air

A “no” result in the rbt reflects the potential for persistence caused by low biological degradability, which only reflects a subset of degradation processes in water, sediment and soil. It does not reflect the reactivity of a chemical in air, where mainly reaction with OH radicals determines persistence. Accordingly, it is possible that a chemical that is readily biodegradable but persistent in air is not identified as a possible P chemical if only the rbt is used as P screening criterion.

Therefore, we propose to complement the screening criterion for biodegradability by a second screening criterion for degradability in air. Because for most chemicals no measured rate constants for the reaction with OH radicals are available, we propose that the estimation software AOPWIN be used to derive an estimate of the atmospheric half-life of organic chemicals under REACH. AOPWIN is publicly available and easily applied. We propose a half-life of 2 days as screening criterion for persistence in air. This criteria value mostly reflects concern about long-range transport in the atmosphere (see below, Section 3.1).

2.4 Uncertainties

There are major uncertainties related to both measurements and estimation of degradation half-lives. In this report, we focus on the uncertainties associated with estimation methods that we propose to use in the P screening and/or actual P evaluation under REACH. The estimation software for reactions with OH radicals, AOPWIN, is discussed here; the estimation software for aerobic biodegradation is discussed in Section 3.4.

The methods used in the AOPWIN software have been developed by R. Atkinson and co-workers (Atkinson et al., 1999). The actual software has been developed by Syracuse Research Inc.; it is available free of charge from the web site of the US EPA (US EPA, 2003). AOPWIN (version 1.91) has recently been compared with other estimation software for reaction with OH radicals (Müller, 2005) and has been found to be the most accurate method and is, at the same time, relatively easy to use. The main limitation of AOPWIN is that its training set is not exactly known and that the program has not been trained for complex molecules. Only degradation of compounds in the gas phase can be estimated but AOPWIN does not provide information about the reactivity of semivolatile organic compounds (SOCs) bound to aerosol particles. However, for many SOCs, sorption to aerosol particles is important and influences their fate in the atmosphere, including long-range transport. Therefore, the application domain of AOPWIN is relatively limited and many chemicals to be assessed under

REACH will lie outside its application domain. This causes considerable uncertainties which are difficult to quantify. In several cases, it has been found that AOPWIN tends to overestimate the reactivity of complex molecules, i.e. it yields half-life results that are too low (Franklin et al., 2000; Krüger et al., 2005). Therefore, we consider it unlikely that AOPWIN will lead to a high number of false positives, but it might lead to a certain number of false negatives. However, this would still be an improvement in comparison to the current situation where there is no screening criterion for air at all.

For the test for ready biodegradability, which we recommend as P screening criterion, a more systematic investigation of cases in which it leads to false negatives is desirable. In particular, the behavior of chlorinated monoaromatic compounds under the conditions of the ready test should be evaluated in more detail.

3 Evaluation of P criteria

The PBT criteria and vPvB criteria in Annex XIII of REACH only include water, sediments and soil but not air[1]. This is a conceptual shortcoming that should be corrected because there might be chemicals with half-lives in all surface media below the criteria but that are highly persistent in air. These chemicals will not be identified with the current criteria. In addition, the current criteria are not consistent with the criteria for POPs as defined under the Stockholm Convention on Persistent Organic Pollutants because these criteria do include an air half-life criterion. The contracting parties of the Stockholm convention are obliged to integrate the criteria into their legislation. The present version of the P criteria of REACH can be considered only an incomplete implementation of the Stockholm convention commitments (or of Directive 850/2004) into the REACH regulation.

Another problem with the current criteria is that they are defined in terms of half-lives with numerical values that are only slightly lower than those used in Annex D of the Stockholm Convention. Because these values are rather high, there might be persistent chemicals which are not classified as P chemicals by the current criteria. For example, the lower bound of half-life estimates for hexachlorobutadiene in water and soil given by Howard et al. (1991) is 28 days, which is below the P criteria for water and soil. However, hexachlorobutadiene has been classified as P chemical by the PBT working group of the European Commission's Technical Committee for New and Existing Substances. Estimates of half-lives in air for hexachlorobutadiene range from 120 to 1200 days so that a half-life criterion for air would certainly identify hexachlorobutadiene as a P chemical.

3.1 Proposal for a P criterion for air

We propose to use a value of 2 days as P criterion for air. The value of 2 days is based on the consideration that transport in air is efficient and that within 2 days transboundary transport can occur (from several 100 to more than 1000 km). It is important to note that this is not a true persistence concern but a concern caused by the mobility of chemicals in air. Therefore, the 2-days criterion reflects a "critical" time scale of transport in air. The criterion is defined in terms of persistence but here persistence is a surrogate for mobility. Our proposal for a half-life criterion in air

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[1] The P/vP criteria from REACH vs. those from the Stockholm Convention are: 40/60 d (freshwater) and 60/60 d (seawater) vs. 60 d (water); 120/180 d (soil) vs. 180 d (soil); 120/180 d (freshwater sediments) and 180/180 d (marine sediments) vs. 180 d (sediments).

corresponds to the long-range transport criterion defined in Annex D of the Stockholm Convention.

Air is the main transport medium of chemicals in the environment and it is therefore important to address not only persistence but also long-range transport. A pure persistence criterion for air should be consistent with persistence criteria for water/soil/sediment (see below); this would then be a value greater than 2 days, depending on the value for water/soil/sediment, see below. However, LRT has a shorter time scale and in order to address LRT as well, the proposed criterion for half-life in air is 2 days.

3.2 Proposals for defining and applying P criteria under REACH

In this section, we propose a possible procedure for identifying P chemicals under REACH. To identify P chemicals, comparison should be made against all single-media half-lives using an "OR" relationship – i.e. if a substance exceeds any of the half life criteria it should be flagged as P. This makes it possible to identify chemicals that are persistent or mobile in air. An "AND" relationship would miss chemicals that are (highly) persistent in water, soil and sediment but are rapidly degraded in air (these chemicals could well cause severe local contamination) and also chemicals that are sufficiently long-lived in the air and, therefore, have high mobility but are not persistent in surface media. These chemicals can well cause transboundary pollution.

Proposal for defining P criteria under REACH

A substance fulfils the persistence/vP criterion (P/vP) if:

- the half-life in marine water is higher than 60 days, OR
- the half-life in fresh- or estuarine water is higher than 40/60 days, OR
- the half-life in marine sediment is higher than 180 days, OR
- the half-life in fresh- or estuarine water sediment is higher than 120/180 days, OR
- the half-life in soil is higher than 120/180 days, OR
- the half-life in air is higher than 2 days.

For chemicals below 100 t/a that are not readily biodegradable, biodegradation half-lives will have to be initially estimated with BIOWIN and the regression equations of Arnot et al. (2005) or Aronson et al. (2006). Simulation tests could be requested or provided based on the results of the BIOWIN and AOPWIN estimations. For chemicals over 100 t/a, half-lives from simulation tests (water, in some cases (K_{oc} high) also soil) will be available unless testing is not technically feasible. For these chemicals, the quality of the measured data has to be evaluated (see Section 3.3 and Appendices 2 and 3). It might be helpful to compare the measured data to estimates obtained with BIOWIN. Half-lives in air have to be estimated with AOPWIN also for these chemicals.

To evaluate the current P criteria defined in Annex XIII of REACH, it is helpful to consider that there are two conceptually different approaches to defining P criteria:

1. REFERENCE CHEMICALS APPROACH: Under this approach, it is assumed that the objective of the P assessment is to avoid chemicals similar to known POPs such as PCBs. These known POPs have different half-lives in different media (typically half lives in the different media are in the order air < freshwater

< seawater and soil < sediment). In this approach, the half-life criteria reflect the half-lives of these identified "reference chemicals" and are different for different media. We call this approach the *reference chemicals approach*.

It is important to note that the half-life criteria in REACH are different for the different media because they are intended to reflect the half-lives of actual chemicals that have been recognized as too hazardous to be released to the environment in any amount (reference chemicals). Other aspects such as systematically slower degradation of chemicals in soil, formation of bound residues in soil etc. are no reason for setting different half-life criteria for different media.

2. MANAGEMENT APPROACH: An alternative approach is to attempt to limit the actual persistence of chemicals in the environment as the goal of the assessment scheme. The objective is to control the presence of chemicals in the environment and, for this purpose, a half-life criterion around 90 days seems to be suitable because contamination by chemicals with half-lives of 90 days or less can be significantly reduced within one year. One year is a reasonable timescale because it is sufficiently short to evaluate and adjust measures for controlling releases of a chemical. Within this approach, all half-life criteria should be equal and be around 90 days. (A half-life criterion for air can be shorter because it is intended to address the mobility of chemicals, which is a different problem that occurs on a shorter timescale.) We call this approach the *management approach* to controlling P chemicals.

The management approach is more comprehensive because it covers all types of chemicals and helps to avoid contamination by any kind of persistent chemical. The reference chemical approach has "loopholes" for chemicals that are persistent in a way different from the reference chemicals, e.g. chlorofluorocarbons, which are highly persistent in air. We therefore suggest that the P criteria under REACH be defined according to the management approach, i.e. a value of 90 days is used for soil, water, and sediment and, to avoid long-range transport in air, a value of 2 days is used for air.

3.3 Uncertainties of measured degradation half-lives

For substances produced or imported in amounts greater than 100 t/a results from simulations tests on ultimate degradation in surface water, degradation in soil and sediment are required in Annex IX of REACH. Simulation test guidelines are available from the OECD (1996) for biodegradability in seawater (OECD 306), for aerobic sewage treatment (OECD 303A), for water and sediment (OECD 308/309), and for inherent biodegradability in soil (OECD 304A). A draft report from a workshop on "Strategies for selecting biodegradation simulation tests and their interpretation in persistence evaluation and risk assessment" (STEP, 2006) has recently been issued. The participants discussed various aspects for selecting simulation tests and environmental conditions for PBT evaluation and proposed a new waste water treatment simulation test. Simulation tests are also used in the pesticide licensing process, e.g OECD 308/309 for water/sediment (see also BBA (1990) and SETAC (1995)). Various test guidelines are also available for aerobic and anaerobic degradation in laboratory and field soils (see Appendix 2). Simulation tests are carried out with radiolabelled compounds. The time after which 50% or 90% of the applied quantity has dissipated or disappeared is used to quantify degradation. Mineralization, expressed as the evolution of $^{14}CO_2$, and the amount of metabolites and bound residues are also relevant information. Dissipation or disappearance times, DT_{50} and DT_{90}, include effects of many different processes (degradation, transport, adsorption, formation of bound residues, even volatilization). Bound (or non-extractable) residues are of particular concern because the chemical species still available in the sample are not identifiable and their (bio)availability not known. The FOCUS group (2005) has issued a report describing how the kinetics of the various fate processes in water and sediment can be separated and "true biodegradation" half-lives, $DegT_{50}$, can be quantified by kinetic modeling. We used data for some pesticides from water/sediment tests to investigate the various fate and transport processes and to derive compartment-specific half-lives for water and sediment (see Appenidx 3). In Appendix 2 we develop and apply a kinetic model by using results from soil simulations tests for several pesticides to derive $DegT_{50}/DegT_{90}$ instead of DT_{50}/DT_{90}. Although the conclusions are based on results for pesticides, they are also valid for the interpretation of simulation test for chemicals under REACH.

3.4 Uncertainties of estimated degradation half-lives

In our case study we estimated degradation half-lives from output from BIOWIN using the regression equation derived by Arnot et al. (2005). Uncertainty in these estimations arises from two sources: (i) uncertainty in the Arnot et al. regression, and (ii) uncertainty in the numerical output from BIOWIN. As for (i), Fenner et al. (2006) calculated the mean squared error from the regression data reported by Arnot et al. (2005). They found a value of 0.7 log units for the mean squared error of the regression equation in the top panel on p. 18 in Arnot et al. (2005), which converts into a factor of five in the half-lives. (ii) The uncertainty in the BIOWIN output was specified by Boethling et al. (1994) in their original publication describing the BIOWIN primary and ultimate degradation survey models. Boethling et al. (1994) report 95% confidence limits on the numerical output of the two models to be approximately 0.5 units. This encompasses 10% of the complete range of possible output from the models, thus at best BIOWIN can separate chemicals into one of 9 "noniles" of biodegradability.

The two conversion schemes from Arnot et al. (2005, p. 18, top) and Aronson et al. (2006, p. 1957) are shown in Figure 6, see also Figure 2 above and Figure A1 in Appendix 1 with results for the 72 example chemicals.

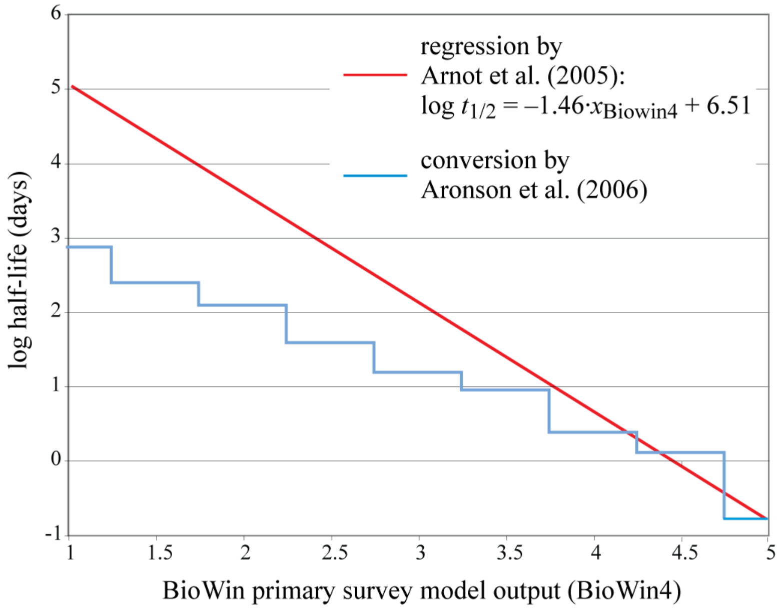

Figure 6: Methods for converting BIOWIN-4 output into half-lives.

Aronson et al. (2006, p. 1959) state that BIOWIN output yields too low half-lives for persistent chemicals, which implies that the regression by Arnot et al. is a better choice.

In the following, we discuss the relationship between BIOWIN and results from the ready biodegradability test in more detail.

The ready test is not meant to provide kinetic information about biodegradation. It seems that the ready test, although it does not provide kinetic information[2], is relatively reliable in the identification of non-persistent chemicals (few false negatives but more false positives). This is supported by the analysis by Aronson et al. (2006, p. 1955), who find that 92.7% of their example chemicals with a degradation of more than 40% in the ready test also have low half-lives but that only 58.3% of the example chemicals with less than 40% degradation in the ready test are actually persistent.[3] However, it has to be kept in mind that there is quite some uncertainty in the empirical half-life data used by Aronson et al. (2006). They compiled data from different data sources such as river die-away tests, simulation tests and field observations) In summary, the studies of Federle et al. (1997) and Aronson et al. (2006) support our recommendation that the ready test be used as a persistence screening criterion in the P assessment under REACH, see Section 4 and Figure 7.

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[2] Federle et al. (1997) observed “almost perfect non-correlation” between rates measured in ready tests and mineralization rates measured in activated sludge, river water and soil. However, they also state “Despite this limitation, ready tests remain very powerful tools for demonstrating the complete biodegradation of a chemical and the existing distribution of degradative microorganisms”.

[3] In our own analysis we investigated the results yielded by the ready test for a selection of persistent chemicals. The chemicals examined in Appendix 2 (see Section 3.3) are all not readily biodegradable (only two of them show noteworthy degradation in the ready-test at all; all other substances are only 0–3% mineralized after 28d). In Appendix 2 we describe the procedure to compare mineralization in a ready-test with that in soil. It shows that for these persistent chemicals no correlation exists between ready test results and mineralization half-lives in soil or DegT_{50}.

3.5 Overall persistence

Although single media half-life criteria are likely to be adopted in the final version of REACH, it is important to recognize that there are many advantages of calculating overall persistence, P_{ov}, using a multimedia model, compared to a single-media half-life approach. Overall persistence includes information about the environmental partitioning of a chemical and thereby assigns realistic weights to the single-media half-lives. It is a conceptually satisfying approach to estimating P since it incorporates limits on the influence of the individual half-lives based on estimated partitioning in the environment. P_{ov} information can also help to identify chemicals that are classified as P because of a high half-life in a compartment to which they might be released but where they do not reside (these chemicals can be considered to be type of "false positive" since they will be identified as P by the single media half-life criteria, but they will not be persistent in the environment). To reflect partitioning information in the P assessment, the PBT profiler (EPA, 2003) uses a Level III-multimedia model to calculate the relative distribution of a chemical and to dermine which half-lives are most relevant. P_{ov} information even goes a step further by considering the temporal remote state, i.e. the environmental partitioning of a chemical that is observed in the long term (Stroebe et al. 2004). The temporal remote state is independent of the emission scenario. In addition, P_{ov} calculations also yield estimates of long-range transport potential in air and/or water.

At this time, a consensus model for calculating P_{ov} is available (OECD P_{ov} and LRTP Estimation Tool) and also an approach that makes P_{ov} results independent of the release compartment (the temporal remote state as described by Stroebe et al. (2004)). P evaluations in terms of P_{ov} can be based either on the management approach (P_{ov} below 90 days, CTD below 4 m/s times 2 days) or on the reference chemicals approach (below P_{ov} of a reference chemical; reference chemicals in this context should be less persistent than the POPs reference chemicals selected by Klasmeier et al. (2006)).

To compare the ranking of chemicals according to P_{ov} with the P evaluation based on the REACH criterion of 40 days for fresh water, we calulated P_{ov} results for the 72 example chemicals with the OECD Tool. With one exception, the chemicals with water half-lives exceeding the 40-days criterion (19 chemicals) are identical to the 19 chemicals with the highest P_{ov} values. Methylchloride is the chemical that is among the high-P_{ov} chemicals but has half-lives in water/soil below 40 days. In other words, the two evaluation schemes are highly consistent when we look at the set of example chemicals. The effect of considering P_{ov} is that volatile chemicals with high half-lives in air are identified as persistent, because their P_{ov} is strongly influenced by the half-life in air. With the half-life criteria for water, soil and sediment, in contrast, these chemicals are not identified unless they have also high half-lives in water or soil. As illustrated by the examples of methylchloride and hexachlorobutadiene, this is not necessarily the case.

3.6 Long-range transport potential

Long-range transport potential describes the tendency of a substance to be distributed over the whole globe. The contamination of remote areas such as the arctic or pristine mountain areas is of particular concern. Persistence is only one of the governing processes; the other is transport with the mobile environmental media air and water. Semivolatile compounds are particularly prone to LRTP, which is considered as a selection criterion in the Stockholm Convention and the UNECE protocol but neither in REACH nor in the present TGD. In the Stockholm Convention, for example, it is suggested to use as screening criterion for LRTP "environmental fate properties and/or model results that demonstrate that the chemical has the potential for long-range environmental transport through air, water and migratory species, with the potential for transfer to a receiving environment in locations distant from the sources of release". LRTP can be calculated with the same multimedia models used to calculate overall persistence, P_{ov}. The approach of the spatial remote state makes it independent of the compartment of release. All of these benefits can be realized by applying The OECD P_{ov} and LRTP Screening Tool to calculate P_{ov} and LRTP as a complementary activity to the formal P screening process under REACH.

3.7 Combined P_{ov}/LRTP criteria

Fenner et al. (2005) compared nine different multimedia models and came to the conclusions that rankings of chemicals according to P_{ov} and LRTP are highly correlated among models and are largely determined by chemical properties. Domains of chemical properties in which model differences lead to different results were identified, and guidance on model selection is provided for model users. Klasmeier et al. (2006) derived a novel approach based on acknowledged POPs as reference chemicals to derive classification boundaries for P_{ov} and LRTP. They recommended adoption of the model-based classification method as a complement to screening against defined half-life criteria. The approach can yield classifications qualitatively different from those based on the single-media half-life criteria. We recommend that P evaluation criteria based on half-life cut-off values should be supported by the additional insights provided by multimedia models.

In addition to the reference chemicals approach used by Klasmeier et al. (2006), it is possible to apply the the management approach to set criteria for persistence and LRTP of chemicals in combined P_{ov}/LRTP evaluations. Applying the management approach merely requires regulators to define acceptable absolute limits on P_{ov} and LRTP for chemicals. As discussed above (p. 14), we recommend a 90-day overall persistence in the environment as a reasonable criterion for P_{ov} based on a management approach since this would allow significant reductions in environmental concentrations to be achieved within the timeframe of one year. Criteria for LRTP could be similarly derived, but they will have to be selected to be consistent with the metric of LRTP used in the modelling study. For example, a volatile chemical with a 2-day half life in air has a characteristic travel distance (CTD) of 500 km. The 2-day half-life in air was defined as a reasonable limit without reference to any specific chemicals, therefore, 500 km would represent a reasonable CTD criteria under the management approach.

4. Proposed P testing strategy

Our proposed strategy for evaluating organic substances for persistence under REACH is summarized in Figure 7. There are three main assessment stages in our proposed strategy:

1. Screening P assessment: All substances are initially categorized to the left or right side of the decision tree based on the ready biodegradability test and the estimated half-life for reaction with OH radicals.
2. REACH-defined P assessment: Substances are evaluated against the defined half-life criteria in REACH by using measured or estimated half-lives derived

from data about the substances available according to production volume, or, in some cases based on additional data submitted by the registrant.

3. Weight of evidence assessment: When the results of the Screening assessment and the REACH-defined assessment are in conflict, a weight-of-evidence assessment is carried out to attempt to identify the reasons for the disagreement and to make a final assessment. Conflicting data can be found in both cases: chemicals that are readily biodegradable can have long half-lives (false negatives from the ready test; relatively unlikely), and chemicals with a "no" from the ready test can have short half-lives (false positives from the ready test; more likely). At this stage all relevant data about the likely persistence of the substance should be considered in addition to the results from simulation tests. This includes, e.g., partitioning, overall persistence and long-range transport potential estimated by models. Also at this stage, information about P_{ov} and LRTP from models compared to criteria values derived from the management approach can be considered.

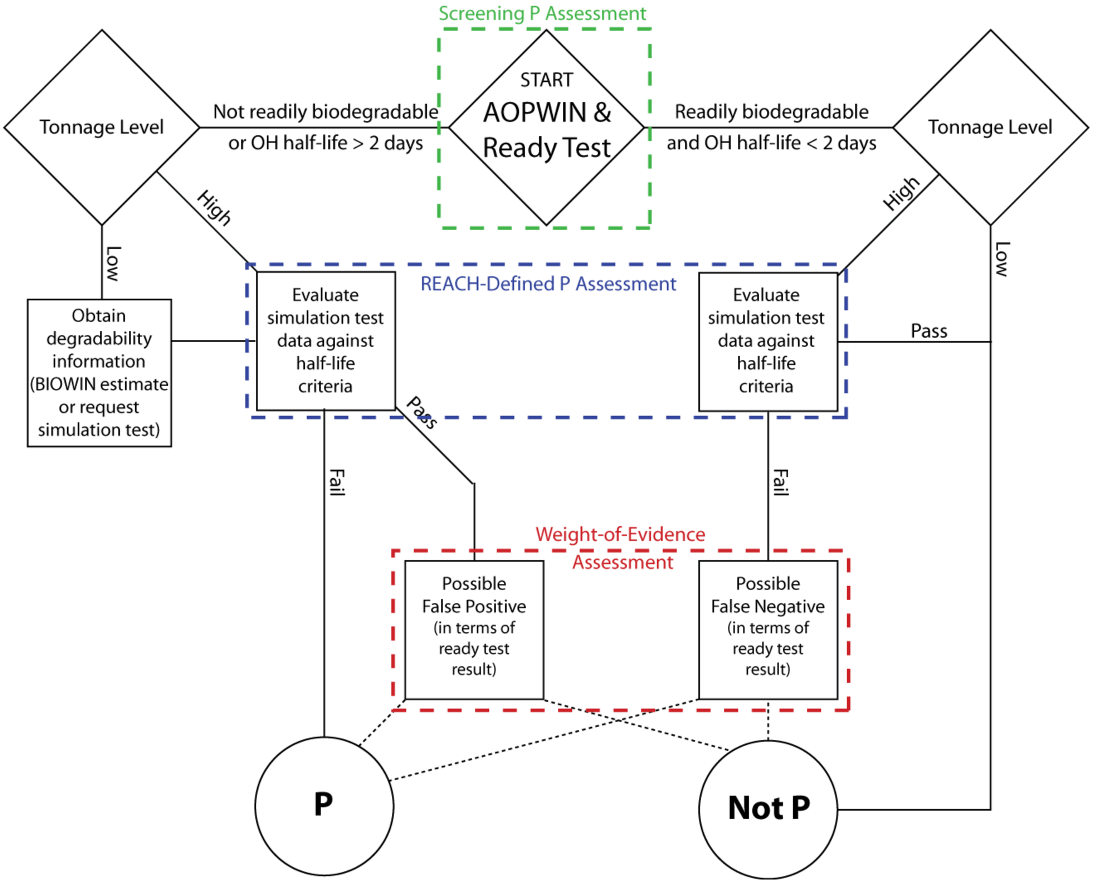

Figure 7: Proposed strategy for evaluation organic substances for persistence under REACH. Diamonds indicate binary decisions which can be made with available data for all substances. Squares indicate decisions or data generation steps that will require expert judgment. The different stages of the evaluation process discussed in the text are identified in the dashed, colored boxes.

The proposed strategy uses results from the ready biodegradability test and AOPWIN as the screening level P assessment. These data are expected to be available or easily accessible for all chemicals registered under REACH. The categorization in the screening assessment places the substance onto either the right or left side of the decision tree. Substances on the right side of the decision tree are most likely on the path to a "Not P" assessment, while substances on the left side are more likely to receive a "P" assessment. Once they are initially categorized at the screening level, the only way a substance can cross from one side of the decision tree to the other is by a weight-of-evidence judgment that it was incorrectly classified by the screening assessment.

Based on our case study of 72 substances, we believe a large majority of the substances placed on the right-hand side of the decision tree by the screening level P categorization will ultimately be assessed as being "Not P" because the ready biodegradability test is expected to produce only a small number of false negatives. It is much more likely that substances placed on the left-hand side of the decision tree will cross over to the right side and ultimately be assessed as "Not P".

Substances at the lowest two tonnage levels, i.e. below 100 t/a, that are placed on the right side of the decision tree by the screening assessment are essentially automatically assessed as "Not P" because it is expected that in most cases there are no other data available for making comparisons against the half-life criteria defined under REACH. If such data are available for the low-tonnage level substances, they should be compared against the half-life criteria defined in REACH.

For high tonnage level substances classified on the right side of the decision tree in the screening level analysis, information about degradation from the simulation tests should be available and can be evaluated against the defined half-life criteria under REACH. As mentioned above, we expect the majority of these substances will pass the criteria and be assessed as "Not P". Some substances may fail the criteria and enter the more detailed weight of evidence assessment since the data from the ready test and the experimentally derived half-lives are in conflict.

All substances classified to the left side of the decision tree enter the P evaluation procedure defined under REACH. For chemicals over 100 t/a, data from simulation tests in surface water and, depending on K_{oc}, in sediment and soil (see Section 1.1) will be available. It needs to be evaluated whether these data actually represent degradation DT_{50} data (see Section 3.4). Where necessary, degradation DT_{50} data should be derived from the measured data on degradation, which can then be compared to the half-life criteria values in Annex XIII of REACH. For chemicals below 100 t/a, there are several options: (i) simulation tests could be requested from the registrant during the evaluation, (ii) half-lives could be estimated with BIOWIN and a conversion of BIOWIN output into half-lives for aerobic biodegradation, or, (iii) additional information could be provided by the registrant to support the evaluation of the substances degradability against the half-life criteria.

Substances on the left side of the decision tree that are judged to pass the half-life criteria are possible false positives from the screening assessment using results from the ready test. Based on a weight-of-evidence approach that should include results from a multimedia model and evaluation against criteria values derived from a management approach, such substances might cross the decision tree to be classified as "Not P". This model-based evaluation could include a calculation of the chemical's fractions in different media so that it can be determined which half-lives are most influential. For these half-lives, improved empirical information could be requested. A suitable model available for that purpose is the OECD P_{ov} and LRTP Screening Tool.

Note that there remains significant scientific uncertainty about how reliable estimates of degradability in the real environment are. Data from simulation tests may represent DT50, and not DegT50. Correlations between BIOWIN and DT50 or DegT50 can be very poor, and there is current scientific debate about whether this conversion works at all. The best conversion scheme (Arnot et al., 2005) has an uncertainty of a factor of at least 5 in half-lives. In the worst case, the uncertainty is so high that a quantitative estimation of half-lives is impossible.

Therefore, an entirely different approach could be used in the weight of evidence assessment. For example, the half-lives or reaction rate constants of a chemical could be compared to those determined for reference chemicals in a well-defined reactivity test system (reference chemicals approach). Green and Bergman (2005) have suggested this approach and have identified as suite of relevant reaction types including oxidation, reduction, nucleophilic substitution, photolysis, and radical reactions. While still highly experimental, we believe this method of assessing environmental persistence holds considerable promise, and that further research in this area should be supported.

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Appendix 1: List of example chemicals

Table A1: Readily biodegradable example chemicals with partition coefficients and half-lives. Partition coefficients are mostly from Howard and Meylan (1997).

chemical	CAS no.	log K_{aw}	log K_{ow}	$t_{1/2,\mathrm{air}}$ AOPWin (hours)	$t_{1/2,\mathrm{ws}}$ Arnot BIOWin primary (hours)	$t_{1/2,\mathrm{ws}}$ Arnot BIOWin ultimate (hours)	$t_{1/2,\mathrm{ws}}$ Aronson BIOWin ultimate (hours)
glycerol	56-81-5	-6.15	-1.76	1.37E+01	7.93E+01	6.04E+01	5.59E+01
theophylline	58-55-9	-17.45	-0.02	1.33E+01	4.49E+02	3.19E+02	2.08E+02
1-butanol	71-36-3	-3.44	0.88	3.00E+01	7.03E+01	5.78E+01	5.59E+01
methyl acetate	79-20-9	-2.33	0.18	9.88E+02	1.24E+02	1.27E+02	5.59E+01
bisphenol A	80-05-7	-9.39	3.32	3.19E+00	7.27E+02	5.29E+02	2.08E+02
methyl methacrylate	80-62-6	-1.86	1.38	1.40E+01	1.41E+02	1.46E+02	5.59E+01
di butyl phthalate	84-74-2	-4.45	4.80	2.77E+01	2.54E+01	6.26E+01	3.00E+01
1-vinyl-2-pyrrolidone	88-12-0	-5.65	0.37	6.90E+00	1.61E+02	2.50E+02	5.59E+01
1,3-dimethyl urea	96-31-1	-7.14	-0.49	8.24E+01	2.87E+02	1.93E+02	2.08E+02
trichloromethylbenzene	98-07-7	-1.97	3.90	7.19E+02	2.20E+03	1.99E+03	3.60E+02
p-tert-butylphenol	98-54-4	-4.31	3.31	6.32E+00	5.69E+02	3.97E+02	2.08E+02
nicotinamide	98-92-0	-9.93	-0.37	1.10E+02	1.81E+02	4.50E+02	5.59E+01
1-diethylaminoethanol	100-37-8	-6.89	0.05	2.60E+00	5.63E+02	2.86E+02	2.08E+02
triacetin	102-76-1	-6.30	0.25	3.02E+01	5.36E+01	1.39E+02	5.59E+01
2-ethylhexylacrylate	103-11-7	-1.75	4.09	1.28E+01	8.58E+01	1.11E+02	5.59E+01
1,4-dichlorobenzene	106-46-7	-1.01	3.52	8.02E+02	1.16E+03	7.36E+02	2.08E+02
isobutyl acrylate	106-63-8	-2.05	2.22	1.87E+01	1.62E+02	1.70E+02	5.59E+01
ethylene diamine	107-15-3	-7.15	-2.00	4.05E+00	1.87E+02	1.47E+02	5.59E+01
glyoxal	107-22-2	-6.87	-1.66	1.01E+01	6.62E+01	1.47E+02	5.59E+01
1-methoxy-2-propanol	107-98-2	-6.13	-0.44	1.38E+01	1.94E+02	1.34E+02	5.59E+01
1-methoxy-2-propyl acetate	108-65-6	-3.85	0.56	2.16E+01	1.70E+02	1.77E+02	5.59E+01
toluene	108-88-3	-0.58	2.70	4.91E+01	3.63E+02	2.25E+02	2.08E+02
n-pentane	109-66-0	1.71	3.39	6.33E+01	1.08E+02	8.48E+01	5.59E+01
Isobutyl acetate	110-19-0	-1.75	1.78	5.58E+01	1.52E+02	1.59E+02	5.59E+01
but-2-yne-1,4-diol	110-65-6	-6.23	-0.93	7.59E+00	1.19E+02	8.68E+01	5.59E+01
dimethyl terephthalate	120-61-6	-5.04	2.25	4.47E+02	1.03E+02	1.72E+02	5.59E+01
catechol	120-80-9	-6.89	0.88	1.11E+01	2.45E+02	1.65E+02	5.59E+01
2-phenoxyethanol	122-99-6	-5.71	1.16	7.86E+00	1.80E+02	1.87E+02	5.59E+01
n-butyl acetate	123-86-4	-1.92	1.80	5.24E+01	6.17E+01	7.63E+01	5.59E+01
methacrylonitrile	126-98-7	-2.00	0.54	3.07E+01	3.23E+02	2.11E+02	2.08E+02
DMAC	127-19-5	-6.27	-0.77	1.58E+01	1.43E+02	2.19E+02	5.59E+01
2-naphtol	135-19-3	-5.73	2.70	1.28E+00	3.30E+02	2.28E+02	2.08E+02
n-butyl acrylate	141-32-2	-1.73	2.36	1.86E+01	6.54E+01	8.15E+01	5.59E+01
ethylacetate	141-78-6	-2.22	0.70	1.51E+02	1.33E+02	1.37E+02	5.59E+01
ethyl acetoacetate	141-97-9	-4.31	0.25	1.30E+02	1.76E+02	1.81E+02	5.59E+01
Imidazole	288-32-4	-3.81	-0.08	7.13E+00	2.61E+02	1.73E+02	2.08E+02

Table A2: Non-readily biodegradable example chemicals with partition coefficients and half-lives. Partition coefficients are mostly from Howard and Meylan (1997).

chemical	CAS no.	log K_{aw}	log K_{ow}	$t_{1/2,air}$ AOPWin (hours)	$t_{1/2,ws}$ Arnot BIOWin primary (hours)	$t_{1/2,ws}$ Arnot BIOWin ultimate (hours)	$t_{1/2,ws}$ Aronson BIOWin ultimate (hours)
methyl chloride	74-87-3	-0.44	0.91	4.97E+03	335.53	240.88	208.08
1,1-difluoro-ethylene	75-38-7	-0.68	1.24	1.13E+02	255.46	169.23	55.92
2-nitroaniline	88-74-4	-5.35	1.85	1.91E+01	758.45	536.48	208.08
2-chlorotoluene	95-49-8	-1.20	3.42	1.41E+02	759.73	475.94	208.08
1,2-dichloro benzene	95-50-1	-1.11	3.38	6.41E+02	1161.21	735.93	208.08
1,2,3-trichloro-propane	96-18-4	-1.78	1.98	7.31E+02	1056.18	958.62	208.08
methyl acrylate	96-33-3	-2.09	0.8	2.72E+01	131.69	135.11	55.92
methylbenzene-sulfonyl chloride	98-59-9	-3.40	3.49	2.10E+02	594.40	405.51	208.08
ethyl benzene	100-41-4	-0.49	3.15	3.62E+01	388.24	242.49	208.08
1,3-diphenyl-guanidine	102-06-7	-9.54	2.89	3.01E+00	1046.64	658.21	208.08
1,2-dichloro-ethane	107-06-2	-1.40	1.48	1.04E+03	595.40	480.53	208.08
phenol, 2,2'-methylenebis 6-(1,1-dimethyl-ethyl)-4-methyl-	119-47-1	-9.49	6.25	6.28E+00	4188.39	2856.03	360.00
1,2,4-trichloro-benzene (*)	120-82-1	-1.24	4.02	4.06E+02	1704.00	1704.00	1704.00
2,4-dichloro phenol	120-83-2	-3.89	2.92	8.61E+01	1098.18	698.82	208.08
butylated hydroxytoluene	128-37-0	-3.77	5.10	1.40E+01	187.31	1179.90	55.92
ethyl acrylate	140-88-5	-1.79	1.32	1.60E+01	140.95	145.83	55.92
3,4-dichlorobut-1-ene	760-23-6	-0.46	2.6	1.26E+01	675.40	553.67	208.08
HHCB	1222-05-5	-2.36	5.90	6.79E+00	2393.88	1703.66	360.00
AHTN	1506-02-1	-2.30	5.7	1.45E+01	2496.62	1762.58	360.00
mtbe	1634-04-4	-1.62	1.24	1.14E+02	497.06	332.48	208.08
clopyralid (acid)	1702-17-6	-9.23	-2.55	7.02E+02	1498.74	1283.31	360.00
tris(2-ethylhexyl)-benzene, 1,2,4-tricarboxylate	3319-31-1	-4.74	11.59	7.83E+00	17.50	91.68	30.00
terbuthylazine (base)	5914-41-3	-5.79	3.04	4.07E+01	4189.80	4169.79	360.00
DEHT	6422-86-2	-3.38	5.11	1.17E+01	43.75	115.37	30.00
nonyl phenol	25154-52-3	-7.01	6.36	4.97E+00	243.23	198.91	55.92
penta BDE (**)	32534-81-9	-3.67	6.76	4.67E+02	29513.13	15925.29	900.00
dimethachlor	50563-36-5	-6.99	2.10	9.52E+00	745.56	1243.48	208.08
metolachlor	51218-45-2	-6.59	3.25	6.89E+00	854.31	1448.70	208.08
thiodicarb	59669-26-0	-7.01	1.57	2.90E+01	1045.23	822.62	208.08
propiconazole	60207-90-1	-6.78	3.72	1.66E+01	5353.37	3749.71	360.00
penconazole (base)	66246-88-6	-6.52	3.73	4.77E+01	2844.47	1867.64	360.00
fenpropidin (base)	67036-00-6	-5.45	2.59	3.41E+00	3918.67	2010.92	360.00
aclonifen	74070-46-5	-5.91	4.37	3.02E+01	1854.14	1943.22	360.00
4-nonylphenol, branched	84852-15-3	-5.89	6.36	4.97E+00	600.83	414.91	208.08
myclobutanil	88671-89-0	-6.76	2.94	5.47E+01	1565.16	948.28	360.00
bromuconazole	116255-48-2	-6.26	3.24	4.45E+01	5447.78	4130.93	360.00
amidosulfuron	120923-37-7	-7.86	0.001	1.88E+00	668.84	1188.07	208.08

Notes: light blue: chemical in list of the PBT working group of the TCNES. Light brown: property data from Beyer and Matthies (2001). *: half-lives from Mackay et al. (1997). **: partition coefficients from Schenker et al. (2005).

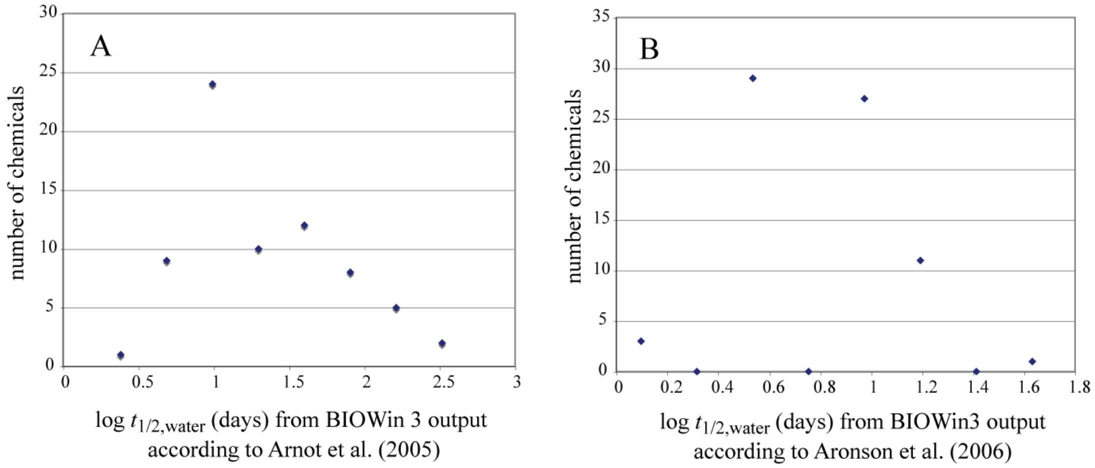

Figure A1: Histograms with estimated biodegradation half-life values of the 72 example chemicals. A: derived from BIOWIN-3 model (ultimate degradation) in combination with the regression equation reported by Arnot et al. (2005, p. 17). B: derived from BIOWIN-3 model (ultimate degradation) in combination with the conversion scheme proposed by Aronson et al. (2006, p. 1957).

Appendix 2: Determination of Soil Biodegradation Half-lives from Simulation Tests

Abstract

The current definition of half-life in soil is not appropriate in the context of PBT assessment as it includes formation of non-extractable residues as a loss process. A pure degradation half-life DegT50 is therefore defined. A first approach for determination of this endpoint by inverse modeling is presented. Experimental data from various soil simulation tests can well be fitted to the model. Several compounds classified as not persistent with the current definition would be classified as very persistent based on DegT50 values. An attempt to derivate DegT50 values from tests for ready biodegradability fails.

Introduction

Persistence is a property of increasing concern in assessment of chemicals. This is particularly the case in combination with bioaccumulation, as no trustworthy prediction about exposure is then possible. The current risk assessment approach of comparing exposure and effect can therefore not be applied to persistent bioaccumulative substances. Furthermore, long-term effects cannot be excluded (UBA, 2005).

Consequently, environmental legislation increasingly attends to persistent compounds, as in the Stockholm Convention limiting or prohibiting the production and use of certain persistent organic pollutants (UNEP, 2001).

Persistence also plays an essential role in the EU legislation proposal REACH (Registration, Evaluation and Authorisation of Chemicals (Commission of the European Communities, 2003)). Within the scope of PBT-assessment, the crucial parameter for persistence of a chemical is its half-life[4] in different compartments. The threshold value for considering a substance as (very) persistent in soil is 120 d (180 d). The notion of half-life should therefore be defined very carefully, and with regard to the issue of persistence.

In this article, it is argued that the current notion of half-life (DT50) in soil is inappropriate in the context of PBT assessment, as it includes formation of non-extractable residues as a loss process. Instead, a half-life restricted to pure degradation processes (DegT50) is proposed. First approaches on how to derive this endpoint from soil simulation tests and tests for ready biodegradability are presented and evaluated.

Non-Extractable Residues

The current approach of DT50 determination refers to the amount of extractable parent compound in soil. However, considerable unextracted amounts remain in the soil and are thus regarded as degraded in this approach. The current knowledge about these non-extractable residues shall therefore be resumed here in order to evaluate whether or not it is justified to consider NER as degraded.

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[4] Some authors distinguish between dissipation half-life (first order kinetics) and DT50 (any kinetics). In this article, both terms are used synonymously, thus adopting the use in REACH.

Definition

The International Union of Pure and Applied Chemistry (IUPAC) defines non-extractable or bound residues (NER) as “chemical species originating from pesticides, used according to good agricultural practice, that are unextracted by methods which do not significantly change the chemical nature of these residues” (Kearney, 1982; Roberts, 1984).

At a DFG workshop in 1996 a modification of this definition was proposed insofar as they “represent compounds in soils, plants or animals which persist in the matrix in the form of the parent substance or its metabolite(s) after extraction. The extraction method must not substantially change the compounds themselves or the structure of the matrix” (DFG, 1998).

Both definitions are problematic as the nature of the extracted fraction depends qualitatively and quantitatively on the employed extraction procedure (Craven and Hoy, 2005). Roberts (1984) therefore stresses that “in each reference to a non-extractable residue, the extraction procedure must be given”.

The operational definition of NER causes not only a problem due to the different extraction procedures employed. Additionally, the extractability of a compound is “not related to any specific parameter, such as bioavailability” (Craven and Hoy, 2005):

On the one hand, the “free”, extractable chemical - however defined - may be reversibly sorbed to soil particles and consequently be less bioavailable (Gevao et al., 2000). On the other hand, it has been reported that NER are to some extent bioavailable to microorganisms, plants, and earthworms (Gevao et al., 2001; Verma and Pillai, 1991; Khan, 1980; Fuhremann and Lichtenstein, 1978).

A number of authors have proposed to develop a different definition of extractability, with milder extraction procedures and being more related to environmentally meaningful measures such as bioavailability (e.g. Craven and Hoy, 2005; Yu et al., 2005; Reid et al., 2000; Alexander, 2000; Calderbank, 1989). However, bioavailability has been shown to be species-dependent (e.g. Yu et al., 2005; Reid et al., 2000; Guerin and Boyd, 1992), so that a single chemical test will never be able to mimic bioavailability (Reid et al., 2000). Craven and Hoy (2005) propose “to determine bioavailability for a wide range of organisms and compounds under a variety of soils and conditions” in order to identify an extraction procedure replicating bioavailability best in most circumstances, yet keeping some conservatism.

State of the Art

The binding of NER may be the result of covalent binding to soil organic matter (SOM) or physical entrapment (Barraclough et al., 2005).

NER may consist of the parent compound, or the metabolites/degradation products, or both, depending on the considered compound (Ostiz and Khan, 1994; Loiseau and Barriuso, 2002; Dec et al., 1997). Due to the nature of NER, their analytical characterization remains a very difficult task, as the required powerful extraction procedures may alter the chemical nature of the compound (Calderbank, 1989). This step will therefore probably not become a routine step in risk assessment (Barraclough et al., 2005). Whereas the nature of NER is mostly unknown, “it is […] generally considered that exposure should be less than that resulting from initial use of a compound, even if all the bound residue was re-mobilised through some mechanism" (Craven and Hoy, 2005).

It is believed that the primary cause of NER release is the activity of microorganisms. Further factors include "changes in agricultural practice and the introduction of certain chemicals that may change the chemistry of the soil" (Gevao et al., 2000). Barraclough et al. (2005) hypothesize that degradation of the organic matter matrix is a prerequisite for release of NER, whether entrapped or covalently bond. Release estimated based on this assumption would be very low even after decades.
Hartlieb et al. (2003) report a decline of pyrene NER in biowaste from 26% of applied radioactivity after 120 d to 23.8% of applied radioactivity after 370 d. This confirms Calderbank's (1989) view that release of NER is a slow process.
On the other hand, Gevao et al. (2001) report release of considerable amounts (up to 24%) of previously non-extractable pesticides after a 28d-period.
In any case, the long-term risk of NER formed after multiple administration of several compounds is yet unclear (Barraclough et al., 2005).

Relevance of NER

The regulatory significance of NER is currently discussed and uncertain (Craven and Hoy, 2005). A great deal of uncertainty is due to the incomplete understanding of the underlying processes. Many studies detect a decline of bioavailability and toxicity during aging of pesticides in soil, as summarized in the review of Reid et al. (2000), but "the extent to which this decline is reversible is still unclear" (Barraclough et al., 2005).
Barraclough et al. (2005) stress that "the difficulty of hazard identification and the problems estimating bioavailability" render conventional procedures for risk assessment inapplicable. "We should [therefore] not be loading soil with chemicals whose future behavior and toxicity we cannot predict".
In contrast, Alexander (2000) emphasizes that the currently used harsh extraction procedures already overestimate bioavailability.

Jones et al. (2000) sum up the double-edged nature of NER assessment:
On the one hand, NER formation may be considered as the first step to deactivation of the pesticide, finally ending with the complete incorporation in the SOM. On the other hand, certain bound residues are formed from potentially toxic/biologically active molecules and persist in soil. Though they are not extractable, they may have long-term effects on soil fertility, or enter the food chain, or be remobilized.

Since formation of NER renders chemicals less active and less bioavailable, it may be sufficient in conventional risk assessment to consider NER as degraded, as the immediate risk emanating from them appears to be marginal.
PBT assessment on the other hand is based on the precautionary principle. Long term exposure of persistent bioaccumulative substances cannot reliably be estimated, and long term effects can never be excluded for chemicals with PBT properties.
As NER may consist of the parent compound and may also be released in the long term, NER in PBT assessment must be considered as undegraded while no further knowledge about their composition and fate exists. DT50 values are therefore inappropriate for use in PBT assessment.

If DT50 values cannot serve as an endpoint in PBT assessment, an alternative endpoint is called for. The idea of taking a “pure” degradation half life (DegT50) including only real degradation processes suggests itself. However, such an endpoint cannot easily be determined analytically, because NER may consist of metabolites, or parent compound, or both, and the analytical procedures for their characterization are too complex to become standard tools.

A straightforward conservative approach would consider all NER as undegraded parent compound. After addition of the amount of NER to the extractable amount of parent compound, the degradation rate constant could then be determined by simple curve-fitting. However, this approach would systematically underestimate the true degradation.

The authors therefore present a first pragmatic approach to determine rate constants for primary degradation, formation of NER from the parent compound and formation of NER from metabolites/degradation products from data of soil simulation tests by inverse modeling.

The developed model was tested with data from soil simulation tests of 8 different ^{14}C-labelled pesticides in different soils and conditions.

Development of a Kinetic Model

The underlying model should be complex enough to contain the basic state variables, but at the same time, it should be kept as simple and general as possible.

Therefore, all processes are assumed to follow first order kinetics. Furthermore, the compartments parent compound (P), non-extractable residues (N), volatile degradation products (V), and metabolites/degradation products (M) are considered. Volatile degradation products can easily be combined to one state variable, as only small amounts of substances other than CO_2 were measured for the considered compounds. Combining the metabolites to one state variable containing identified and non-identified degradation products is a way of simplifying the model and of increasing the comparability of the different compounds.

Volatile degradation products and NER are considered as sinks. In fact, release from bound residues has been observed (see above), but in most literature reports it does not play a role for the observed time scales. Direct mineralization of the parent compound turned out to be an unnecessary pathway for the considered compounds, as the respective rate constant was mostly 0 and no considerable ameliorations of the fit were achieved in the other cases. This pathway was therefore eliminated from the model.

The resulting model structure is shown in Figure 1.

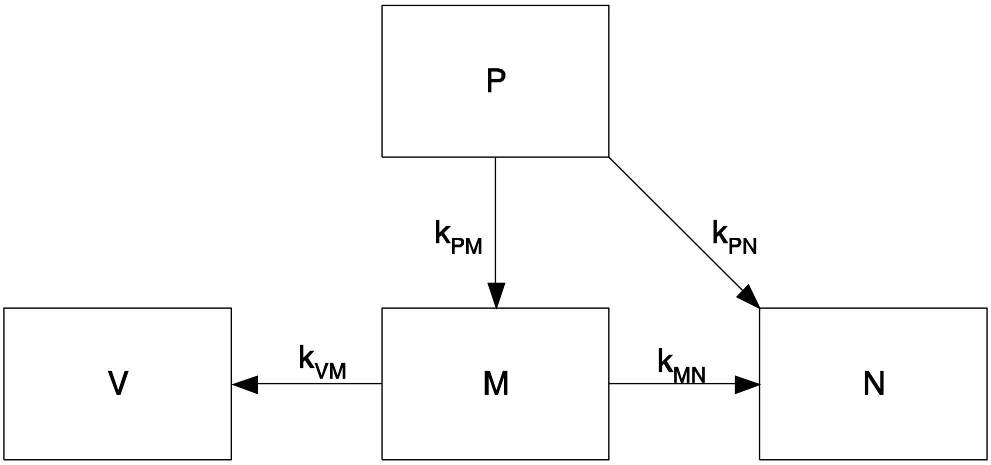

Figure 1: Model structure

This can be expressed in terms of a system of linear differential equations:

$$\frac{dP(t)}{dt} = -(k_{PM} + k_{PN}) \cdot P(t)$$

$$\frac{dM(t)}{dt} = k_{PM} \cdot P(t) - (k_{MN} + k_{MV}) \cdot M(t)$$

$$\frac{dN(t)}{dt} = k_{PN} \cdot P(t) + k_{MN} \cdot M(t)$$

$$\frac{dV(t)}{dt} = k_{MV} \cdot M(t)$$

where P(t), M(t), N(t) and V(t) are the respective state variables in % of applied radioactivity (without correction for 100% recovery), and k_{xy} [d^{-1}] are the rate constants for a flow from compartment X to compartment Y.

The system was solved analytically with the initial conditions $P(0)=P_0$, $M(0)=0$, $N(0)=0$, $V(0)=0$.
The half-life for pure biodegradation, DegT50, and the respective DegT90 value can be read from this model as

$$DegT50 = \frac{\ln(2)}{k_{PM}}$$

$$DegT90 = \frac{\ln(10)}{k_{PM}}$$

The classical DT50 and DT90 values are obtained as

$$DT50 = \frac{\ln(2)}{k_{PM} + k_{PN}}$$

$$DT90 = \frac{\ln(10)}{k_{PM} + k_{PN}}$$

Fitting Procedure

Least-square-fitting of the data was performed using the computer program Scientist for Windows (Version 2.0). The program uses a modified Powell algorithm. Starting values for M, N, and V were set to 0, the starting value for P, P_0, was optimized together with the rate constants. The parameter range for P_0 was constrained to [80, 120] (%), the parameter range for all rate constants was constraint to [0, 0.5] (t^{-1}). Starting values were 95 % for P_0 and 0.01 t^{-1} for all rate constants. If visual inspection of the resulting fit raised suspicion that the found optimum was only a local one, the fitting procedure was repeated with appropriately changed starting values, but in the same parameter ranges.

Data

Data from laboratory studies in aerobic soils were provided by the German Federal Environment Agency (Umweltbundesamt). The data set was inhomogeneous with respect to extraction procedures, test guidelines and test conditions. However, many studies were conducted according to BBA guideline IV 4-1 (BBA, 1986). All data sets were fitted, but only those under standard conditions (20°C and 60 % field capacity or 40 % maximum water holding capacity, non-sterile soil) were used for determination of DegT50 and DT50 values.

The number of studies fitted and used for half-life determination for the different chemicals is presented in Table 1.

Table 1: Number of studies fitted and used for half-life determination

	fitted	Standard conditions
Aclonifen	5	4
Bromuconazole	4	2
Dimethachlor	10	7
Ethofumesate	4	4
Fenpropidin	11	7
Metolachlor	13	8
Penconazole	10	6
Propiconazole	4	2

Data sets contained measurements at 6 - 12 different time points.

Data were treated as recommended by the FOCUS work group on degradation kinetics (FOCUS, 2005).

Data for metabolites were calculated as Extractable minus Parent.

The Root Mean Square Error (RMSE), defined as

$$RMSE = \sqrt{\frac{\sum_{i=1}(C_i - O_i)^2}{n}}$$

$C_i = calculated\ values$

$O_i = observed\ values$

$n = number\ of\ values$

was calculated in order to compare the goodness of the different fits.

Results and Discussion

Table 2 resumes the median RMSE values for the fits of the different data sets.

Table 2: Median RMSE values

	P	M	N	V
Aclonifen	6,47	2,25	6,74	0,51
Bromuconazole	2,07	1,80	2,10	0,37
Dimethachlor	2,64	2,84	2,21	0,64
Ethofumesate	2,16	1,67	3,67	0,91
Fenpropidin	5,10	2,48	2,35	2,05
Metolachlor	3,37	2,86	1,42	1,24
Penconazole	3,88	2,73	1,65	0,59
Propiconazole	6,14	4,60	3,00	1,18

As determination of a RMSE value identifying an acceptable fit is difficult,
Figure 2 shows a fitted data set with representative RMSE error (3.26 for P, 2.69 for M, 2.61 for N and 0.81 for V) in order to allow a visual assessment of a fit with representative quality. The study was performed in compliance with Commission Directive 95/36/EC of 14 July 1995 amending Council Directive 91/414/EEC: Annex II: 7.1.1 and under consideration of BBA guideline IV 4-1 (BBA, 1986). In this example, extraction procedures included extraction at room temperature with acetonitrile/water 8:2, reflux extraction (at 80°C for 2 hours) with acetonitrile, neutral harsh extraction with acetonitrile/water 8:2 extraction (at 80°C for 2 hours) and acid harsh extraction with acetonitrile/ 0.1 N HCl 9:1 (at 80°C for 2 hours).

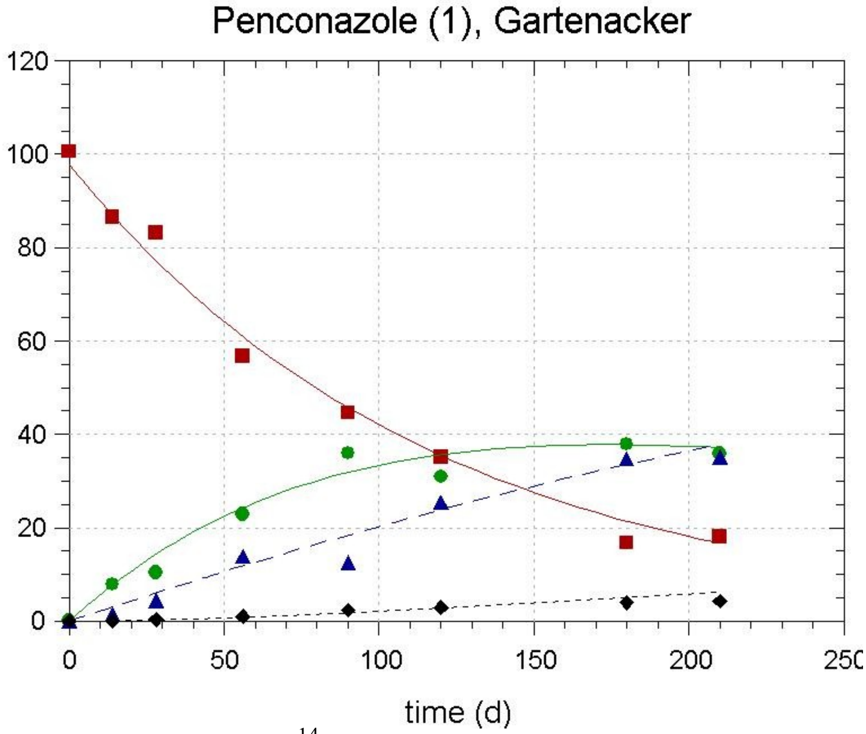

Figure 2: Degradation of ^{14}C-labelled Penconazole in soil under aerobic laboratory conditions [in % applied radioactivity]. Solid line, squares: Parent compound. Long dashes, circles: Metabolites. Medium dashes, triangles: NER. Short dashes, diamonds: Volatile degradation products.

This fit, which is representative in terms of RMSE shows that the model generally fits the data of all substances well. Only for Aclonifen, Propiconazole, and Fenpropidin problems occur in some fits. This is reflected by the median RMSE, which is markedly higher for these three substances. In case of Fenpropidin, these problems can clearly be assigned to extremely varying recoveries. When corrected for 100% recovery, the data for Fenpropidin can be fitted very well. In case of Aclonifen the data themselves seem to be problematic, with maximum metabolite amounts at time 0 and sudden increases of the amount of parent compound. In case of Propiconazole, data uncertainties probably inhibited a better fit.

As the data can well be fitted to the model, it can be assumed that it is not oversimplified. Particularly, the assumption of first order kinetics and the combination of all metabolites/degradation products to one state variable had no negative influence on the model results.

However, more detailed models may be required in other cases if considerable amounts of metabolites with cascading pathways are formed, or if metabolites formed in parallel exhibit a very different kinetic behavior, or if different kinetics is observed. For some chemicals, it may also be necessary to include a pathway for direct mineralization of the parent compound.

As expected, decrease of NER could not be observed in any of the data sets, thus confirming the approach of regarding NER as a sink for the considered time scales. Furthermore, the different extraction procedures (and therewith different definitions of NER) did apparently not affect the goodness of fit.

The DT50 for the study in Figure 2 is 82 d, the DegT50 is 112 d. This exemplifies that on the one hand substances that are classified as not persistent with the DT50 approach may be considered persistent with the DegT50 approach. On the other hand, it shows that the formation of relatively large amounts of NER does not necessarily lead to a greatly increased DegT50. This is particularly visible taking into account that the conservative approach of considering all NER as parent compound would result in a DegT50 longer than 210 d.

For a better handling of the results, the median DT50 and DegT50 values from studies under standard experimental conditions were calculated for the 8 pesticides. If the number of values was even, the geometric mean of the two median values was calculated for the rate constants. Median DT50/90 and DegT50/90 values are summarized in Table 7.

Table 3: Comparison of DegT50/90 and DT50/90 of the eight pesticides

	DegT50 [d]	DT50 [d]	DegT90[d]	DT90[d]	Deg/DT
Aclonifen	321	79	1068	262	4.1
Bromuconazole	1370	504	4553	1674	2.7
Dimethachlor	10	5	33	18	1.9
Ethofumesate	364	100	1209	331	3.6
Fenpropidin	125	93	415	310	1.3
Metolachlor	24	15	79	51	1.6
Penconazole	229	136	761	453	1.7
Propiconazole	111	87	368	290	1.3

Though the absolute values must be interpreted very carefully, as the experimental conditions do not correspond to the field conditions, it is obvious that DegT50 values are often considerably larger than DT50 values. Particularly, the DT50 values of Aclonifen, Ethofumesate, and Penconazole are below 180d, while their DegT50 values are beyond this threshold defining substances as “very persistent” according to the REACH legislation proposal.

While DegT50 values can well be estimated with the present model,
the estimation of DegT90 values has to be judged more critically in the case of Dimethachlor and partly Metolachlor. For these substances, bi-phasic kinetics for the degradation of the parent compound seem to be more appropriate, as its concentration is systematically overestimated in the terminal phase. This may result in an underestimation of the DegT90 values if determined with the present model. For DegT50 values, this influence is negligible.

Determination of DegT50 Values from Ready-Tests

As soil simulation tests are laborious and time-consuming, it would be tempting to derive biodegradation rates from less complex tests such as the screening tests for ready biodegradability (“ready-tests”) defined by the OECD (1996). Since most data are available for the “modified Sturm test” (OECD 301b test) this test will particularly be considered here.

First investigations by Federle et al. (1997) yielded “almost perfect noncorrelation” between rates in ready-tests and mineralization rates in activated sludge, river water and soil. The use of Aronson et al. (2006) for binning chemicals into persistence categories based on half-life in water was only successful for readily degradable substances. It shall be investigated here whether the presented DegT50 approach may lead to a better predictability of half-lives from ready test results.

The chemicals examined in this study are all not readily degradable. Only two of them show noteworthy degradation in the ready-test at all: Fenpropidin (15.8% at 10 mg/l, 4.7% at 20mg/l after 27d) and Aclonifen (22% at 5 mg/l, 0% at 10 mg/l after 28d). All other substances are only 0-3% mineralized after 28d.
In order to compare mineralization in the ready-test to mineralization in the soil, model results for the mineralized amount were determined taking the median rate constants as parameters and assuming P(0)=100. The mineralized amount after 180 d was used for comparison.

Degradation was fastest for Fenpropidin (50%) and slowest for Aclonifen (0%). DegT50 of these two compounds was in the middle of the DegT50 range of the 8 compounds. Degradation of the chemicals showing no mineralization in the ready test ranged from 3% to 43%. Obviously, no correlation between ready-test result and mineralization in soil or DegT50 can be established for these 8 compounds. Table 4 summarizes these results.

Table 4: Mineralization in ready-test and soil, and DegT50. Mineralization in soil was determined with model runs using median rate constants.

Substance	Ready-test result	% mineralization in soil after 180d	Median DegT50 [d]
Aclonifen	5 mg/l: 22% 10mg/l: 0%	0,0	315
Bromuconazole	< 1%	2,6	1386
Propiconazole	0-3%	3,1	110
Penconazole	0% (29d)	4,3	231
Ethofumesate	0%	18,1	365
Metolachlor	0%	28,2	24
Dimethachlor	0% (29d)	43,1	10
Fenpropidin	10 mg/l: 15.8% 20 mg/l: 4.7 % (27d)	50,3	124

These results confirm the finding that no degradation half-lives can be derived from ready-test results of not readily degradable substances though it may not be impossible to extrapolate biodegradation rates of chemicals passing the ready-test.

Conclusions and Outlook

The current approach for determination of DT50 of chemicals in soil is not appropriate for use in PBT assessment as the DT50 considers NER as degraded. Instead, the use of a true degradation half-life DegT50 is recommended. Determination of this rate constant by inverse modeling yields good fits thus suggesting that the model structure is not oversimplified.

Application of the DegT50 approach in PBT assessment would result in classifying several previously non-persistent substances as persistent. Determination of the DegT50 using tests on ready biodegradation fails. It may however be possible for readily degrading substances which were not considered in this work.
Adaptations of the model structure may be required in some cases. Examination of more substances is therefore necessary in order to determine how generally this model can be applied. Furthermore, soil simulation tests in combination with experimental determination of the composition of NER for some substances will be required in order to soundly validate the model.

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Appendix 3: Determination of Biodegradation Half-lives from Water/Sediment Simulation Tests

In the framework of the registration of pesticides, experiments in standardized water-sediment test systems are required for substances which are not readily biodegradable. These experiments are useful to evaluate the dissipation of the substances under realistic and practice-relevant conditions (BBA, 1990; SETAC, 1995, OECD Nr. 308/309). Experiments are conducted with radio-labeled compounds in cylindrical vessels containing 2-2.5 cm of natural sediment and 6 cm of water above. Two water-sediment systems of different origin and with different properties were investigated in parallel. Active ingredients are spiked onto the surface of the water phase after allowing the system to acclimate for a certain amount of time. Radioactivity of the parent compound and of identified metabolites is analyzed separately in water and sediment over a time period of 90-150 days in regular intervals. Test data are exploited to estimate DT_{50} and DT_{90} values for the disappearance of the active ingredient from water, from sediment and from the total sediment-water system by means of regression analysis. However, this analysis does not distinguish the different processes governing the fate of the compound in the test system. One of the major drawbacks of the experimental setup is that kinetically limited transport of the compound from the water phase into the sediment competes with the loss by biodegradation. Thus, DT_{50} values for the water phase do not distinguish between transport and degradation. It must also be pointed out that the experimental setup allows for settling of suspended solids during the acclimatization phase. Thus, the microbial biomass in the water phase during the experiment is most likely very low and biodegradation is negligible in the bulk water phase. In this context, it is not feasible to assign dissipation times for water to primary degradation of the active ingredient in water or sediment or both without kinetic modelling.

A compartment model that allows for separate fitting of the kinetic rate constants for transport and degradation has been used to analyze data from water-sediment tests for eight pesticides. For all investigated substances, which are resistant against hydrolysis and stable under UV-light, a satisfying agreement of experimental data and model results could be achieved with the assumption of no degradation in bulk water. None of these data sets gave a significantly better fit if degradation in water was allowed. It is thus not surprising that estimated half-lives for transport from water to sediment are always very close to the reported DT_{50} values (water) in the official documents. However, this finding has very important consequences for the derivation of degradation rate constants from such experiments. It must be concluded that biodegradation rates for bulk water cannot be derived from water-sediment tests, because this process (biodegradation) apparently does not occur under the experimental conditions of the tests.

On the other hand, this implies that true loss processes largely occur in the sediment. Abiotic loss processes are generally of minor importance in this compartment and, thus, biodegradation is most likely responsible for the decrease of the active ingredient in the sediment. The compartment model allows for estimation of a first-order degradation rate constant for bulk sediment in each test system. This rate constant describes the only true removal process in the system. However, formation of bound residues could not be modeled since only the percentage at the end of the study has been reported. Percentages of bound residues vary between the two parallel experiments and tend to be higher for fast than for slowly degradable pesticides. This supports the assumption that unidentified metabolites are the major part of the bound residues. Data are summarized for a number of selected substances in Table 2.

Table 2: Half-lives (DegT$_{50}$) for bulk sediment determined by fitting experimental data to a kinetic model and DT$_{50}$ values for water and the whole system from official assessment protocols. Data are given for two parallel experiments.

	DT$_{50}$ [days] bulk water	 whole system	DegT$_{50}$ [days] bulk sediment
Benalaxyl	17 / 58	108 / 203	95 / 109
Bromuconazole	2 / 5	226 / 312	180 / 290
Dimethenamide	20 / 28	23 / 33	5.5 / 11
ethofumesate	36 / 47	105 / 156	6 / 154
metazachlor	14 / 17	16 / 21	1.3 / 1.4
myclobutanil	11 / 19	367 / 391	235 / 728
propamocarb	14 / 157	14 / 19	2.3 / 9.3
quinoclamine	4.8 / 4.4	18 / 22	3.0 / 1.9

DT$_{50}$ values for the whole system tend to be slightly higher than estimated bulk sediment half-lives, but result in the same ranking.

There remains the question of whether half-lives for bulk sediment derived from the test results can be used in persistence assessment procedures. This would require the transferability of the values from the experimental test system to average environmental conditions as applied in aquatic fate models for pesticides (FOCUS) and multimedia regional exposure models for chemical risk assessment (EUSES). However, for many of the investigated compounds, estimated rate constants even varied significantly between the two parallel experiments due to the non-standardized test design, e.g. for ethofumesate. First, this is due to the fact that biodegradation is restricted to the dissolved, bioavailable fraction of the compound in the bulk sediment which varies in dependence of the sorption capacity of the solid phase. Second, the sediment material may exhibit different biological degradation potential even after acclimatization to the test conditions. The effect of sorption can be considered in the model if distribution coefficients between pore water and solid material were known or could be estimated. The second factor is much more difficult to evaluate, as independent parameters that quantitatively describe the biodegradation potential of natural samples are not available. The problem with the transferability of bulk sediment rates is best illustrated by the results for ethofumesate. Half-lives in bulk sediment are different by a factor of approximately 30 for the two investigated water-sediment systems. This is due to the completely different properties of the two sediments (biomass-C, organic carbon) as noted down in the test protocols.

We conclude that the results of experiments in water-sediment test systems cannot be used to extrapolate kinetic rate constants for biodegradation in water, but are useful to evaluate the potential degradation behavior in sediment. However, bulk sediment degradation rate constants derived by fitting the data to a simple compartment model show large variability between different sediment samples. Transfer of such results to other than the test conditions (e.g. average environmental conditions) is a critical step that would require detailed knowledge about the effect of sorption and consideration of the large natural variability of biomass activity and biological degradation potential for the compounds of interest.