

Umweltforschungsplan  
des Bundesministeriums für Umwelt, Naturschutz, Bau und Reaktorsicherheit

Environmental Research of the  
Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety

Project (UFOPLAN) *FKZ 371265416*

**Guidance for the precautionary protection of raw water destined for drinking water extraction from  
contaminants regulated under REACH**

**Leitlinien  
für den vorsorglichen Schutz des Rohwassers zur Trinkwassergewinnung  
vor Kontaminationen durch Chemikalien  
im Rahmen der REACH-Verordnung**

by

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ON BEHALF OF THE FEDERAL ENVIRONMENTAL AGENCY

IM AUFTRAG DES UMWELTBUNDESAMTES

Dessau, November 2014



## Berichtskennblatt

<b>Berichtsnummer</b>	UBA-FB
<b>Titel des Berichts</b>	<b>Leitlinien für den vorsorglichen Schutz des Rohwassers zur Trinkwassergewinnung vor Kontaminationen durch Chemikalien im Rahmen der REACH-Verordnung</b>
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<b>Fördernde Institution</b>	Umweltbundesamt Postfach 14 06 06813 Dessau-Roßlau
<b>Abschlussdatum</b>	30. November 2014
<b>Forschungskennzahl (FKZ)</b>	<i>FKZ 371265416</i>
<b>Seitenzahl des Berichts</b>	204
<b>Zusätzliche Angaben</b>	Zusätzlich wurden im Rahmen des Projekts ein Leitfaden („practical guide“) erstellt und ein digitalisiertes Bewertungstool unter KnowSEC entwickelt
<b>Schlagwörter</b>	Rohwasser; Trinkwasser; Mobilität; Persistenz; Toxizität; PMT Substanz; REACH; Bewertungskonzept; Entscheidungsunterstützung; Bewertungs-Software; Ontologie, KnowSEC

## Report Cover Sheet

<b>Report No.</b>	UBA-FB
<b>Report Title</b>	<b>Guidance for the precautionary protection of raw water destined for drinking water extraction from contaminants regulated under REACH</b>
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<b>Funding Agency</b>	Federal Environmental Agency Postfach 14 06 06813 Dessau-Roßlau
<b>Report Date</b>	30 November 2014
<b>Project No. (FKZ)</b>	<i>FKZ 371265416</i>
<b>No. of Pages</b>	204
<b>Supplementary Notes</b>	Additionally within this project a „practical guide“ was developed and a digital assessment tool was established within KnowSEC software
<b>Keywords</b>	raw water; drinking water; mobility; persistence; toxicity; PMT substance; REACH; assessment concept; decision support, assessment tool, ontology, KnowSEC

## Kurzbeschreibung

Innerhalb der Europäischen Chemikaliengesetzgebung REACH wird der vorbeugende Trinkwasserschutz unzureichend berücksichtigt. Dieser Schutzgedanke sollte beim Rohwasser, aus dem Trinkwasser gewonnen wird, ansetzen. Im vorliegenden Projekt wurde ein Bewertungskonzept erarbeitet, mit welchen Kriterien eine unter REACH zu registrierende Substanz als PMT Substanz und damit als „*rohwasserkritisch*“ identifiziert werden soll. Kriterien für die Stoffeigenschaften Persistenz (P), Mobilität (M) und Toxizität (T), die zur Identifizierung als PMT Substanz führen, wurden definiert. Es gilt, Stoffe mit diesen inhärenten Eigenschaften mit hoher Priorität im Rohwasser zu vermeiden. Das Bewertungskonzept nutzt die unter REACH generierten Daten. Dieses Konzept war so zu konkretisieren, dass eine „regelbasierte Wissensbasis“ entsteht, die die Erstellung eines digitalisierten Bewertungstools ermöglicht. Die Persistenz (P) Definition fokussiert auf das Frischwasserkompartiment und beruht im Wesentlichen auf den entsprechenden P Kriterien aus Anhang XIII REACH. Kriterien zur Mobilitätsbewertung (M) wurden vor allem über einen Modellierungsansatz entwickelt: Als entscheidend für die Mobilität erwies sich der auf den organischen Kohlenstoffgehalt normalisierte Adsorptionskoeffizient  $K_{OC}$ . Aus den Modellierungsdaten konnte für persistente Stoffe ein Abschneidekriterium für M von  $< 4.5$  log-Einheiten abgeleitet werden. Es wurde ferner eine Mindestlöslichkeit  $> 150 \mu\text{g/L}$  als Voraussetzung für eine mögliche Mobilität festgelegt. Das Entscheidungsschema für die Toxizität (T) umfasst die in Anhang XIII, REACH, festgelegten Kriterien für die Humantoxizität und weitere Aspekte, insbesondere die Einführung eines DNEL-basierten Abschneidekriteriums („Derived No Effect Level“  $< 9 \mu\text{g/kg} \times \text{d}$ ) als Maß für die Effektstärke (chronisch, oral). Die Expositionshöhe geht bei dem gewählten Ansatz nicht in die PMT Kriterien ein, dient jedoch als Abschneidekriterium, wann (k)eine PMT Bewertung vorgenommen werden sollte. 93 Substanzen wurden bereits nach dem Konzept analysiert und daraus PM oder PMT Substanzen ermittelt. Anhand dieser Beispielsstoffe und über die Einordnung von Substanzen aus dem Gewässermonitoring konnte die Eignung des Bewertungskonzepts gezeigt werden.

## Abstract

Within the European regulation on chemicals (REACH) precautionary protection of drinking water is insufficiently addressed. Protection should be linked already to raw water, from which drinking water is generated. In the present project, an assessment methodology is proposed specifying under which circumstances a compound, which is to be registered under REACH, should be regarded a PMT substance and “*critical in raw water*”. We define the degree of persistence (P), mobility (M), and toxicity (T), which leads to classification of a chemical as a PMT substance. There is a high priority to avoid substances with these inherent properties in raw water. The concept uses the data generated under REACH registration. The approach had to be specified to permit the development of a digital assessment tool. The definition for persistence (P) focusses on the fresh water compartment and mainly uses the respective P criteria from Annex XIII, REACH. Criteria for mobility (M) were primarily developed by a modelling approach. It is demonstrated that the best parameter to define mobility is the organic carbon normalized adsorption coefficient ( $K_{OC}$ ). For persistent substances a cut-off criterion for M was derived with  $< 4.5$  log units. Furthermore a minimum water solubility of  $> 150 \mu\text{g/Liter}$  was found to be prerequisite for mobility. The decision tree for toxicity (T) includes criteria from Annex XIII, REACH, for human toxicity and further aspects. Specifically, a DNEL („Derived No Effect Level“ ) cut-off of  $< 9 \mu\text{g/kg} \times \text{d}$  as a measure for substance inherent potency (chronic, oral exposure) was introduced. Exposure assessment is not part of the PMT assessment. However, exposure categories are used as cut-off to define as to when PMT assessment may (not) be necessary. 93 substances were evaluated according to this assessment approach and respective PM or PMT substances were identified. With those example substances and further assignment of compounds detected in monitoring programs, we were able to demonstrate suitability of the proposed concept.



## Zusammenfassung

Es besteht ein grundlegendes gesellschaftliches Interesse daran, zur Trinkwassergewinnung vorgesehenes Rohwasser frei von chemischen Verunreinigungen zu halten. Allerdings wird zu Chemikalien, die unter der europäischen Verordnung zur Registrierung, Bewertung, Zulassung und Beschränkung chemischer Stoffe REACH (1907/2006 EG) registriert sind, derzeit nur unzureichend aufbereitete Information zur Beurteilung geliefert, ob diese Stoffe eine mögliche Auswirkung auf das Rohwasser haben. Zugleich bietet REACH viele hilfreiche Daten, die für die Ermittlung entsprechender Stoffeigenschaften und die Bewertung möglicher Emissionen in das Rohwasser nützlich sein könnten.

Im vorliegenden Projekt wurde ein Bewertungskonzept erarbeitet, mit welchen Kriterien eine unter REACH zu registrierende Substanz als PMT Substanz und damit als *rohwasserkritisch* identifiziert werden soll. Wir definieren Kriterien für die Stoffeigenschaften Persistenz (P), Mobilität (M) und Toxizität (T), die zur Identifizierung als PMT Substanz führen. Es gilt, Stoffe mit diesen inhärenten Eigenschaften mit hoher Priorität im Rohwasser zu vermeiden.

Unser Bewertungskonzept nutzt die unter REACH generierten Daten, um eine PMT Substanz zu identifizieren. Dieses Bewertungskonzept war so zu konkretisieren und zu differenzieren, dass eine „regelbasierte Wissensbasis“ entsteht, die die Erstellung eines digitalisierten Bewertungstools ermöglicht. Dieser Bericht enthält eine Darstellung und Begründung des Bewertungskonzepts zur Ermittlung von PMT Substanzen und charakterisiert die Prinzipien des daraus entwickelten Bewertungstools.

Ferner wurden im vorliegenden Projekt Stoffbeispiele bewertet, die den PMT Kriterien (oder zumindest PM Kriterien) entsprechen. Die Identifizierung der Stoffbeispiele diente einerseits der Überprüfung der Aussagekraft des Konzepts und andererseits der Veranschaulichung der Relevanz der Thematik.

Zugleich wurde im Rahmen dieses Projekts ein Leitfaden („practical guide“) erstellt, der es den Akteuren (insbesondere dem Registrierer unter REACH) ermöglicht, ohne das elektronische Bewertungstool die Logik der PMT Ermittlung nachzuvollziehen und eine entsprechende Bewertung durchzuführen. Der Leitfaden ist nach einem Acht-Stufen-Konzept gegliedert und erläutert Begriffe und Vorgehensweise in der Reihenfolge der erforderlichen Entscheidungsschritte. Dieser Leitfaden ist nicht Teil des vorliegenden Berichts.

## Definition und Überprüfung der Persistenz

Persistenz wird über ein Entscheidungsablaufschema festgestellt, das auf den P Kriterien aus Anhang XIII REACH in Verbindung mit den einschlägigen Leitliniendokumenten der ECHA beruht (R.11; R.7b). Entsprechend der Zielsetzung dieses Projekts erfolgte eine Konkretisierung auf das Süßwasserkompartiment. Zur Identifizierung der Persistenz wird in unserem Bewertungskonzept nach einem gestuften Verfahren vorgegangen. Folgende Stufen werden berücksichtigt:

Stufe 1	Screening-Test auf Bioabbaubarkeit (OECD 301;OECD 310); ggf. Einbezug von „enhanced biodegradation screening test“ und Test auf inhärente Bioabbaubarkeit; ggf. unter Einbeziehen zusätzlicher Bedingungen nach OECD 302 B und C
Stufe 2	Hydrolysetest (z.B. nach OECD 111)
Stufe 3	Simulationstests zum Abbau (Mineralisierung) im Oberflächenwasser (z.B. nach OECD 309)
Stufe 4a	Übernahme des Ergebnisses zu P aus vorliegender PBT Bewertung
Stufe 4b	Abschätzung der Persistenz aus quantitativer Struktur-Wirkungsbeziehung (QSAR); BIOWIN 2 & BIOWIN 3 oder BIOWIN 6 & BIOWIN 3

Die höheren Stufen müssen nur beschränkt werden, wenn die Persistenz nicht bereits auf niedrigerer Stufe bewertbar ist. Bei der Bewertung der Persistenz ist zu beachten, dass einige Testsysteme nur den Abbau der

Muttersubstanz erfassen. Deswegen ist auch die Persistenz der Transformationsprodukte zu prüfen. Ferner ist zu berücksichtigen, dass Hydrolysetests nicht immer bei geeigneter Temperatur von 12 °C durchgeführt wurden, so dass dann eine Umrechnung des Ergebnisses erforderlich ist, um es vergleichbar zu machen.

Auf diese Weise kann in der Regel mit den unter REACH in den Registrierungsdossiers berichteten Daten (ggfs. unter Ergänzung durch QSAR-Berechnungen) die Persistenz einer chemischen Substanz bewertet werden.

### **Definition und Überprüfung der Mobilität**

Eine quantitativ eingegrenzte Definition zur Mobilität von chemischen Substanzen im Wasser liegt bisher nicht vor. Mobilität wird allgemein als „Tendenz einer Substanz, sich in der Umwelt zu bewegen“ beschrieben. Zu Beginn dieses Projektes wurde diskutiert, diese Eigenschaft entsprechend über die Wasserlöslichkeit, den Oktanol-Wasser-Verteilungskoeffizienten ( $K_{OW}$ ) oder den auf organischen Kohlenstoff normierten Adsorptionskoeffizienten ( $K_{OC}$ ) zu definieren. Auch der aggregierte „Purification Factor“ (der die teilweise Entfernung der im Oberflächenwasser gelösten Substanz durch Abbau, Adsorption und Verflüchtigung beinhaltet) könnte eine Rolle spielen.“

Eine im Rahmen von REACH häufig verwendete Modellierungssoftware von ECETOC („ECETOC-Targeted Risk Assessment“ TRA) ermöglicht es, den prozentualen Anteil einer Substanz im Oberflächenwasser und im Grundwasser zu berechnen, wenn jeweils die gleiche Menge unter standardisierten Bedingungen in eine Kläranlage emittiert wird. Dieser Anteil wird als ein aussagekräftiges Maß für die Mobilität angesehen. Dabei wird sowohl der direkte Übergang aus der Kläranlage ins Oberflächenwasser betrachtet als auch der Übergang über den indirekt exponierten Boden in das Grundwasser; beide Pfade können zur Belastung des Rohwassers führen und für beide ist daher die Erfassung der Mobilität von Interesse. Im vorliegenden Projekt wurde deshalb für 64 Substanzen, für die Persistenz angenommen wurde (kein Bioabbau), berechnet, welcher der physikalisch-chemischen Eigenschaften (Wasserlöslichkeit,  $\log K_{OW}$ ,  $\log K_{OC}$ , mit/ohne Berücksichtigung des „Purification Factor“) sich am besten zur Kennzeichnung der so definierten Mobilität eignet. Es wurde sichergestellt, dass diese Substanzen heterogene Molekulargewichte und Wasserlöslichkeiten auswiesen, um eine gewisse Repräsentativität zu erzielen. Der prozentuale Anteil einer Substanz im Oberflächenwasser und im Grundwasser wies bei Überschreitung einer bestimmten Mindestwasserlöslichkeit (siehe unten) keine gute Korrelation mit der Wasserlöslichkeit auf. Auch die Korrelation mit der Flüchtigkeit (Henry-Konstante) war nur schwach, mit nur leicht verbessertem gesetzmäßigem Zusammenhang bei Gegenüberstellung mit dem  $\log K_{OW}$ . Aufgrund der engen Korrelation zwischen Wasserlöslichkeit und  $\log K_{OW}$  ergibt sich diese Aussage nicht unvermutet. Als jedoch der  $\log K_{OC}$  als maßgebliche Stoffeigenschaft geprüft wurde, zeigte sich sowohl für das Grundwasser wie für das Oberflächenwasser eine sehr gute Korrelation. Es ergab sich, dass der  $\log K_{OC}$  ein aussagekräftiges Maß für die Mobilität darstellt. Wir schlussfolgern, dass das Ausmaß der Mobilität im Rohwasser umgekehrt proportional mit dem Ausmaß der „Nettoadsorption“ an Feststoffe in Zusammenhang steht, wobei die Nettoadsorption sowohl Adsorptions- wie Desorptionsvorgänge über die Zeit beinhaltet. Abschließend konnte ein  $\log K_{OC}$  von ca. 4,5 aus der Verteilung der 64 Substanzwerte abgelesen werden, bei dessen Überschreitung sowohl der Anteil einer eingeleiteten Substanz ins Oberflächenwasser wie derjenige ins Grundwasser gleichermaßen deutlich abnehmen. Der Wert:  $\log K_{OC} = 4,5$  wurde aufgrund dieser Analyse als Mobilitätskriterium festgelegt:

Unter REACH wird regelmäßig der  $\log K_{OW}$  ausgewiesen und auch der  $\log K_{OC}$  im Registrierungsdokument in der Regel berichtet, jedoch oft aus dem  $\log K_{OW}$  berechnet. Während dies (berechnete Werte) für die Bewertung neutraler organischer Substanzen unter bestimmten Umständen zulässig ist, und darüber hinaus für diese Substanzgruppe eine Abschätzung des  $\log K_{OC}$  nach OECD Richtlinie 121 erfolgen kann, benötigt die Bewertung von ionisierbaren Stoffen weitergehende Daten aus echten Adsorptions-Desorptionsstudien nach Testrichtlinie OECD 106. Für die Feststellung, ob es sich um eine ionisierbare Substanz und um eine Säure oder Base handelt, gibt es neben den nicht immer hinreichend interpretierbaren Informationen aus den Registrierungsdossiers unter REACH auch geeignete Softwareprogramme, die für die Dateninterpretation herangezogen werden sollten.

Wie ausgeführt, ist eine Mindestwasserlöslichkeit vorausgesetzt, die von uns mit 150 µg/Liter festgelegt wird (Abschnitt 2.2.3).

**Persistente Verbindungen sind als *mobil in Wasser* zu werten (M), wenn ihr  $\log K_{OC} < 4.5$  ist und eine Mindestwasserlöslichkeit von  $>150 \mu\text{g/L}$  gegeben ist.**

Wenn diese Wasserlöslichkeit unterschritten ist, ist nicht von einer Mobilität auszugehen. Allerdings spielt auch hier eine Rolle, ob es sich um eine ionisierbare oder nicht-ionisierbare Substanz handelt. Bei ionisierbaren Substanzen ist die Wasserlöslichkeit stark vom pH-Wert abhängig, so dass für Säuren, Basen und zwitterionische Verbindungen gesonderte Differenzierungen zur Mindest-Wasserlöslichkeit in Abhängigkeit vom pH-Wert zu beachten sind.

Auch bei Uferfiltrat handelt es sich um Rohwasser, das eine wichtige Trinkwasserquelle darstellt. Eine Modellierung der jeweiligen Mobilität ist jedoch nur standortspezifisch möglich und bietet damit kein generisches Verfahren. Die für das Oberflächenwasser berechnete Mobilität kann jedoch als „schlimmster Fall“ für die Abschätzung der Mobilität im Uferfiltrat herangezogen werden. Deshalb ist es nicht erforderlich, diesen Pfad über das Uferfiltrat in die Ableitung einer Mobilitätsdefinition einzubeziehen.

Bei der Ausweisung des Abschneidekriteriums über den  $\log K_{OC} (< 4,5)$  fällt auf, dass der gleiche Nominalwert von 4,5 auch bei PBT Substanzen genannt ist: bei den Screening-Kriterien für PBT wird ein  $\log K_{OW} > 4,5$  im REACH-Leitfaden als Abschneidekriterium für Bioakkumulation genannt. Es ergibt sich die Frage möglicher Überschneidungen („Kann eine PMT Substanz zugleich eine PBT Substanz sein?“). Wir vernachlässigen an dieser Stelle die Kriterien P und T. In der Tat besteht für neutrale, nicht-ionisierbare organische Verbindungen eine positive Korrelation von  $\log K_{OC}$  mit  $\log K_{OW}$ . Diese ist, je nach Verbindungsgruppe, unterschiedlich ausgeprägt. Der Zusammenhang zwischen beiden Größen gilt jedoch nicht in dieser Weise für geladene oder ionisierbare Stoffe (umweltrelevanter pH-Bereich). Entsprechend gibt es für neutrale organische Verbindungen tatsächlich einen Überlappungsbereich von Substanzen, die sowohl „mobil“ ( $\log K_{OC} < 4,5$ ) wie „bioakkumulativ“ ( $\log K_{OW} > 4,5$ ) sein können. Verbindungen mit einem  $\log K_{OW} > 4,5$  sind jedoch relativ hydrophob, so dass die Wasserlöslichkeit gering ist (vgl. Abschneidekriterium bei der PMT Bewertung von  $\leq 150 \mu\text{g/Liter}$ ). Die mit zunehmendem  $\log K_{OW}$  abnehmende Wasserlöslichkeit begrenzt damit diesen Überlappungsbereich. Bei der Bioakkumulation ist zudem darauf hinzuweisen, dass für eine abschließende Aussage der Biokonzentrationsfaktor von  $> 2000$  heranzuziehen ist. Dennoch kann zwar eine marginale Überlappung des „M“ und des „B“ Kriteriums nicht ausgeschlossen werden. Der Schwerpunkt unserer Betrachtungen wird jedoch auf PMT Substanzen liegen, die kein relevantes Bioakkumulationspotenzial besitzen.

### **Definition und Überprüfung der Toxizität**

Das Toxizitätskriterium zur Identifizierung von PMT Substanzen muss einerseits gängige Definitionen von „toxisch“ abdecken, wie sie unter REACH bezüglich Humantoxizität (zum Beispiel im PBT Assessment nach Anhang XIII, REACH) herangezogen werden, andererseits aber auch für bisher nicht eingestufte Substanzen Eigenschaften beinhalten, die aus Sicht der Bewertung von Wirkungen auf die menschliche Gesundheit als besorgniserregend gelten müssen. Entsprechend wurden im Rahmen dieses Projektes Stoffe als „toxisch“ (T) bezeichnet, die eine (oder mehrere) der folgenden Eigenschaften aufweisen:

- Substanz ist eingestuft als kanzerogen, keimzellenmutagen oder reproduktionstoxisch (nach Verordnung 1272/2008 EG; „CLP Verordnung“) in den Kategorien 1A oder 1B,
- Substanz ist eingestuft als keimzellenmutagen oder reproduktionstoxisch (nach Verordnung 1272/2008 EG; „CLP Verordnung“) in Kategorie 2,
- Substanz ist eingestuft als kanzerogen (nach Verordnung 1272/2008 EG; „CLP Verordnung“) in Kategorie 2 (getrennt von letztgenannter Gruppe wegen unterschiedlicher Konsequenz, siehe unten),
- Substanz ist eingestuft mit „kann Säuglinge über die Muttermilch schädigen“ (Kennzeichnung mit Gefahrenhinweis H (H362) ohne Symbol) oder Warning, STOT RE 1,2 (H372: Schädigt das Organ/ die Organe bei längerer oder wiederholter Exposition oder H373: Kann das Organ/ die Organe schädigen bei längerer oder wiederholter Exposition)

- Substanz zeigt einen relevanten Strukturverdacht auf Gentoxizität und Kanzerogenität,
- Substanz weist einen niedrigen derived no adverse effect level (DNEL) bei oraler Aufnahme (Langzeitexposition, Allgemeinbevölkerung) aus mit  $DNEL \leq 9 \mu\text{g/kg}$  Körpergewicht und Tag,
- (nicht eingestufte) Substanz, für die kein DNEL vorliegt oder ableitbar ist, muss wegen ihrer Substanzstruktur bei quantitativer Strukturwirkungsanalyse (QSAR-Software: TOXTREE) der Cramer-Klasse III (reaktive Substanzen mit niedrig anzunehmendem DNEL) zugeordnet werden,
- Substanz steht in einer ausgewiesenen Liste mit Warncharakter (z.B. in Trinkwasserverordnung),
- Substanz ist endokrin wirksam oder es besteht ein Verdacht auf endokrine Aktivität (ebenfalls nach Ausweis in einer maßgeblichen Liste).

Bei einigen dieser Kriterien erfolgt die Zuordnung zur Eigenschaft „toxisch“ nur vorläufig (Kennzeichen:  $T_{\text{Screen}}$ ) und muss durch eine qualifizierte toxikologische Bewertung bestätigt werden. Diese ist jedoch nicht in eine einfach formalisierbare Entscheidungsabfolge auf Basis von unter REACH ausgewiesenen Informationen zu überführen und wird somit im Rahmen dieses Projekts nicht näher charakterisiert. Dabei handelt es sich um Kanzerogene der Klasse 2, um Substanzen mit Strukturverdacht auf eine gentoxische und kanzerogene Wirkung, um (möglicherweise) endokrin wirksame Substanzen, um Substanzen, bei denen Wirkstärkeklassen mit QSAR abgeleitet wurden (je mögliche Gründe für Zuweisung von  $T_{\text{Screen}}$  auf niedriger Stufe eines PMT assessment). Eine Substanz kann demnach durch den Bezug auf mehrere Endpunkte gleichzeitig als „toxisch“ ( $T$  oder  $T_{\text{Screen}}$ ) bezeichnet werden.

Es ist darauf hinzuweisen, dass auch maßgebliche Transformationsprodukte von einer Substanz, die im Wasser abgebaut wird, in ihrer Toxizität zu beschreiben sind, wobei in der REACH Registrierung oft nur die Muttersubstanz benannt und hinreichend toxikologisch charakterisiert ist. Hier ergibt sich eine zusätzliche Ermittlungspflicht.

### **Die Bedeutung der Exposition für eine PMT Abschätzung unter REACH**

Eine differenzierte Expositionsabschätzung ist bei der Bewertung der PMT Kriterien nicht eingeschlossen und widerspricht dem Kerngedanken, dass die intrinsischen Stoffeigenschaften unabhängig von der Expositionshöhe sind. Tonnage-abhängige Überlegungen stehen nicht im Vordergrund.

Expositionsabschätzungen im Rahmen der Bewertung der PMT Kriterien haben jedoch zwei Funktionen:

1. Sie sollen den Abschätzungsaufwand gering halten, wenn aufgrund auszuschließender oder niedriger Exposition die Fragestellung nach PMT Kriterien nicht relevant ist,
2. Sie sollen Markierungen liefern, die die Begriffe *rohwassergängig*, *rohwasserrelevant* und *rohwasserkritisch* voneinander abgrenzen, wenn zugleich PM oder PMT Eigenschaften vorliegen.

Als einer der ersten Schritte beim PMT Assessment erfolgt demnach eine Abfrage, ob vorhersehbare Einträge in die verschiedenen Umweltmedien auszuschließen sind („Exposure“, Stufe E1). Diese Substanzen können von der weiteren Bewertung ausgeklammert werden. Dazu zählen im Allgemeinen nur Substanzen, die nur als „Zwischenprodukt unter streng kontrollierten Bedingungen“ gehandhabt werden. Es ist zu beachten, dass alle Stoffe mit vollständiger Registrierung nach Artikel 10 unter REACH oder Stoffe, die im Verfahren gemäß Richtlinie 67/548/EWG angemeldet wurden, die weitere PMT Abschätzung durchlaufen und an dieser Stelle nicht ausgegrenzt werden. Wurde ein Stoff auf Stufe E1 von der weiteren Betrachtung ausgeschlossen, ist diese Entscheidung in geeigneten Zeitabständen zu überprüfen. Ein Stoff, bei dem ein Eintrag in die Umwelt möglich ist und der die Kriterien P und M erfüllt, wird als *rohwassergängig* bezeichnet.

In der späteren Stufe E2 wird nochmals eine grobe Abschätzung der Exposition vorgenommen. Es wird eingrenzt, ob die bei der Registrierung eines Stoffes ausgewiesenen Umweltemissionskategorien

(„environmental release categories“; ERCs) in Verbindung mit der unter REACH registrierten Gesamttonnage zuverlässig dafür sprechen, dass nur sehr niedrige Emissionen in die Umwelt erfolgen. Hier liefert REACH-Leitfaden R.16 entsprechende Anhaltspunkte. Wenn zum Beispiel nur die ERCs 6A, 6D oder 11A<sup>1</sup> genannt sind, ist eine weitere Betrachtung der PMT Eigenschaften nur erforderlich, wenn eine Tonnage von mehr als 10000 Tonnen registriert wird. Ein rohwassergängiger Stoff (PM Stoff), der die jeweilige Tonnageschwelle übersteigt, wird als *rohwasserrelevant* bezeichnet und hinsichtlich der Toxizität näher geprüft, ob er auch das T Kriterium erfüllt. Wird die Emission als zuverlässig niedrig eingeordnet (Tonnageschwelle in Verbindung mit ERCs unterschritten), ist eine weitere Analyse der Toxizitätseigenschaften nicht erforderlich. Die Substanz wird als rohwassergängige PM Substanz mit niedriger Priorität aus dem weiteren Verfahren ausgeklammert.

Ist die *rohwasserrelevante* Substanz zugleich *toxisch* (PMT Substanz), wird von einer *rohwasserkritischen* Substanz gesprochen, was weitere Bewertungsschritte nach sich zieht. Diese Betrachtungen zu rohwasserkritischen (PMT) Stoffen sind nicht Gegenstand des vorliegenden Projekts.

Liegt zu Beginn der Bewertung der PMT Kriterien bereits eine vollständige Expositionsschätzung (Stufe E3) vor, wie sie unter REACH im Rahmen der Registrierung unter bestimmten Bedingungen erfolgen muss, so erleichtert dies meist die Identifizierung des P und M Kriteriums, da in diesem Falle mit einer guten Datenlage zu rechnen ist. In anderen Regelwerken wird eine modellierte oder gemessene Umweltkonzentration von 0,1 µg/Liter im Rohwasser als Relevanzkriterium diskutiert. Im vorliegenden Rahmen wurde noch kein abschließend konsentierter Wert vorgeschlagen.

### Anwendungsdomäne

Nicht alle Substanzen, die unter REACH registriert werden, können mit dem hier vorgestellten Verfahren derzeit auf ihre PMT Eigenschaften geprüft werden.

- Anorganische Stoffe einschließlich Metalle sind weder für ein PBT Assessment noch für ein PMT Assessment zugänglich.
- Substanzen mit unbekannter oder variabler Zusammensetzung (UVCB) und aus mehreren Komponenten bestehende Stoffe („multiconstituent“ substances) sind aufgrund ihrer möglichen Komplexität derzeit schwieriger hinsichtlich ihrer PMT Eigenschaften zu bewerten und daher ausgeklammert.
- Organometalle sind üblicherweise nicht stabil im Wasser oder regieren dort; es handelt sich generell um reaktive Substanzen. Mit dem vorliegenden Bewertungskonzept können aber die Reaktionsverbindungen bewertet werden.
- Oberflächenaktive Substanzen verhalten sich möglicherweise deutlich anders als ihre einzelnen Moleküle, so dass eine Bewertung der Mobilität mit dem vorliegenden Bewertungskonzept nicht möglich ist.
- Bei Übergangsmetallen mit organischen Liganden kann der Bioabbau nur für den organischen Teil abgeschätzt werden.
- Bei ionischen, zwitterionischen und ionisierbaren organischen Substanzen ist eine Bewertung nur bedingt im Rahmen des vorliegenden Konzepts möglich, nämlich dann, wenn gemessene log  $K_{OC}$ -Werte vorliegen. (siehe hierfür Ausführungen zur Bewertung der Mobilität)

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<sup>1</sup> So werden bei ERC 11A („wide dispersive indoor use of long-lasting articles, low release“) nur Emissionen ins Wasser von 0,05% unter REACH angenommen, so dass unterhalb hoher Tonnagen keine weitere PMT Prüfung erforderlich scheint.

## Mängel in Registrierungsdokumenten unter REACH

Die derzeit üblicherweise in Registrierungsdokumenten unter REACH zu findenden Informationen enthalten einige Einschränkungen, die auch die Anwendbarkeit des vorgestellten Ansatzes limitieren:

Transformationsprodukte von unter REACH registrierten Substanzen können von ihren PMT Eigenschaften her besondere Relevanz besitzen. Zum Beispiel erweist sich Methyl-Triclosan als persistenter und stärker bioakkumulierend als die Muttersubstanz Triclosan. Allerdings fehlen in den Registrierungsdokumenten unter REACH in der Regel entsprechend genaue Hinweise auf die Identität von Transformationsprodukten und deren Eigenschaften. Abbaupfade können mit vorliegender frei verfügbarer Software auch selten mit hinreichender Genauigkeit modelliert werden, so dass sich hier eine relevante Informationslücke ergibt. Im Zuge des vorliegenden Bewertungskonzepts wird jeweils darauf hingewiesen, wenn die Prüfung gezielt auf Transformationsprodukte erfolgen sollte. Solche Hinweise können zumindest dort, wo Daten vorliegen, zu deren Berücksichtigung führen. Darüber hinaus könnte sich daraus eine Ermittlungspflicht ableiten, wenn entsprechende Lücken identifiziert werden.

Unter REACH wird derzeit bereits im Rahmen der Registrierung bei Umsetzung des Expositionsszenarios „Humans via the environment“ eine Exposition des Menschen über das Trinkwasser berechnet. Tatsächlich handelt es sich dort um eine Abschätzung der Exposition gegenüber Rohwasser, da eine Trinkwasseraufbereitung nicht thematisiert wird; der Terminus Rohwasser ist unter REACH jedoch nicht verwendet. Allerdings wird diese Abschätzung normalerweise nur vorgenommen, wenn eine Tonnage von mehr als 1000 Jahrestonnen vorliegt oder wenn eine eingestufte Substanz mit einer Tonnage von mehr als 100 Jahrestonnen zu bewerten ist und diese Einstufung eine relevante Toxizität belegt.

Da die hier aufgestellten Kriterien für P und M derzeit noch keine Berücksichtigung unter REACH finden und da das T Kriterium eingeschränkter definiert ist, wird demnach unter REACH derzeit die Belastung des Rohwassers durch PMT Substanzen im Registrierungsdossier nicht dokumentiert. Eine *gesonderte Bewertung* der Rohwasserbelastung durch einen registrierten Stoff findet derzeit im Rahmen von REACH auch dann meist nicht statt, wenn die entsprechende modellierte Konzentration im Rohwasser dokumentiert ist (unter REACH als *Trinkwasser* bezeichnet). Diese wird überwiegend derzeit unter REACH nur zusammen mit anderen Belastungen (insbesondere über die Nahrung) aggregiert bewertet, wenn das Szenario „Humans via the Environment“ überhaupt erfasst ist. Es handelt sich dann derzeit unter REACH um eine *risikobezogene* Bewertung anhand der *risk characterisation ratio* (RCR). Die Ausweisung der Belastungssituation über das Rohwasser ist jedoch im vorliegenden Projekt von sekundärer Bedeutung, da ein „*Hazard*“- Ansatz vorgestellt wird. Verunreinigungen des Rohwassers mit PMT Stoffen sind zu vermeiden, auch wenn eine  $RCR \ll 1$  belegt würde.

## **Bewertungstool**

Im Rahmen des Sachverständigengutachtens FKZ 3600 10602 und des Forschungs- und Entwicklungsvorhabens UFOPLAN 3711 63 4203 wurde am Umweltbundesamt im für die Bewertung von unter REACH registrierten Chemikalien zuständigen Fachgebiet das System KnowSEC konzipiert und eingeführt.

Das System erlaubt die Dokumentation und Entscheidungsunterstützung im Rahmen von stoffbezogenen Entscheidungen. KnowSEC wurde als Intranet-basiertes und semantisches Wiki-System umgesetzt. Es kann somit über den Web-Browser eine zentrale Version der Infoseite einer Substanz gewählt, Informationen zu der Substanz abgerufen und auch neue Informationen abgelegt werden. Neben informellem Freitext ist es auch möglich formale Entscheidungen zu dokumentieren, wobei das Treffen der Entscheidungen neben der Ablage in Memos zusätzlich mithilfe eines Frage-Antwort-Dialogs unterstützt wird.

Das Bewertungstool zur Bestimmung der PMT Eigenschaft von Stoffen wurde im Rahmen des vorliegenden Projekts als weiteres Modul für die Entscheidungsunterstützung mittels Frage-Antwort-Dialogs in KnowSEC integriert. Dort steht es neben Modulen zu den Themen wie Relevanz aufgrund politischer, regulatorischer oder wissenschaftlicher Überlegungen, Hinweisen zu möglichen Einträgen in die Umwelt (Exposition), sowie der von Rohwasser unabhängigen Bewertung von Persistenz, Bioakkumulation und Toxizität im Umweltbundesamt den Mitarbeitern zur täglichen Arbeit bereit. Langfristig ist auch der Einsatz des Tools außerhalb des Umweltbundesamtes unabhängig von KnowSEC möglich und angedacht.

KnowSEC erlaubt das Erstellen neuer Module zur Entscheidungsunterstützung direkt im System über die Oberfläche im Web-Browser. Fragebögen mit darin enthaltenen Fragen und Antworten, sowie das Herleitungswissen für Entscheidungen können von Experten der Domäne ohne Änderungsbedarf der Software im laufenden Betrieb selbst erstellt und gegebenenfalls auch geändert werden.

Fertige Module stehen auf der Infoseite einer Substanz zum Aufruf bereit. In einem Dialog beantwortet der Benutzer Fragen zum vorliegenden Themenbereich, während das System diese Antworten anhand der hinterlegten Bewertungskriterien auswertet und entsprechende Entscheidungen auch bereits während der Eingabe herleitet. Entscheidungen wie z.B. „kritisch in Rohwasser“ bzw. PMT werden dem Benutzer angezeigt. Speichert der Benutzer die Beantwortung der Fragen, so werden auch die hergeleiteten Entscheidungen für die aktuelle Substanz im System abgelegt. Sie werden anschließend auf der Infoseite der Substanz angezeigt und stehen auch für durch Benutzer definierte, sich automatisch aktualisierende Übersichtslisten in KnowSEC bereit. Beispielsweise existiert eine Liste mit allen Substanzen, die aufgrund entsprechender Nutzereingaben im System und den in diesem Projekt erarbeiteten Kriterien als PMT Substanzen eingestuft werden.

Wie in diesem Bericht dargestellt, umfasst die Bewertung von Substanzen im Kontext von Rohwasser die drei Hauptaspekte Persistenz, Mobilität und Toxizität. Zusätzlich kann über eine Betrachtung der Exposition die weitere Bearbeitung für die vorliegende Substanz abgekürzt werden, wenn eine Exposition der Substanz

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<sup>2</sup> Konzeption und Entwicklung eines Prototyps zur Entscheidungsunterstützung bei der Identifizierung umweltrelevanter Chemikalien und notwendiger regulatorischer Maßnahmen im Rahmen der REACH-Verordnung

<sup>3</sup> Klärung der technischen und rechtlichen Möglichkeiten und Erarbeitung von Lösungen zur Nutzung von unter REACH generierten Daten für umweltrelevante Vollzugsmaßnahmen auf allen Ebenen der deutschen Behörden bzw. Gesetzesvollzüge

in die Umwelt beispielsweise ausgeschlossen werden kann. Weiterhin gibt es Substanzen, die aufgrund von besonderen Eigenschaften nicht bewertet werden können.

Analog zum Leitfaden („practical guide“) umfasst das Modul in KnowSEC also die folgenden Aspekte bzw. Fragebögen:

- Exposure Evaluation (Stufe E1): Kann Exposition in die Umwelt aufgrund von Nutzung nur als „Zwischenprodukte unter streng kontrollierten Bedingungen“ ausgeschlossen werden?
- Substance Characterisation: Liegt die Art der Substanz im Kompetenzbereich des Moduls?
- Persistence: Ist die Substanz im Wasser persistent?
- Mobility: Ist die Substanz im Wasser mobil?
- Exposure Evaluation (Stufe E2): Kann der Stoff wegen einer vernachlässigbar geringen Exposition der Umweltkompartimente auf Grundlage der registrierten ERCs und Tonnagen ausgeschlossen werden?
- Toxicity: Ist die Substanz im Wasser toxisch?

Pro Fragebogen werden Entscheidungen im Kontext dieses Fragebogens getroffen, z.B. „P Criterion fulfilled“ oder auch „No relevant exposure potential for raw water“. Diese Entscheidungen werden anschließend zu Gesamtentscheidungen der Art „Critical in raw water“ zusammengefasst. Das Wissen zur Herleitung der Entscheidung wurde in Form von ausführbaren Flussdiagrammen sowie textuellen Regeln in KnowSEC hinterlegt.

Um wie beschrieben die Bearbeitung einer Substanz frühzeitig abbrechen zu können wird die Einhaltung der gegebenen Reihenfolge der Fragebögen empfohlen. Auch bei einer von der Reihenfolge abweichenden Bearbeitung werden jedoch stets Entscheidungen hergeleitet, die ausgehend von den aktuell dem System bekannten Fakten korrekt sind. Wird beispielsweise der Fragebogen „Persistence“ vor dem Fragebogen „Substance Characterisation“ bearbeitet, so kann es aber vorkommen, dass vorher bereits etablierte Entscheidungen zurück genommen werden müssen. Es könnte sich herausstellen, dass die Substanz zu einer Klasse gehört, die nicht im Kompetenzbereich des Moduls liegt.

### **Validierung des Ansatzes mit Beispielsubstanzen**

Nach Erstellung des oben beschriebenen Bewertungskonzeptes und der Umsetzung in das Bewertungstool wurde für 93 Substanzen überprüft, ob es sich um PM oder PMT Substanzen handelt, a) um praktische Beispiele über die Aussagekraft der gewählten Kriterien zur Verfügung zu haben, b) um zu prüfen, ob auch solche Substanzen, die in Monitoring-Programmen auffällig waren, sich als PM Substanzen erweisen würden, c) um ggf. das Konzept zu optimieren, wenn die Beispielsubstanzen keine sinnvolle Auswahl liefern würden.

Zunächst wurden 84 Substanzen bewertet, bei denen ein Screening nahegelegt hatte, dass es sich um PM oder PMT Substanzen handeln würde. Diese Substanzen wurden entsprechend des Bewertungskonzeptes bewertet. Es ergab sich:

21 der 84	Chemikalien waren PM Substanzen, zusätzliche
12 der 84	Chemikalien waren PMT oder PMT <sub>Screen</sub> Substanzen, also solche PMT Substanzen, bei denen noch eine Absicherung durch Expertenmeinung erforderlich wäre, ob sich das T Kriterium erfüllt (7 PMT Substanzen; 5 PMT <sub>Screen</sub> Substanzen). Bei
3 von 12	PMT oder PMT <sub>Screen</sub> Substanzen lag nach Prüfung der ERC in den

Registrierungsunterlagen eine niedrige Exposition (→E2 Bewertung) vor (so dass sie nicht als *rohwasserrelevant* oder *rohwassergängig* eingeordnet werden müssen), während sich

9 von 12

als *rohwasserkritisch* erwiesen. Bei diesen PMT oder PMT<sub>Screen</sub> Substanzen handelt es sich um

Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoat  
 4-Aminophenol  
 Cyanide  
 1,2-Dichloroethan  
 Trichloroethen  
 Tetrachloroethen  
 Dibutylhydrogenphosphat  
 Triclosan  
 Naphthalin

Mit der Methodik konnte demnach eine relevante Anzahl von PM und PMT Substanzen identifiziert werden. Es wird deutlich, dass einige der gelisteten Stoffe nur durch die gewählte systematische Suchstrategie als kritisch erkannt wurden. Allerdings wurde festgestellt, dass die Dokumentation der Daten in den REACH Dossiers selten so gut aufbereitet war, dass eine schnelle routinemäßige Auswahl anhand der oben entwickelten Kriterien möglich gewesen wäre. Oft war eine gründliche Analyse von Einzelstudien und eine vergleichende Prüfung verschiedener divergierender Einzeldaten erforderlich, um eine qualifizierte Aussage zu treffen.

Ein weiterer Datensatz von 9 Substanzen wurde aus Monitoring-Programmen zusammengestellt. Hier war durch den Nachweis in Grund- oder Oberflächengewässern die Wahrscheinlichkeit groß, dass P oder M Kriterien erfüllt wären. Die nähere Prüfung zeigte:

- 2 von 9 Stoffen erwiesen sich als PMT Stoffe (die T Eigenschaft spielt bei der Frage des Nachweises in Monitoring Programmen jedoch nicht notwendigerweise eine Rolle). Es handelte sich um das Biozid DIURON, das auch unter REACH registriert ist und um 2,4,6-Trinitrotoluol
- 4 von 9 Stoffen erwiesen sich als PM Stoffe (das Flammschutzmittel Trichloropropylphosphat, das Korrosionsschutzmittel Benzotriazol und Tolyltriazol (z.B. in Geschirrspülmitteln im Gebrauch) sowie der Süßstoff Acesulfam K (alle ohne T Eigenschaft)).
- 2 von 9 Stoffen waren zwar nicht PM, aber die registrierte Menge war so hoch, dass ein Wiederfinden dieser Stoffe in Monitoring Programmen trotz nicht erfüllter PM Kriterien plausibel ist (das Bisphenol A und der Komplexbilder NTA) , und bei
- 1 von 9 Stoff war die Datenlage für eine abschließende Beurteilung der PMT Eigenschaften unzureichend (4- Benzophenon).

Dieses Ergebnis zur Analyse der Monitoringdaten demonstriert, dass die Befunde beim Monitoring sich adäquat in der Bewertungsmethodik begründen lassen. Die meisten vorgefundenen Stoffe erwiesen sich tatsächlich als PM(T) Stoffe und in den beiden Ausnahmefällen war diese Ausnahme gut begründbar. Für einige Stoffe ist Zusatzwissen erforderlich, das bei einer Routineanwendung des Bewertungstools möglicherweise nicht immer einbezogen werden kann.

Wir haben auch eine Substanzliste mit prioritären Stoffen aus Sicht eines Vorgängerprojekts zur gleichen Thematik auf Übereinstimmung oder Unterschiede zum hier vorgelegten Konzept überprüft. Das frühere Projekt beinhaltete 340 Stoffe; dabei waren jedoch 80% Pflanzenschutzmittel, Biozide oder Pharmaka, so dass hierzu kein Vergleich durchgeführt werden konnte. Unter den 19 Substanzen mit vollständigen

Registrierungsdossiers waren ionisierbare Stoffe ausgeklammert, so dass die Auswirkungen dieser wichtigen Stoffgruppe, für die vermutlich maßgebliche Unterschiede festgestellt worden wären, nicht darzustellen waren. Dennoch zeigte sich auf Basis von nur 3 in ihrer Reihenfolge eingeordneten Stoffe deutlich, dass im Vorläuferprojekt Auswirkungen durch Doppelbewertungen einzelner Kriterien auftraten und dass weder der Vergleich mit anderen Stoffen zur korrekten Reihung führte noch PM Eigenschaften der Einzelsubstanz korrekt zugewiesen wurden.

Zusammenfassend zeigt sich an den Stoffbeispielen, dass durch die hier vorgestellte Methodik ein deutlicher Fortschritt in der Konsistenz und Nachvollziehbarkeit der Bewertungen erreicht werden konnte. Die vorgestellten Stoffbeispiele aus Monitoring und aus Substanzlisten von REACH registrierten Stoffen zeigen, dass mit der Ausweisung von PM(T) Substanzen eine wichtige Information bereitgestellt wird, die einen verbesserten Schutz vor besorgniserregenden Verunreinigungen des Rohwassers durch unter REACH registrierte oder zu registrierende Stoffe ermöglicht.

## Executive Summary

There is a fundamental social interest to prevent contamination of raw water used for drinking water production by chemical substances. However, the European directive on registration, evaluation, authorisation and restriction of chemicals (Directive No 1907/2006 (EC); REACH) currently do not sufficiently take into account, if a chemical substance potentially poses threat to raw waters. At the same time, information provided for a registered substance under REACH may be valuable for qualified assessment of substances' raw water contamination potential.

Persistency, mobility and toxicity of a substance make that substance critical to raw water. In the present project, an assessment methodology is proposed specifying under which circumstances a compound, which is to be registered under REACH, should be regarded a PMT substance and "*critical in raw water*". We define the degree of persistence (P), mobility (M), and toxicity (T), which leads to classification of a chemical as a PMT substance. A PMT substance which *may* occur in raw water in more than just very low concentrations is characterised as *critical in raw water*. There is a high priority to avoid substances with these inherent properties in raw water.

Our approach uses data generated under REACH together with software freely available over the internet to identify PMT substances. To enable the development of a digital evaluation tool, a "rule based knowledge system" was created by substantiating and differentiating the established PMT assessment methodology. This report contains the rationale of the assessment concept to determine PMT substances and outlines the principles of the electronic assessment tool.

Further, to verify practicability and relevance of the assessment concept as well as to demonstrate the importance of the issue, compounds meeting the properties required for a PMT (or, at least, PM) substance, were determined.

In addition, within the framework of this project also a "practical guide" was developed which enables stakeholders (especially registrants under REACH) to follow the logic of PMT assessment and to apply criteria to determine if a compound meets requirements qualifying it as PMT – without the software based tool developed in the project. The guide is structured according to an eight-step-procedure; all necessary terms are defined and the procedure is illustrated accordingly in sequence of the respective decisions. This "practical guide" is not part of this report.

### Persistence: definition and assessment

Persistence in regard to PMT properties was defined largely following the definition as provided by REACH in regard to PBT properties, that is REACH Annex XIII as well as REACH guidance documents, especially REACH guidance R.11 on PBT assessment. Corresponding to the target of raw water protection, it was substantiated in regard to the fresh water compartment. To verify persistence, a tiered approach is applied, with the following steps:

- Step 1: Evaluation of screening tests on biodegradability: a) tests on ready biodegradability (OECD 301; OECD 310), including b) "enhanced biodegradation screening tests" based on these guidelines and c) tests on inherent biodegradability (OECD 302 B and C) under consideration of specific criteria as given by REACH guidance R.11.
- Step 2: Test on hydrolysis as a function of pH (OECD 111)
- Step 3: Simulation tests on biodegradation (mineralisation) in water (e.g. according to OECD 309)
- Step 4a: Adoption of existing conclusion on P from PBT assessment performed under REACH

Step 4b: Estimation of persistence using quantitative structure-activity relationships (QSAR):  
BIOWIN 2 & BIOWIN 3 or BIOWIN 6 & BIOWIN 3

The higher tiers are necessary only as far as degradability/ persistence could not conclusively be demonstrated already at lower tiers. Attention has to be paid to the fact, that some test systems may consider only the decline of the parent but not mineralisation. In this case, stable transformation products may be formed which would have to be assessed themselves for P, M, and T properties (however, often data on transformation products as provided by REACH may not suffice to do so). In case of hydrolysis, temperature correction must be considered if the test temperature was inappropriate to conclude on environmental conditions.

Applying this tiered approach, in most cases a conclusion on persistence of a chemical based on data provided by REACH (occasionally supported by QSAR) can be achieved.

### **Mobility: definition and assessment**

A definition of mobility of chemicals in water including quantitative measures is lacking up to now. Mobility is described more generally as “the tendency of a chemical to move in the environment”. It is discussed in this report to define mobility of a chemical in water by either one of the following properties: water solubility, the octanol-water partition coefficient ( $K_{ow}$ ), the organic carbon normalized adsorption coefficient ( $K_{oc}$ ). Also the influence of an aggregated value, the so –called “purification factor” (that models removal of the dissolved fraction of a substance from surface water due to degradation, adsorption and volatilisation) was evaluated.

ECETOC developed a software for exposure modelling under REACH (“ECETOC-Targeted Risk Assessment”, TRA, Version 3.0), which is often applied. This software allows for calculation of the percent fraction of input concentration of a sewage treatment plant found in surface water and groundwater, respectively. Using the same input concentrations for different chemicals under standardized conditions (especially zero biodegradation assumed), the size of the respective fractions of a chemical in surface water and ground water compared to other chemicals is assumed to be a meaningful relative measure for the mobility of this chemical. A characteristic of this measure for mobility is, that the direct emission from the sewage treatment plant to the surface water is considered as well as the indirect emission to groundwater via adsorption on sewage sludge and application of this sludge on fields. Both pathways may be relevant in terms of raw water contamination and must be considered while defining an encompassing measure for mobility.

In the present project we therefore used 64 substances and estimated their relative mobility using TRA under standardized conditions as described. Then, correlation of partitioning to raw water (surface water and groundwater, respectively) with different physico-chemical properties (water solubility, Henry’s law constant,  $\log K_{ow}$ ,  $\log K_{oc}$  including/excluding purification factor) was investigated. For the 64 sample substances it was ascertained that their molecular weight, water solubility,  $\log K_{oc}$  and Henry’s law constant were heterogeneous and spanning a wide range to achieve sufficient representatives.

The percent fraction of a substance in surface water and groundwater was not or very weakly correlated with water solubility given that a minimum water solubility was exceeded. Also correlation with Henry’s law constant was weak and only a slightly better correlation was achieved with  $\log K_{ow}$ . This came not unexpectedly taking the close correlation of  $\log K_{ow}$  with water solubility. However, using  $\log K_{oc}$  as the dependent variable, correlation was high, for surface water as well as for groundwater. It turned out that  $\log K_{oc}$  is a meaningful measure for mobility, and that the extent of mobility is inversely proportional to the extent of net adsorption to solids, with net adsorption including adsorption / desorption events integrated

over time. Finally, from the results with the 64 sample compounds used for the model calculations, a value for  $\log K_{OC}$  of approximately 4.5 could be derived from which on a significant decline in surface- and groundwater concentrations could be observed with further increasing  $\log K_{OC}$ . As such, the value of  $\log K_{OC} = 4.5$  was set as the criterion for mobility:

Under REACH, regularly  $\log K_{OW}$  is reported, however, also  $\log K_{OC}$  may be given in the registration document. But this value often is calculated based on  $\log K_{OW}$ . This may be appropriate for neutral, non-ionisable organic compounds, but is certainly not for ionic or ionisable compounds. Neither is the HPLC screening methodology according to OECD 121 appropriate for this group of substances. For these difficult compounds only the batch equilibrium method (OECD 106 or equivalent) is appropriate for determination of adsorption. To determine, if a substance is ionisable in the environmentally relevant pH range and if acid functionality, alkaline functionality or both is decisive, an appropriate software tool available over the internet exists and is described. A further important prerequisite for mobility is, as mentioned above, a minimum water solubility, which was empirically derived to be around 150  $\mu\text{g/L}$ .

**Persistent compounds are regarded as mobile in water, if their  $\log K_{OC}$  is  $< 4.5$   
and their water solubility is  $> 150\mu\text{g/L}$ .**

With a value for water solubility smaller or equal to 150  $\mu\text{g/L}$  immobility is to be assumed. However, for ionisable compounds it is important to consider if the pH prevalent for determination of water solubility was appropriately chosen to capture the water solubility of the ionised state. Thus, the methodology was sufficiently differentiated as to cover the interdependency of water solubility and pH for this compound class.

Bank storage water is also raw water and an important source for drinking water. Bank storage water is not specifically addressed for the purposes of this project, because it is considered to be a special (“worst case”) form of surface water.

It is striking, that the cut-off for mobility (i.e.  $\log K_{OC} < 4.5$ ) is the same numerical value as the cut-off for the screening criterion on bioaccumulation (i.e.  $\log K_{OW} > 4.5$  according to REACH guidance document R.11). The interesting question arises if there could be an intersection of these properties (mobility and bioaccumulation), i.e. implicating eventually compounds being PMT and PBT at the same time. We do not elaborate here on T and P. With regard to M and B, we show that an overlap is theoretically possible. This is due to the positive correlation of  $\log K_{OC}$  with  $\log K_{OW}$  for neutral, organic compounds. This correlation is differentially manifest dependent on the exact substance class (structure types and heteroatoms present). However, at  $\log K_{OW} 4.5$ , water solubility is already low due to significant hydrophobicity, and the theoretically possible overlap will, in practice, be reduced due to a decline in water solubility (often below the cut-off of 150  $\mu\text{g/L}$ , see above) with increasing  $\log K_{OW}$  beyond 4.5. Further, a  $\log K_{OW} > 4.5$  is a screening criterion on bioaccumulation, and the actual criterion of  $\text{BCF} > 2000$  according to REACH, Annex XIII, may not be fulfilled for all compounds close to this cut-off. Therefore, while some marginal overlap of M and B may be demonstrated, our focus is on PMT substances without significant bioaccumulation potential.

### **Toxicity: definition and assessment**

The toxicity criterion for characterisation of PMT substances should at the one hand incorporate generally accepted definitions for “toxic” as used within REACH with regard to human health (e.g., within PBT assessment), on the other hand it should also be applicable on up to now non-classified compounds being

nonetheless of health concern. Correspondingly, in the framework of this project substances fulfilling one or more of the following properties were assigned T for *toxic* (classification according to REGULATION (EC) No 1272/2008):

- Substances classified as carcinogen, germ cell mutagen or reproductive toxicant (CMR) Cat. 1A, 1B
- Substances classified as germ cell mutagen or reproductive toxicant Cat 2
- Substances classified as carcinogen Cat. 2 (differentiated from substances mentioned above by screening-level assignment - see below - and possible further differentiation by experts assessment)
- Substance is classified with H362 (“may cause harm to breast-fed children”)
- Substances classified for specific target organ toxicity upon repeated exposure (STOT RE) Cat. 1 or 2
- Substance has structural determinants implicated with genotoxicity and carcinogenicity
- The derived no adverse effect level (DNEL) for oral exposure (long-term, general population) is  $\leq 9\mu\text{g}/\text{kg}$  body weight and day
- For substances without appropriate DNEL derived (in case, classification does not lead to assignment of T as outlined above): Cramer Class III assigned (reactive compounds, low DNEL assumed) according to quantitative structure activity relationship (QSAR; e.g. implemented in TOXTREE software)
- Substance part of a qualified toxic substance inventory (e.g. drinking water directive)
- Substance shown or suspected to have endocrine disrupting properties (part of a decisive list which yet has to be established)

For some of these criteria assignment of T is provisional ( $T_{\text{screen}}$ ) and still has to be confirmed by a qualified toxicological expert assessment. This, however, is beyond a simplified formalized decision based approach using information given under REACH, and as such cannot be characterized further within the framework of this project. This applies to carcinogens of category 2, to substances with structural determinants implying mutagenic or carcinogenic action, to (suspected) endocrine disrupting compounds, and to substances with Cramer Class III as a substitute for a low DNEL. A substance can be assigned T or  $T_{\text{screen}}$  based on more than one criterion.

It should be noted that also transformation products possibly formed by degradation processes not leading to full mineralisation have to be assessed for toxicity as well, given that these are sufficiently characterized to enable this. Under REACH however, only the parent compound will be sufficiently identified and toxicologically characterized to allow an assessment. In such cases, in addition an obligation arises to determine the necessary data for relevant transformation products.

### **Relevance of exposure for PMT assessment under REACH**

The assessment of PMT properties is linked to the “hazard” of a possible raw water contamination based on intrinsic properties of a substance. It should essentially be identified independently from exposure assessment, which is performed, e.g., in the course of a registration under REACH.

However, estimation of exposure in the framework of an assessment of PMT properties has two functions:

1. Reduce the work-load, if environmental exposure can virtually be excluded: then, the question on fulfilment of PMT properties becomes irrelevant.

2. Provide discrimination benchmarks between substances being *pervious* to raw water or *relevant in* raw water. To be *pervious* only requires classification on P and M (with no information on exposure, just based on intrinsic properties of a substance) , but, in case of *relevance* , more than just very low exposure may, in fact, occur.

Both aspects need to be further illustrated:

One of the first steps in assessment of PMT properties is the question, if there is the possibility of environmental exposure at all, i.e. exposure tier 1 (E1) passed. Exposure via raw water can generally only be excluded for substances used as “intermediates under strictly controlled conditions”. It must be emphasized, that all compounds having a full registration (maybe in addition to their use as intermediate) or which are registered as new substances (according to Directive 67/548/EEC) will *not* be exempted from a further assessment of PMT properties. Was a compound dismissed from further investigations at tier E1, it has to be checked at appropriate points in time if meanwhile a full registration was performed in parallel. If it may not be excluded that a compound reaches raw water at all, it will be analysed if it fulfils criteria for P and M. If yes, it will be assigned as *pervious to raw water*.

At tier E2, again a screening on potential exposure is performed. It is determined whether assumed exposure to the environment will be very low or (possibly) not. A *pervious* substance (PM substance) showing not clearly very low exposure is called *relevant in raw water*. The decision criterion is based on the “environmental release categories” (ERCs) reported for registered substances under REACH and the respective total tonnage per year for this substance. REACH guidance R.16 provides criteria, which were applied for discrimination. For example, if only ERCs 6A, 6D or 11A<sup>4</sup> are mentioned in the published registration dossier, further discussion on PMT properties is not warranted, if tonnage is not above 10000 tonnes per year. A (PM) substance, which is *not relevant in* raw water, will not be further studied with respect to toxicity. A (PM) substance, which is *relevant in* raw water and *toxic* (additionally T criterion fulfilled), will be called *critical in raw water* and is a PMT substance.

If a complete exposure assessment already exists (e.g., from a registration procedure apart from PMT assessment), the two first tiers of exposure assessment may be skipped. Based on exposure tier E3 (which is a detailed exposure assessment including the scenario “humans via the environment”), it may be decided, whether a PM(T) assessment should be performed. As discussed in other regulatory framework, a modelled or measured raw water concentration of 0.1 µg/Litre may be an appropriate cut-off. Within this project, however, no final value has been proposed.

### Applicability domain

Not all substances, which are registered under REACH, may be assessed with the provided methodology regarding their PMT properties:

- Inorganic substances including metals cannot be assessed for PBT or PMT classification
- Substances with “unknown or variable composition” (UVCB) or multi-constituent substances were not yet specifically considered because of their possible complexity. They are currently out of the applicability domain of PMT classification.

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<sup>4</sup> For example, in ERC 11A („wide dispersive indoor use of long-lasting articles, low release“) only emission to water of 0.05% are listed in this REACH guidance. This permits the exclusion of substances with this use from further consideration at tonnages below 10000 tons/year.

- Organometallic compounds usually are not stable in water or are reactive. Therefore, priority should be given to PMT assessment of the reaction products.
- Surfactants may behave potentially different from their single contained molecules. Therefore assessment of mobility will not be possible.
- For transition metals with organic ligands, only biodegradation of the organic part may be assessed.
- In case of ionic, zwitter ionic or ionizable organic compounds assessment within this framework is only feasible, if a measured  $\log K_{OC}$  is available. The only respective procedure for determination is the “batch equilibrium method” according to OECD 106 (or comparable guidelines).

### **Reporting gaps in REACH registration documents**

The original information usually provided in REACH registration documents has some relevant restriction, which limit the feasibility of the proposed approach:

Transformation products from substances registered under REACH may be highly relevant with regard to their PMT properties. However, within REACH registration documents usually respective detailed information on identity and properties of transformation products is lacking. Degradation pathways may be rarely modelled with sufficient precision. We propose that the assessor of PMT properties should give notice if a supplementary assessment on transformation products including their assessment should be performed. If gaps are identified this should prompt further investigations. The current structure within the reporting file (IUCLID) does not promote the (voluntary or obligatory) implementation of adequate (and sufficiently detailed) documentation, where structured fields could be marked specifically, if test results from the parent compound need to, but do not, address the respective aspect of transformation products.

Currently, under REACH, exposure concentration in raw water is calculated, if the exposure scenario “humans via the environment” is considered. This concentration, in fact, is in raw water, because water treatment is not addressed in this modelling approach. However, within the nomenclature of REACH, the term *raw water* is not known and therefore the result is called concentration in *drinking water*. However, this calculation is only requested, if the registered tonnage is higher than 1000 tons/year or if the tonnage is higher than 100 tons/year *and* the substance is classified as “toxic” or as a CMR substance. In many cases, raw water concentrations were not reported (e.g., if a *persistent* and *mobile* substance, as defined in this project, is present). There only is an aggregated assessment of “drinking water” in combination with food and only for this more complex exposure a *risk characterisation ratio* (RCR) is calculated, if “humans via the environment” is looked at. However, information about raw water concentrations and the RCR are only of secondary importance within this project, because contamination should also be avoided, if RCR is clearly below one.

## Assessment tool

In the context of the expert evaluation report FKZ 3600 1060<sup>5</sup> and the research and development grant UFOPLAN 3711 63 420<sup>6</sup>, the system KnowSEC was designed, implemented, and deployed within the section of the German Federal Environmental Agency responsible for the assessment of chemicals registered under REACH.

The system allows for the documentation and decision support of substance-related decisions. KnowSEC was implemented as an intranet-based semantic wiki. Group members are able to view information on substances via a central info page mechanism. Also new information can be added easily. Besides informal text, the users are also able to store explicit decisions on substances. The decision making process is supported by memos and interactive question-answer interviews.

With the current project, the assessment tool for PMT properties of substances in raw water was added to KnowSEC as a decision support module named "Raw Water Protection". There, besides modules on domains like relevance (based on political, regulatory, or research related considerations), exposure (indications for release of chemicals to the environment), and the raw water independent assessment of persistence, bioaccumulation and toxicity, it can be used by the UBA employees for their daily work.

KnowSEC allows the creation of new decision-support modules directly within the web-based system. Questionnaires and the contained questions and answers as well as the respective derivation knowledge can be added and edited by domain specialists without changes to the software during standard daily operation of the system.

Finished modules are available for decision-support on the info pages of the known substances of the system. In an interview the user answers questions about the present domain, whereas the system uses these answers in combination with the provided assessment criteria to derive decisions like "critical for raw water" for the user during the input. If the user saves the changes in the interview, the derived decisions are shown in a summary on the info page of the current substance. Also, the decisions will be used to automatically update overviews and lists in KnowSEC, which can be created and changed by the users. For example there are lists with all substances that are currently known by the system to fulfill the PMT criteria established in this project.

As described in this report, the assessment of substances in the context of raw water comprises the three main aspects persistence, mobility, and toxicity. Additionally, the consideration of exposure allows shortcuts in the assessment of substances, and some substances have to be excluded from assessment because of special properties not covered in this project.

Therefore, analogous to the practical guide, the module "Raw Water Protection" in KnowSEC comprises the following aspects or questionnaires:

- Exposure Evaluation (Tier 1): Can exposure to the environment be excluded due to usage only as "intermediates under strictly controlled conditions"?
- Substance Characterisation: Is the module competent to assess the given substance?
- Persistence: Is the substance persistent in water?
- Mobility: Is the substance mobile in water?
- Exposure Evaluation (Tier 2): Can the substance be excluded because of insignificant exposure to the environment based on registered ERCs and tonnages?
- Toxicity: Is the substance toxic in water?

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<sup>5</sup> Conception and development of a prototype for decision support for the identification of environmentally relevant chemicals and necessary regulatory measures in the context of REACH

<sup>6</sup> Clarification of technical and juridical possibilities and development of solutions for the usage of data generated under REACH for environmentally relevant management options on all planes of German agencies and laws

For each questionnaire, respective decisions are derived, e.g. "P Criterion fulfilled" or "No relevant exposure potential for raw water". Those decisions are then aggregated into overall decisions like "Critical in raw water". The knowledge to derive the decisions are defined using executable flow charts and text rules.

To get the previously described shortcuts for the assessment of a substance, compliance to the given order of questionnaires is recommended. An assessment independent of the given order will still yield decisions that are correct on the basis of the information currently known to the system. If for example the questionnaire "Persistence" is assessed prior to the questionnaire "Substance Characterisation", it is possible that decisions will be retracted, because the substance is then known to be of a class not covered by the module.

### Validation of the approach with example substances

After the concept to identify PMT substances had been established and after it had been transformed into the assessment tool, we analysed for a range of substances, whether those would, in fact, be PM or PMT substances according to the definitions and substance intrinsic data illustrated above, a) because examples could show that the selected criteria really are meaningful, b) because we were interested to know whether substances observed in monitoring programs of surface water, groundwater or sewage treatment plant effluents would fit to our definition of PM substances, c) because we intended to improve the proposed methodology where needed if examples showed any flaws.

First we made a selection of 84 substances, for which a prior screening procedure indicated, that those would probably be PM or PMT substances. Therefore, the 84 substances were analysed more closely. Finally, the following results were obtained:

21 of 84	chemicals really were PM substances. A additionally
12 of 84	chemicals were PMT or PMT <sub>Screen</sub> substances, i.e., PMT substances, for which the T criterion should be confirmed at a higher expert level (7 PMT, 5 PMT <sub>Screen</sub> ). For
3 of 12	PMT or PMT <sub>Screen</sub> substances a very low exposure was shown with E2 criteria (ERCs in combination with tonnage); therefore they were not further analysed, and
9 of 12	were found to be critical in raw water (PMT or PMT <sub>Screen</sub> ). Those were Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoate 4-Aminophenol Cyanide 1,2-Dichloroethane Trichloroethene Tetrachloroethene Dibutyl hydrogen phosphate Triclosan Naphthalene

Therefore, with this methodology a relevant number of PM or PMT substances were identified. It becomes evident, that some of these substances were not identified to be a problematic substance before. However, we also learned that information in REACH IUCLID dossiers rarely is documented in a way that a fast routine selection according to the criteria would have been possible. Instead, often a thorough examination of the single data and an evidence based selection from contradicting information was necessary to get qualified results.

A second set of substance consisted of 9 compounds from monitoring programs. Because of the occurrence in significant concentrations in ground- or surface water, it was hypothesized that they should be P or M substances or PM substances. A more detailed analysis demonstrated:

- 2 of 9                      Substances were PMT substances (the T property, however, was not included because it was not the reason for monitoring). Those were the biocide diurone, which is also registered under REACH, and 2,4,6-trinitrotoluene
- 4 of 9                      Substances were PM substances (the flame retardant Trichloropropyl phosphate, the corrosion inhibitor benzotriazole and tolyl triazole (used, e.g., as a dishwashin agent) and the sweetener Acesulfam K).
- 2 of 9                      were not PM, however, the registered amount was that high, that detection in monitoring studies was plausible (the antioxidant bisphenol A and the complexing agent NTA) , and for
- 1 of 9                      substance, data were incomplete and did not permit final conclusions regarding PM properties (UV screen 4- benzophenone).

This result from the monitoring studies demonstrated that monitoring results were largely in agreement with our hypothesis. Most detected substance really were PM(T) substances and for both exemptions the result was still plausible. Some of the substances needed additional input, which may not be available with routine application of the assessment tool.

We also analysed a list of substances proposed as priority substances as result of an earlier project on the same issue. The earlier methodology and results were compared to this projects' methodology. The comparison was only possible with major limitations. The earlier study analysed 340 compounds, but 80% were plant protection products or pharmaceuticals, which were not addressed here. Only 19 substances with full REACH registration were found. Ionizable substances were almost excluded in the earlier study, which were an important reason not to use  $\log K_{OW}$  (as in the earlier study) but to use the  $K_{OC}$  as criterion for mobility assessment in the present project. It can be demonstrated that double counting of criteria in the earlier project led to biases in ranking and improper assignments of PM classification.

Taken together, the presented substance examples show that significant progress in plausibility and consistency of assessments was achieved with the current project compared to the prior analysis. Presented examples from monitoring and from REACH lists for registered substances in this project demonstrated that the identification of PMT substances provides relevant additional knowledge and can be used to improve protection from contaminations by substances registered under REACH in raw water.



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## 1 Introduction

Provision and conservation of clean drinking water is one of the key objectives of public and environmental health policy. To effectively implement such a policy,

- we have to define, what we call *clean* drinking water, and
- we have to identify chemical substances, which contribute to the contamination of drinking water.

Apart from pharmaceuticals, cosmetics, pesticides and biocides an important source for contamination of drinking water resources are chemicals, which are manufactured, placed on the market and used according to the European Community regulation on chemicals (REACH; EC 1907/2006). We provide a methodology for identification of substances with a potential for contaminating raw waters used as a source for drinking water which are emitted by registrants (manufacturers, importers), formulators or other downstream users including end-users as actors under REACH.

Raw water is a generic term for the various sources of drinking water without considering potential water treatment<sup>7</sup>. In most cases, raw water therefore may be groundwater or surface water (lakes, rivers) or bank storage water (dune recharges). We focus on raw water instead of drinking water, because the objective should be reached not by initially contaminating the raw water and subsequently reverse this contamination by remediation/ water treatment. We don't want to rely on the respective *end of pipe* instruments, which may or may not be fully effective.

A positive definition of what means *clean* within the framework of this project is not straight forward. A contamination level of zero is intended, but may not be universally manageable because, e.g., of the limit of determination, geogenic occurrences or some precautionous and proportionate *limit of significance*. In order to use a term which is operational and to focus on manageable goals we provide a definition of the opposite, i.e., a level of contamination which is *not sufficiently clean*, i.e., the respective substance is regarded as

- *relevant* (in its contribution to contamination) *in raw water*, or even
- *critical* (in its contribution to contamination) *in raw water*.

The potential occurrence of such contaminations in raw water calls for action by the manufacturer/ importer or other actors under REACH (e.g., risk management measures, regulatory intervention).

Basically, REACH provides a regulatory framework, which is established according to precautionary principles (Art. 1(3), REACH). Therefore, the terms *relevant in raw water* and *critical in raw water* should be defined in an extensive understanding:

We will call a substance as being *relevant in raw water*,

- i) if it is *pervious to raw water* according to its physicochemical properties, and
- ii) if uses combined with annual tonnage level as given in REACH registration dossiers do not demonstrate only low environmental releases.

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<sup>7</sup> Raw water: "untreated water of any kind" (<http://www.agwt.org/content/ground-water-and-water-wells-definitions-and-explanations>); "water that has not been treated" (GEMET - GEneral Multilingual Environmental Thesaurus).

We will call a substance as being *critical in raw water*,

- i) if it is *pervious* to raw water according to its physicochemical properties,
- ii) if it is *toxic*, and
- iii) if uses combined with annual tonnage level do not indicate only low environmental releases.

A substance *pervious to raw water* is to be characterized by certain physicochemical properties with regard to *persistence* and *mobility*.

Within the context of this report a chemical substance is regarded to be *persistent* (indicated by the capital letter “P” if it fulfils criteria as defined in section 2.1. A chemical substance is regarded as *mobile* (indicated by the capital letter “M”) within this project, if it fulfils criteria derived and defined in section 2.2 of this report. A chemical substance is regarded as *toxic* (indicated by the capital letter “T”) if it fulfils criteria as defined in section 2.3 of this report.

A substance that is *persistent, mobile and toxic* according to these definitions will be called a PMT substance.

As indicated above, a *persistent* and *mobile* substance (“PM substance”) will be called *pervious* to raw water. Similar terms with similar meaning in literature are P<sup>3</sup> substances (polar persistent pollutants; PPP) or PPOP substances (“polar persistent organic pollutants”) (see e.g. Loos, et al., 2009; Loos, et al., 2010; Reemtsma and Jekel, 2006). However, we use a somewhat broader definition for the purposes of this project.

If, however, a substance is confirmed to be *critical in raw water*, the consequences may include a full exposure assessment. If, then, the qualified exposure assessment results in a *predicted exposure concentration* (PEC<sub>drinking\_water</sub>) of more than 0.1 µg/Litre or if other decision criteria are fulfilled, this may trigger further demands for action (risk management measures, possible activities by the competent authorities, etc.). The used threshold of 0.1 µg/Litre is a German guidance value for a concentration of substances in raw water (“gesundheitsbasierter Orientierungswert”, GOW), below which generally no adverse health effects are expected (Dieter, 2009; 2011; 2014). For most substances, exposures at or below 0.1 µg/Litre are regarded as insignificant.

Basically, a PMT substance, which occurs in raw water, may set up a scenario that “gives rise to equivalent concern” as for other *substances of very high concern* (“SVHC” acc. to Article 57f, REACH). However, the special conditions and details of consequences for substances critical in raw water are not further discussed in this project. The possibility to reduce contaminations during raw water treatment and the extent of such reductions may be one important factor, which may give further weight to demand regulatory action by competent authorities in addition to activities by the registrant.

The methodology used in this project is linked to some defaults and conventional assumptions, which may not be determined by mere scientific means. Because precaution may be understood differently by the different actors under REACH, and because terms like “some exposure”, “low water solubility” or “significant toxicity” may be interpreted heterogeneously, we provide *flexible* definitions. We used cut-off levels which are regarded justified and agreeable to many actors under REACH. However, as we provide full transparency on the criteria for selection of such defaults, as a matter of principle, modifications of cut-off levels are possible and may be justified, based on new evidence or if an altered level of protection is desired. However, a full understanding of the relevant scientific background is recommended before considering respective changes. Similarly, the user can be interested to generate a list of PM substances instead of PMT substances or may want to know details about the occurrence of *toxic* substances without consideration of

persistence or mobility. The methodology used in this project may, thus, be adapted to generate such modified priority lists.

The methodology may be used to assess PMT properties and (potential) exposure of contaminants in raw water. Because of the heterogeneity of the physicochemical properties, many different parameters had to be considered. However, because of the complexity of some processes we had to limit the approach and exclude some types of substances and some types of exposure pathways potentially leading to contamination of raw water for the time being. These demarcations will be addressed in more detail in section 2.5 of this report.

The methodology is based on a tiered assessment if appropriate. Such a stepwise approach is justified in order to avoid unnecessary data generation and compilation, if the output at a low (less complex) tier already is sufficient to decide on the criterion in question. A tiered approach may also be helpful for the exposure assessment, which is currently foreseen with a two-tiers approach for *exposure* (E1 and E2). For criteria and procedure we refer to section 2.4.

This methodology with the substance assessment according to the definitions given above is outlined in a comprehensive way in the flowchart (Figure 1) below. Although some minor shortcuts and additional options are eliminated in the flowchart for reasons of clarity, this structure shows the logical backbone of this project. The rationale for the various definitions and all details are elaborated and explained in section 2 of this report. Note that the PMT assessment procedure focuses to the blue shaded block (PMT assessment) and is supplemented by the two tiers of the exposure assessment (E1, E2). All further steps linked to a substance critical in raw water (red shaded block at the bottom of the scheme) are beyond the scope of this project and have to be implemented separately.

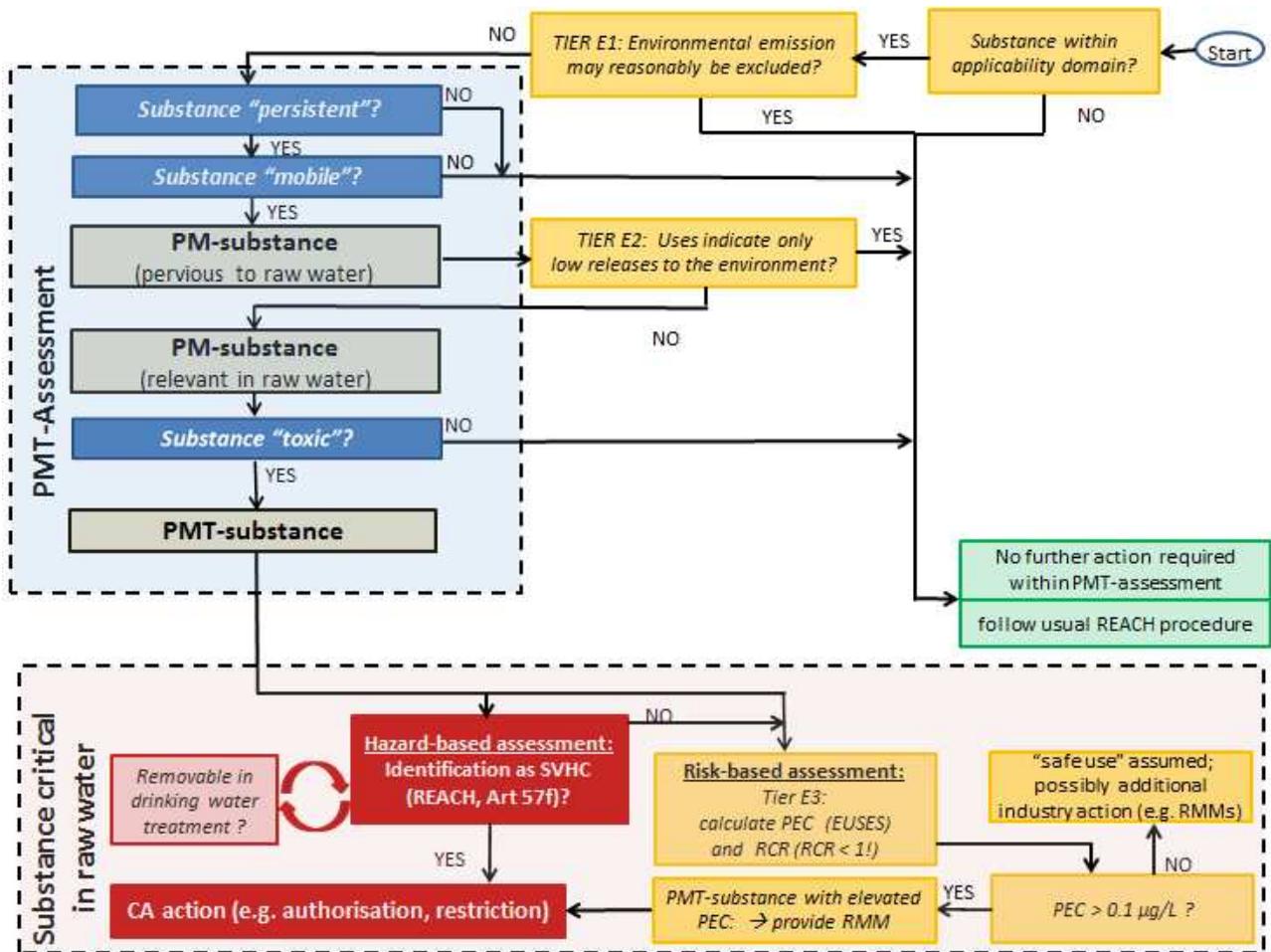


Figure 1: The decision process to identify PM or PMT substances (substances *pervious* to raw water; substances *relevant* in raw water; substances *critical* in raw water) for substances registered under REACH regulation.

This decision structure is explained in detailed in section 2, and transformed into a rule based decision structure and into an assessment tool as indicated in section 3.

This decision tool was then applied on a) a compound list derived from the list of REACH registered substances and b) compounds determined in monitoring studies to be present in relevant concentrations in surface waters, groundwater or STP effluents being at the same time REACH registered. Accordingly, relevant or critical substances were explicitly identified by the methodology developed (see section 4).

## 2 Concept to Assess PMT Substances

### 2.1 Persistence assessment

#### 2.1.1 Data availability under REACH

Data necessary for estimating persistence of chemicals which will be available under REACH depending on the tonnage level valid for the registration are summarized in Table 1.

Table 1: Data requirements under REACH in regard to parameters determining persistence

1-10 t/year (Annex VII)	≥ 10 t/year, data <u>additionally required</u> (Annex VIII)	≥ 100 t/year, data <u>additionally required</u> (Annex IX)
Ready biodegradability  Needs not to be determined if - the substance is inorganic	Hydrolysis as a function of pH  Needs not to be determined if - the substance is readily biodegradable - the substance is highly insoluble in water	Simulation testing on ultimate degradation in surface water Needs not to be determined if - the substance is highly insoluble in water, or - the substance is readily biodegradable
		Soil simulation testing Needs not to be determined if - the substance is readily biodegradable or - if direct and indirect exposure of soil is unlikely.
		Sediment simulation testing Needs not to be determined if - the substance is readily biodegradable or - if direct and indirect exposure of sediment is unlikely.
		Identification of degradation products, unless the substance is readily biodegradable

Data on ready biodegradability should generally be present for all registered organic compounds, i.e. already at the lowest tonnage level (1-10 t/year). Together with tests outlined below these tests are termed *biodegradation screening tests* in contrast to the higher tier simulation tests of REACH Annex IX. Seven test guidelines are available, namely technical guidance OECD 301 A-F and OECD 310 (suitable for volatile compounds). According to REACH guidance document R.7B, due to the stringency of these tests (small amount of inoculum originating from predominantly domestic STP, no pre-adaption to test chemical, 28 days duration limit) reliable positive test results (guidance specific pass levels met) may be taken to demonstrate ready biodegradability even if other, negative test results are available at the same time.

The following pass levels have to be fulfilled in these OECD 301 tests within 28 days in order to assume a chemical to be readily biodegradable:

- 70% removal of dissolved organic carbon (DOC, 301 A & E) or
- evolution of 60% of theoretical carbon dioxide (ThCO<sub>2</sub>, 301 B) or
- consumption of 60% of theoretical oxygen demand (ThOD, 301 C & D & F).

In addition, for pure substances these pass levels have to be achieved within a 10-day window, starting at a degradation of 10% and not exceeding the 28 days limit. Exceptions are the closed bottle test (301 D), where a 14 day window is applicable instead, and the MITI (I) test (not required).

For compounds demonstrated to be readily biodegradable, all further test requirements foreseen at higher tonnage levels can be waived, i.e. in principal no further tests are mandatory under REACH. For substances determined to be not readily biodegradable, at the next tonnage level (at and above 10 t/a) a test on hydrolysis as a function of pH (OECD 111) has to be performed. If relevant hydrolysis is observed, hydrolysis products should be identified: at least those representing 10% or more of the applied dose.

In contrast to REACH Annexes VII to IX, according to REACH guidance document R.7B also the following further screening-type tests on biodegradability can be considered for persistency assessments, however cannot be used for classification and labelling and may not be regarded as ready biodegradability:

For *Enhanced Biodegradation Screening Tests* beyond others the following modifications on tests for ready biodegradability are suggested in REACH guidance R.7B to increase biodegradation potential:

- Elongation of test duration up to 60 days
- Use of larger test vessels to increase microorganism diversity without changing inoculum density
- Testing at different biomass concentrations using concentrated microbes of environmental waters
- Using low level pre-adaption

Enhanced Biodegradation Screening Tests showing biodegradability (pass level reached) may be used to demonstrate that a substance is not fulfilling P criteria of REACH Annex XIII. However, in contrast to test results from tests on ready biodegradability according to the OECD guidelines this type of test cannot be used to derive rate constants needed for exposure estimation under REACH using e.g. EUSES/TRA (see section 2.2.3, Exposure estimation with ECETOC TRA).

Very similar to these enhanced biodegradation screening tests and often available are the third type of screening tests, tests on *Inherent Biodegradability* (OECD 302 A-C). These tests are more favourable for biodegradation as e.g. higher amounts of inoculum are used and mixed inoculum of different sources may be applied including industrial sewage treatment plants or locations, where a variety of chemical substances are consumed and discarded. While also OECD 302 A is one of the tests on inherent biodegradability, it differs considerably from 302 B and C tests in that a pre-adaption step is included to increase degradation potential and the total incubation time is principally not limited (other than 302 B and C: 28 days). In contrast to the other two tests the OECD 302 A (SCAS Test) under REACH is neither accepted to prove non-persistence (PBT/vPvB-assessment, REACH guidance R.11) nor can be used in the exposure assessment to derive a degradation rate constant, i.e. degradation rate equals zero even if pass levels are fulfilled (EC, 2003; RIVM, 2004). For the other two tests, under the following criteria inherently biodegradable substances may be assigned rate constants for exposure estimation under REACH (often termed “inherently biodegradable fulfilling specific criteria”):

- Zahn-Wellens (OECD 302B):  $\geq 70\%$  mineralisation (DOC removal) within 7 d; log phase no longer than 3d; removal before degradation occurs must be below 15%; pre-adapted inoculum must not be used.
- MITI II test (OECD 302C):  $\geq 70\%$  mineralisation ( $O_2$  uptake) within 14 days; log phase no longer than 3d; pre-adapted inoculum must not be used.

Test results fulfilling these specific criteria also demonstrate non-persistence with regard to the PBT assessment under REACH (ECHA, European Chemicals Agency, 2012c). For applicability of these test systems regarding assessment of persistence please see REACH guidance R.11. According to REACH guidance document R.7B (ECHA, European Chemicals Agency, 2012a), degradation  $< 20\%$  (i.e. lack of degradation) in these tests on inherent biodegradability may be taken as sufficient information to confirm

persistence in regard to PBT/vPvB assessment under REACH, such that higher tier simulation tests would be dispensable (ECHA, European Chemicals Agency, 2012c).

Moreover, as it is quite often the case, results of tests on ready biodegradability may be taken to demonstrate inherent biodegradability, if pass levels for ready biodegradability were just barely missed (slightly below 60% or 70%, respectively) or the 10-day window criterion was failed.

In conclusion, screening tests on ready biodegradability are the minimum data required under REACH for all registered substances (except inorganic compounds). In principle, if a substance could be demonstrated to be readily biodegradable, further higher tier data on biodegradation are not strictly required for this substance. Those data are however mandatory if the chemical safety assessment indicates the need for further data. If a substance turned out to be not readily biodegradable, at least for substances above 10 t/a in addition data on hydrolysis as function of pH would have to be generated. Higher tier testing always depends on the outcome of the chemical safety assessment. Results from simulation tests need to be provided in case substances not being “readily biodegradable” and when direct or indirect exposure of the environmental compartment of concern cannot be excluded. The exact test type also depends on the chemical safety assessment: Tests are selected according to the environmental compartments considered of highest relevance (distribution modelling).

### 2.1.2 Parameters determining persistence

#### Background

Persistence defined in a general way is “the ability of a chemical substance to remain in a particular environment in an unchanged form” (US-EPA, 2012<sup>8</sup>). More specifically, persistence is mostly defined according to half-lives in different environmental compartments, most often water, sediment and soil. Half-lives used in different regulatory frameworks are summarized in Table 2. While assessing single compartment specific degradation rates a chemical may fulfil the P criterion for a certain compartment while criteria for other compartments may be missed (i.e. not P for those compartments). Also in this respect multimedia models could help to prioritize compartments for a certain chemical: Compartments predicted to contain the highest mass fractions could be given the greatest weight while assessing degradability of a certain compound (Boethling, R., et al., 2009).

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<sup>8</sup> [www.epa.gov/dfe/pubs/tools/ctsa/ch5/mod5-3.pdf](http://www.epa.gov/dfe/pubs/tools/ctsa/ch5/mod5-3.pdf)

Table 2: Half-lives for identification of POPs from different regulatory frameworks

Compartment of concern	Regulatory framework			
	UNEP	CEPA	EU PBT	EU vPvB
Water	60 d	182 d	40 d freshwater	60 d
Sediment	180 d	365 d	120 d freshwater	180 d
Soil	180 d	182 d	120 d	180 d
Other	Sufficient other evidence for persistence		Marine water: 60 d; marine sediment: 180 d	

UNEP: United Nations Environmental Program – Stockholm Convention on Persistent Organic Pollutants, Annex D (2009); CEPA: Canadian Environmental Protection Act (data taken from Boethling et al. (2009)); EU PBT, EU vPvB: Cut-off criteria for PBT and vPvB as defined in EU REACH Annex XIII.

Most important are degradation events in sewage treatment plants, followed by degradation in surface waters and soil (see specific sub-chapters below). Most important in this respect are biodegradation and hydrolysis. If a chemical is *ultimately biodegraded*, it is *completely metabolized to CO<sub>2</sub> and water* (aerobic biodegradation). Screening tests on ready (OECD 301 tests) and inherent (OECD 302 tests) biodegradability generally assess ultimate biodegradability in that either O<sub>2</sub>-consumption or CO<sub>2</sub>-production is compared to theoretical values deduced from structure (or chemical oxygen demand). Another means is to measure the decrease in DOC (dissolved organic carbon concentration due to the chemical assessed). Care must be taken here that not adsorption events reducing DOC (adsorption on test vessel walls or activated sludge particulates) are taken for biodegradation<sup>9</sup>. Higher tier tests simulating e.g. biodegradation of chemicals in sewage treatment plants (OECD 303A), surface water (OECD 309) or soil (OECD 307) may assess both, ultimate and primary biodegradation. Often these tests are restricted to primary biodegradation if radioactively labelled materials are not available and specific analytics for parent compounds are applied. *Primary biodegradation* – like hydrolysis – leads to *degradation products (transformation products)* which may or may not (rapidly) biodegraded. Due to oxidation events playing a major role for degradation or the nature of hydrolysis, transformation products most often are more polar than the parent and may therefore be of higher mobility in water.

In conclusion, if a chemical is assessed to be readily or inherently biodegradable according to OECD 301 and OECD 302 test guidelines, it can be assumed that it is fully metabolized to CO<sub>2</sub> and transformation products will be most probably of no concern. In contrast, rate constants or half-lives on hydrolysis or primary biodegradation events yield only information on degradation of the parent and often no information is available on transformation products. Further, for chemicals with potential for adsorption to organic

<sup>9</sup> Note that OECD 301 A (DOC Die-Away) and 301 E (Modified OECD Screening) relate to dissolved organic carbon. These tests are inappropriate for highly adsorptive compounds and generally require an adsorption control incubation in parallel for adsorbing compounds.

matter, sediment and soil, care must be taken not to take elimination (i.e. disappearance from the water phase or formation of non-extractable residues in soil and thus disappearance from eluate) as degradation. This is especially of concern for higher tier tests (simulation tests) and makes these tests often difficult to interpret.

## Surface Water

### *Conclusions from REACH and EUSES/TRA calculations, respectively*

Annex XIII, REACH specifies criteria for persistence with regard to the PBT assessment under REACH. Decisive for the freshwater compartment is a half-life of > 40 days specifying a particular compound as persistent. With regard to experimental data on biodegradability available under REACH, this criterion is directly applicable for tests on hydrolysis (OECD 111) and simulation tests for mineralisation in surface waters (OECD 309 or similar tests), only. But, in most cases available data are limited to screening test data on biodegradability.

For environmental exposure estimations under REACH, however, screening test results on biodegradability are assigned generic half-lives, which in turn could be compared to criteria given by Annex XIII, REACH to judge on persistence. This approach is investigated in this section, and it is demonstrated below that, in fact, it is not an option for determining persistence with regard to PMT assessment. The similar holds true for groundwater with regard to degradation events in soil (see corresponding section).

As pointed out above, screening tests on ready biodegradability and – alternatively - inherent biodegradability are the minimum data generally available and needed for exposure estimation under REACH using EUSES or TRA (see also section 2.2.3, Exposure estimation with ECETOC TRA). Translation tables (see Table 3 to Table 5) are used within these programs to transform test results to compartment specific rate constants or half-lives. It must be emphasised here that translations from screening test results to half-lives in sewage treatment plants, surface water, soil and sediment (see section 2.1.3 on bank storage water) are very conservative. Thus guidance R.16 states that “the general experience is that a substance passing a test for ready biodegradability may under most environmental conditions be rapidly degraded and the estimated half-lives for such substances should therefore be regarded as a “realistic worst-case concept”.

**Table 3: Biodegradation in sewage treatment plants (rate constants for SimpleTreat model; water phase) - Data taken from REACH guidance document R.16, amended with half-lives calculated assuming pseudo-first order rate constants**

Test result	Rate constant k [h <sup>-1</sup> ]	t <sub>1/2</sub> [h]
Readily biodegradable	1	0.7
Readily biodegradable, but failing 10-day window	0.3	2.3
Inherently biodegradable, fulfilling specific criteria	0.1	6.9
Inherently biodegradable, <b>not</b> fulfilling specific criteria	0	infinite
Not biodegradable	0	infinite

Most relevant input in surface waters is sewage treatment plant effluent. Table 3 shows the rate constants and half-lives for degradation in sewage treatment plants derived by default from screening test results when performing exposure assessments under REACH. These rate constants and half-lives are valid only for the water-dissolved fraction of a substance and partitioning between water and sludge phase must be taken into

account. An approximate quantification of the impact of adsorption to sludge and particulates is possible using the screening-type tables given in R.16 (following the banding approach in analogy to Table 8 shown below, section 2.2.2).

The very conservative nature of rate constants deduced from screening tests becomes obvious in comparing suggested half-lives with cut-off values for P or vP given in REACH Annex XIII (PBT/vPvB assessment) in regard to surface water (see Table 4): A half-life of 50 days is assigned to a readily biodegradable compound failing the 10-day window requirement. According to P criteria (DegT<sub>50</sub> freshwater >40 days) this substance would have to be regarded as *persistent* – which is in contradiction to P assessment according to REACH guidance R.11. Similarly, an inherently biodegradable substance which – according to REACH guidance R.11 – would have to be regarded as *not* P given that specific criteria are fulfilled<sup>10</sup>, would have to be classified as vP (DegT<sub>50</sub> freshwater > 60 days) taking the half-life of 150 days assigned according to Table 4. As the guidance points out, rate constants and half-lives given in Table 4 do not have to be further adapted depending on adsorption behaviour of a substance “due to the well-established practice to conclude on biodegradability in the environment from such data.” For comparison of extrapolation factors between compartments to derive rate constants for readily biodegradable compounds used under REACH, by US-EPA as well as derived by dedicated experimental results, see Table 6 in section 2.1.2, Groundwater below.

**Table 4: First order rate constants and half-lives for biodegradation in surface water based on screening test results on biodegradability - data taken from REACH guidance document R.16. Values need not to be corrected for adsorption.**

Test result	Rate constant k [d <sup>-1</sup> ]	t <sub>1/2</sub> [d]
Readily biodegradable	4.7*10 <sup>-2</sup>	15
Readily biodegradable, but failing 10-day window	1.4*10 <sup>-2</sup>	50
Inherently biodegradable, fulfilling specific criteria	4.7*10 <sup>-3</sup>	150
Not biodegradable	0	infinite

Therefore, even for readily biodegradable compounds for which no further higher tier tests on biodegradability are mandatory when compared with the requirements of annexes VIII to X of the REACH legislation, it may make sense to perform simulation tests on degradation in surface waters, as this will yield more realistic half-lives which may reduce the calculated environmental concentration considerably compared to calculations based on these very conservative generic rate constants.

In conclusion, direct assessment of persistence according to the half-life criterion of 40 days specified by Annex XIII, REACH and based on generic half-lives assigned to screening test results according to REACH guidance document R.16 (translation tables) is no option to judge on the persistence of a compound in surface water.

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<sup>10</sup> e.g. for OECD 302 B: ≥ 70% mineralisation (DOC removal) within 7 d AND log-phase ≤ 3 d AND removal before degradation occurs < 15% AND no pre-adapted inoculum used.

## ***Conclusions from other projects and literature evaluation***

### *Approach by IfW*

Preceding projects on raw water relevance (IfW, 2010; 2011) postulated, that for industrial chemicals found in drinking water the relevant contamination pathway would be the one from sewage to surface waters, while other pathways and especially the sludge to field pathway could be disregarded (IfW, 2011). While not any supporting proof for this assumption is provided, the screening model focusses on the contamination pathway by effluents only.

In spite of this, the assessment of persistence considers data on biodegradability in the following rank order:

1. Soil
2. Sediment
3. Laboratory tests
  - a) Percolation experiments (e.g. test filters)
  - b) Batch experiments
4. Groundwater
5. Surface water
6. Sewage treatment plants simulation tests
7. Data from QSAR.

As such, according to IfW-approach the highest weight is assigned to degradation data with regard to media influencing groundwater (soil) or bank storage water (sediment) concentrations of chemicals, in spite of the fact that predominantly degradation in sewage treatment plants and surface waters will determine concentrations in surface waters. In addition, if data on anaerobic degradation are available, the overall degradation class will be determined by these data if a lower anaerobic degradation is observed. This worst-case assessment does not consider that most important degradation pathways for surface water concentrations are aerobic: This holds true for the sewage treatment plant as well as degradation in surface waters itself. Anaerobic degradation events are important only for the lower sediment layers, the groundwater and anaerobic digestion of sewage sludge.

Depending on the DegT<sub>50</sub> derived for a substance following the described prioritisation of degradation data, an index is derived as outlined in Table 9 (section 2.2.2, Surface Water). This index is directly added to the indexes connected to mobility, i.e. no separate assessment of persistence is performed. This approach has the severe draw back that an a priori exclusion of rapidly biodegradable substances is not possible. Rather, given a high mobility the mobility score may mask biodegradability and the substance would be regarded of e.g. intermediate concern for surface waters while an exclusion based on biodegradability data would have been possible and reasonable.

### *Approach by Götz et al.*

Götz et al. (2010) targeted aquatic micro-contaminants for monitoring in Switzerland. In this regard degradation is assessed. Chemicals demonstrated to be readily biodegradable or having hydrolysis half-lives

below 1 day are given low priority and are assigned to exposure category VI (surface water distribution, however rapidly biodegraded). For chemicals where no such data were available, it was assumed they were not rapidly degradable (worst case assumption) and QSAR was applied to further differentiate their potential for persistence. Using US-EPA's BIOWIN 3 module contained in the EPI suite TM platform, numeric values may be transformed into half-life categories. Compounds with BIOWIN 3 values  $< 1.75$  (corresponding  $\text{DegT}_{50}$  180 days<sup>11</sup>) were classified as highly persistent chemicals, whereas chemicals with values  $\geq 1.75$  (corresponding  $\text{DegT}_{50} \leq 60$  days<sup>11</sup>) were classified as moderately persistent chemicals. According to these two categories, compounds predicted to distribute into surface water were assigned either exposure categories I and II (highly persistent compounds, depending on emission scenario: continuous input versus periodic/complex input) or exposure categories III and IV (moderately persistent compounds, depending on emission scenario: continuous input versus periodic/complex input).

Thus, relying on screening data on biodegradability only, fortified by data on hydrolysis and – given that those data were not available – QSAR screening, a classification independent from mobility was performed allowing for targeted assessment of those compounds predicted to be highly or moderately persistent *and* predicted to partition into surface waters. This seems to be a valid approach of assessing biodegradability potential in regard to surface water relevance.

## Groundwater

### *Conclusions from REACH and EUSES/TRA calculations, respectively*

For the persistence criterion in regard to groundwater relevance of chemicals under REACH the following considerations apply:

In principle, groundwater may be recharged from surface water or from precipitation and percolation through soil. Under REACH, for groundwater only the second pathway (precipitation and percolation) is considered. This is a valid approach, as surface water is assessed separately (see above) under REACH and for drinking water (actually raw water) a worst case scenario is assumed in that the estimated concentrations for surface water (plus purification factor, see section 2.2.3, Exposure estimation with ECETOC TRA, and Table 20 for details) and groundwater are compared to one another and the higher concentration taken. Further, it is a safe assumption that groundwater recharged from surface water will contain equal concentration or less of any industrial chemical than the surface water it is recharged from. This is due to possible adsorption processes during passage of sediments and ground. On the other hand, anaerobic degradation in the sediment is not a priority taken into consideration while assessing persistence but may contribute to lower concentrations in groundwater.

Thus, the most important pathway for common chemicals -registered under REACH for which there is no dedicated direct exposure on land (agricultural soil) is the sludge to field pathway: Surplus sludge from sewage treatment plants frequently is applied on fields (see section 2.2.2, Groundwater) and especially adsorbing not readily biodegradable chemicals contained in the sludge may accumulate in soil over time, eventually leaching into groundwater.

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<sup>11</sup> A banding approach is used here: Nominal (verbal) output of BIOWIN 3-results (e.g. "months", i.e. discontinuous by nature) is transformed to half-life categories according to recommendations by US-EPA

Thus most important experimental results to determine the degradability of a compound and thus its potential for persistence in water are the following:

1. Aerobic biodegradation in sewage treatment plants
2. Possibly: Anaerobic degradation in sludge digesters (not common practice and not taken into account for exposure assessment under REACH)
3. Aerobic degradation on soil
4. Anaerobic degradation in deeper soil layers, saturated soils or groundwater (not taken into consideration for exposure assessment under REACH)

Thus especially for substances with high adsorption potential the sludge to field pathway may gain importance and biodegradation on soil may become relevant for estimation of groundwater concentrations. The general assumption for exposure assessment under REACH is that only the freely dissolved fraction present in the water phase will be available for degradation, translating into overall decreasing rate constant with increasing adsorption to soil. While this may not hold true for some substances, it certainly is a reasonable worst case assumption. A draw back regarding these assumptions under REACH however is, that on the one hand for adsorbing substances decreased rate constants for biodegradation are assumed due to preferential partitioning to solids. On the other hand, combined with repeated sludge applications and a sufficiently low biodegradation rate by integration over 10 years high accumulating concentrations in soil are estimated which translate via equilibrium partitioning into comparatively high concentrations in pore water. Due to pore water equalling groundwater under REACH, groundwater contamination will be predicted.

However, while all these assumptions may very well be correct, as long as these processes take place in the upper (aerobic) soil layer high pore water concentrations due to high accumulated overall concentrations in soil translate into a comparatively high freely dissolved fraction which in turn may be readily biodegraded *before* deeper layers and finally groundwater is reached. In addition, soil acts like a chromatography column retarding those compounds at the most which are of highest adsorption and (predicted) slowest biodegradation (due to the assumption that the adsorbed fraction is not biodegraded). However, adsorption is an equilibrium process: The available freely dissolved fraction in pore water may be low, will however steadily replenished from the adsorbed fraction while biodegradation proceeds. Thus, biodegradation may be slowed down – concurrently however dwell time in upper aerobic soil layers will be elongated compared to no or only slightly adsorbing substances and will at least partly compensate for slower biodegradation rate constants.

Apart from these model-specific draw backs soil biodegradation rate is surely important in regard to a potential for groundwater contamination. Due to missing half-life data for soil in most cases (see section 2.1.1) a banding approach is used transforming screening test results into soil specific half-lives depending on adsorption properties (see Table 5).  $K_{p_{soil}}$  is the soil-specific adsorption coefficient, calculated from  $K_{OC}$  and the organic carbon (OC) fraction ( $K_{p_{soil}} = K_{OC} * \% OC/100$ ).

**Table 5: Half-lives (days) for (bulk) soil based on results from standardised biodegradation test results - Data taken from REACH guidance document R.16**

<b>Kp<sub>soil</sub> [L/kg]</b>	<b>Assumed half lives in days for substances being:</b>		
	<b>Readily biodegradable</b>	<b>Readily biodegradable, failing 10-day window</b>	<b>Inherently biodegradable, fulfilling specific criteria</b>
≤ 100	30	90	300
> 100 ≤ 1000	300	900	3,000
> 1000 ≤ 10,000	3,000	9,000	30,000
etc.	etc.	etc.	etc.

These default half-lives (first order rate constants can be derived by the formula  $K = \ln 2 / t_{1/2}$ ) are highly conservative: Non- to moderately adsorbing, inherently biodegradable substances fulfilling specific criteria have an assigned half-life of 300 days, which would qualify them as very persistent (vP) according to REACH annex XIII (PBT/vPvB assessment). In contrast, according to REACH guidance R.11 (PBT/vPvB assessment), inherently biodegradable compounds fulfilling specific criteria are clearly regarded as not fulfilling even the P criterion (i.e. half-life in soil below 120 days). For the next adsorption band, even readily biodegradable substances fulfilling the 10-day window requirement would have to be regarded as vP in soil from their assigned half-life.

Thus, even for readily biodegradable compounds for which no further higher tier tests on biodegradability are required according to annexes VIII to X of the REACH legislation, it may be necessary to perform simulation tests for the soil compartment in order to reduce the calculated environmental concentration considerably compared with calculations based on these very conservative generic rate constants derived from screening test results.

Finally, to demonstrate that passing a ready test may be very well taken as a good indicator of fast biodegradation in different compartments of the environment in spite of these high half-lives assigned to even readily biodegradable compounds per default within the exposure assessment under REACH, a comparison of extrapolation factors between media is available in Table 6.

Table 6: Comparison of extrapolation factors used for readily biodegradable substances to extrapolate DegT<sub>50</sub> between media and actual factors determined experimentally by Federle et al. (1997)

Authority / Source	Extrapolation factor DegT <sub>50</sub> STP to DegT <sub>50</sub> surface water for readily biodegradable substances	Extrapolation factor DegT <sub>50</sub> surface water to DegT <sub>50</sub> soil for readily biodegradable substances	Overall extrapolation factor DegT <sub>50</sub> STP to DegT <sub>50</sub> soil
US-EPA	120	1	120
EU-REACH	520 (based on EU half-life STP of 0.69 h) or 360 (based on US-EPA half-life STP of 1 h)	2 (lowest adsorption band)	1040 (based on EU half-life STP) 720 (based on US-EPA half-life STP)
Federle et al. (1997), n = 9	0.71 to 25 (mean 2.7)	0.31 to 7.1 (mean 0.88)	Experimental: 2.1 to 14.3 (mean 5.3)

Extrapolated half-lives for readily biodegradable substances for sewage treatment plants (STP), surface water and soil in line with EU-methodology were compared to US-EPA *Interim Guidance for Using Ready and Inherent Biodegradability Tests to Derive Input Data for Multimedia Models and Wastewater Treatment Plants (WWT) Models (9/1/2000)*<sup>12</sup> and factors between media were calculated. These are juxtaposed to factors derived from experimental values by Federle et al. (1997) who compared experimental data de novo generated under carefully controlled conditions for 9 compounds for the following biodegradation test setups: Ready biodegradability (OECD 301 B, CO<sub>2</sub> evolution) – batch activated sludge test – river water test – soil mineralisation test. For the latter 3 tests, radioactive material had been used. Half-lives for the activated sludge test (STP) were between 1.16 and 0.17 days.

In conclusion, while US-EPA is more conservative in deriving half-life for STP from ready-tests (1 day compared to 0.69 days under EU-REACH), even when comparisons are based on the more conservative value from US-EPA resulting half-lives in soil are more conservative by a factor of 6 for soil and a factor of three for surface water. While Federle et al. (1997) included only 9 substances in their evaluation, it is of high interest that obviously differences between media are not as high as indicated by the default extrapolation factors in use. Interestingly, they found especially high first order rate constants in the test on ready biodegradability for those substances with high water solubility, while results in environmental media (with much lower test item concentrations) were rather the other way round. Thus water solubility seems especially relevant for biodegradation in screening tests but of lower impact under conditions more close to those found in environmental media.

<sup>12</sup> <http://www.epa.gov/opptintr/exposure/pubs/half-life.htm>

As a result from these considerations, we do abstain from considering separately aerobic degradation within soil or anaerobic degradation events in groundwater. Rather it is assumed to be sufficient to consider aerobic degradability in the water phase, also with regard to groundwater.

### **Bank storage Water**

While dedicated concepts for assessment of bank storage water were developed (Scheytt, et al., 2011), necessary input data (e.g. anaerobic degradation rates) are seldom available. For simplification and as a worst case, bank storage water may be regarded as a special form of surface water. This is already pointed out in the section on groundwater. For bank storage water the same holds true like for groundwater derived from surface water (see section on groundwater above).

### **Transformation Products**

Transformation products or metabolites may be formed by hydrolysis or primary biodegradation events. While mineralisation (formation of CO<sub>2</sub>), if complete, will lead to complete disappearance of the compound, disappearance of the parent by hydrolysis or primary biodegradation leads to transformation products which may or may not further be biodegraded under environmental conditions. The tests on hydrolysis as a function of pH (OECD 111), the simulation test for sediment (OECD 308), the simulation test for surface water (OECD 309) and simulation test for soil (OECD 307) are the testing guidelines which definitely foresee characterisation of degradation products. However, especially in the simulation tests in effect identification is often restricted to very basic information, e.g. approximate mass peaks, and mostly definite identification of compounds is lacking. Information like this is hardly to use in regard to this project. REACH foresees characterisation of degradation products only for substances registered above 100 t/a and technical completeness check provided with the software does not cover this point. It is thus highly questionable if any noteworthy data will be available for substances registered. However, for substances fulfilling PBT criteria under REACH, guidance documents are much more definite and data availability in regard to transformation products may be better.

#### **2.1.3 Persistence assessment in this project**

Within the context of this project a substance is regarded as being a PMT substance, if it is estimated to be *persistent* (P), *mobile* (M), and *toxic* (T) in raw water according to an assessment scheme based on intrinsic properties of a chemical substance. The following section describes assessment parameters for persistence to be used in identifying those substances. The order of the sub-chapters roughly represents the decision tree structure (the stem rather than the branches).

#### **Biodegradation screening test (Persistence Tier 1)**

Failure of biodegradation is the sine qua non condition for raw water relevance. Substances shown to be biodegradable therefore need not to be further characterized with regard to their mobility and toxicity properties. Most relevant in regard to raw water (surface water and groundwater, see section 2.1.2) are the following degradation processes:

- aerobic degradation in sewage treatment plants
- aerobic degradation in surface waters
- aerobic degradation in soil

while aerobic and anaerobic degradation processes in sediment (bank storage water, groundwater) and anaerobic degradation in groundwater are of lower impact in most cases and will not be regarded in the screening as

- chemicals will only arrive there if not sufficiently biodegraded in sewage treatment plants, surface water and soil
- anaerobic degradation is generally assumed to be considerably slower than aerobic degradation processes
- data on anaerobic degradation will seldom be available under REACH as the choice of test compartment and conditions depends on intrinsic substance properties and the outcome of the environmental fate and behaviour assessment
- no reliable QSAR predictions are possible.

As outlined in section 2.1.2, especially compounds successfully screened in tests on ready biodegradability but also inherently biodegradable substances (fulfilling specific criteria) may with high probability be assumed to be rapidly biodegraded in aerobic environmental compartments or at least to be not *persistent*. These screening test data should normally be available for all registered substances (i.e. even lowest tonnage band), are easily to interpret and therefore the first tier in screening assessment of persistence.

Thus, in line with the persistence criteria defined in REACH annex XIII together with screening criteria on persistence outlined in REACH guidance on PBT assessment (R.11) compounds assessed to be

- Readily biodegradable fulfilling the 10 day window according to OECD 301 / OECD 310 testing guidelines or equivalent
- Readily biodegradable not fulfilling the 10 day window according to OECD 301 / OECD 310 testing guidelines or equivalent
- Fulfilling pass levels for ready biodegradability in *enhanced ready biodegradability tests* (see section 2.1.1)
- Inherently biodegradable within 28 days as deduced from test on ready biodegradability if pass levels are just barely missed (<60% but  $\geq 50\%$  within 28 day of theoretical CO<sub>2</sub> evolution or O<sub>2</sub> consumption; <70% but  $\geq 60\%$  for DOC removal)
- Inherently biodegradable fulfilling specific criteria (see section 2.1.1) according to OECD 302 B and C testing guidelines

are regarded to be not *persistent* in water and are not further considered in the screening procedure for identification of PMT substances.

All other substances are regarded as *persistent* in the first tier.

### Hydrolysis (Persistence Tier 2)

For substances which failed the biodegradability screening test on ready biodegradability, data on hydrolysis as a function of pH should normally be available under REACH for tonnage levels above 10 t/a.

Half-lives determined according to OECD 111 should be compared to cut-off criteria for P under REACH. For environmentally relevant results, hydrolysis half-life determined at pH 7 and at a temperature sufficiently close to 12°C should be chosen. Minor temperature adaptations may be performed according to the following formula:

$$\text{DegT50}(12^\circ\text{C}) = \text{DegT50}(T) \times e^{(0.08 \times (T-12))}$$

with T being the temperature in °C at which hydrolysis was determined.

Transformation of pseudo first-order rate constants to half-lives can be performed according to:

$$\text{DegT}_{50\_hydr\_water} = \ln 2 / k_{hydr\_water}$$

$k_{hydr\_water}$  being the first-order rate constant for hydrolysis in water.

With a thus determined relevant half-life  $\leq 40$  days the substance is regarded as not P in water and not further assessed in the screening procedure.

However, under these circumstances (no relevant mineralisation in screening tests, but efficient hydrolysis) transformation products of the hydrolysis reaction are obviously not readily biodegraded and might be of concern. If for the mother compound higher tier simulation tests would be available assessing ultimate biodegradation (mineralisation) and relevant mineralisation would have been observed, concern for transformation products could be waived. Generally however, higher tier simulation tests will often not be available.

Some of the transformation products of hydrolysis reactions will have been registered for their own under REACH (e.g. fatty acids esters will hydrolyse to fatty acids and alcohol, which themselves may have been registered). These would be covered then anyway by the proposed classification approach for identification of PMT substances.

### Higher tier simulation tests (Persistence Tier 3)

The last resource of experimental data in regard to persistence would be higher tier tests (simulation tests) for surface water, soil, or sediment. These will often be available for compounds assessed to be not readily biodegradable and for which no relevant hydrolysis under environmentally relevant conditions had been observed. They may be more difficult to interpret compared to screening level tests: According to ECETOC (2011) “it is ... difficult to assess and interpret many of the higher tiered biodegradation studies designed to generate DegT<sub>50</sub> values or half-lives as they have no validity criteria or positive reference controls.” Possible further draw-backs are that only primary biodegradability may have been assessed or elimination may be higher than mineralisation due to e.g. non-extractable residues or volatilisation. Some of these issues are discussed in the review by Boethling et al. (2009).

In these tests, half-lives for the respective compartments are directly determined and can be compared with REACH cut-off criteria for persistence (Annex XIII REACH, see section 2.1.2, Table 2). Persistence in the context of a general raw water contamination potential may however only be assessed by simulation tests on degradation in surface waters (OECD 309 or equivalent). While concentrations in the water phase are separately assessed in the sediment simulation test (OECD 308), it cannot be decided in final conclusion whether a decline in concentration is caused by degradation or rather adsorption to sediment particulate matter in case the test substance is not radiolabelled. Therefore, simulation tests for sewage treatment plants, soil or sediment are *not* considered here.

### Thus, evaluating simulation test data on degradation in surface waters,

- ➔ compounds with **simulation test half-lives (DegT<sub>50</sub>)  $\leq$  40 days (mineralisation)** for freshwater are regarded as **not P in water and no further action is required** within PMT assessment.
- ➔ If the half-life criterion ( $\leq 40$  days) for degradation was met in regard to **primary biodegradation only**, major transformation products have to be identified and quantified as far as possible according to OECD 309. While the **parent compound is regarded as not P** in water and not further assessed

for M and T properties, identified **major transformation products must be assessed for MT-properties instead**. Due to the lack of biodegradation observed in the simulation test (mineralisation half-life > 40 days), persistence may be assumed by default for major metabolites. Thus, PMT assessment is continued with the assessment for mobility (M).

- ➔ **Parent compounds with DegT<sub>50</sub> > 40 days for ultimate *aPMT nd* primary biodegradation are definitely regarded as P**. PMT assessment is continued with the assessment of mobility (M).

#### **PBT assessment under REACH (Persistence Tier 4a)**

There may be situations, where only non-guideline tests are available, with or without a negative test on ready biodegradability. Assessment of reliability and results of these tests often requires expert knowledge. Therefore, under these circumstances the result of the persistence assessment as part of the PBT assessment according to the REACH legislation and the specific technical guidelines is adopted, as far as available.

This however only under the prerequisites that within the PBT assessment

- more than just a negative test on ready biodegradability and / or non-hydrolysis has been taken into account
- and a clear conclusion on P is given.

In principle, for PBT assessment all relevant data should have been considered in a weight of evidence approach. Thus, ideally, a conclusion on P derived by an expert's assessment would already have been reached.

However, persistence assessment under REACH differs from the one elaborated for PMT assessment, in that also compartments other than water are taken into account (sediment, soil, atmosphere - as far as data being available), weighted according to (predicted) environmental distribution of a compound. Still, under the specified conditions data will mostly be of higher relevance than QSAR results, which will be used only as a last resort.

Thus, in case the P assessment performed as a part of the PBT assessment under REACH can be adopted,

- ➔ for compounds determined to be ***not P in water***, **no further action is required** within PMT assessment
- ➔ compounds **assessed to be P have to be further assessed for mobility**.

In case the P assessment performed as a part of the PBT assessment under REACH cannot be adopted (see conditions outlined above), QSAR assessment (persistence tier 4b) may be applied to decide upon persistence.

#### **QSAR assessment of P (Persistence Tier 4b)**

Compounds

- having been assessed as P from screening biodegradation tests on ready biodegradability *but lacking inherent tests or enhanced screening tests*,
- being without data on hydrolysis or having been assessed as P from test on hydrolysis but
- lacking higher tier data on biodegradation and

- for which no PBT assessment is available or the respective P assessment is inconclusive or of low relevance (e.g. only negative test on ready biodegradability and / or non-hydrolysis considered)

are further assessed for persistence using QSAR. The rationale is that failing a test on ready biodegradability does not mean in all circumstances that a compound is really persistent in the environment due to the stringency of those tests. However, compounds assessed in tests on *Inherent Biodegradability* or *Enhanced Biodegradation Screening Tests* which failed the respective pass levels are assumed to be *persistent* and tier 4b is not performed.

For the persistency screening by QSAR, BIOWIN-programs within the EPI Suite software package are used.

BIOWIN 1-7 are all based on molecular fragment constants that were developed using multiple linear or non-linear regression analyses, depending on the model. From 295 compounds 36 molecular fragments were derived which affect biodegradability. The 37th variable is molecular weight. BIOWIN 1 and 2 predict aerobic fast biodegradation (ready biodegradability), are based on the same data set and represent the linear and non-linear mode, respectively. A biodegradation probability assumed with BIOWIN 1 and 2 greater than 0.5 is considered as fast biodegradable, a biodegradation probability less than 0.5 is considered as not fast biodegradable. These results give however no information on the potential for complete, ultimate biodegradability in wider time frames. This is covered by BIOWIN 3 results. Based on a training set of 200 compounds, experts rated the time frame for complete ultimate biodegradation on a scale of 1 to 5: 5 - hours; 4 - days; 3 - weeks; 2 - months; 1 - longer. Based on these ratings, the program output is scaled, e.g. > 1.75 - 2.25 corresponding to "months", < 1.75 "recalcitrant". BIOWIN 5 and 6 also address ready biodegradability, the training set of compounds however is based on the MITI test on ready biodegradability (OECD 301C). 884 chemicals (385 readily biodegradable, 499 not readily biodegradable) were used to derive the fragment probability values used for the QSAR model. Biowin 5 is the linear, Biowin 6 the nonlinear model.

EPI Suite is freely available from US-EPA (<http://www.epa.gov/oppt/exposure/pubs/episuite.htm>) and may easily be installed on PCs with Windows® operating system. For BIOWIN calculations, a SMILES<sup>13</sup> code is needed which can be retrieved from the REACH registration dossier, [ChemIDplus](#) or using the OECD QSAR Toolbox<sup>14</sup>. To our knowledge, all compounds fulfilling the applicability domain of this PMT assessment scheme (see section 2.5.1) technically can be assessed using BIOWIN. However, according to REACH the applicability domain of the BIOWIN modules has to be checked in addition. Pursuant to the BIOWIN user information included with the program, no clear domain is applicable here. However, the user should check if the compound to be assessed is within the molecular weight range of the training set compounds and in addition, if functional groups of the compound are sufficiently represented by the 36 fragments of the model library (documentation included with the program). Further, for use within a regulatory context of REACH, a documentation of the model according to the OECD principles (OECD, 2004) is required (QSAR model reporting format) including a documentation of model application for the target compound (QSAR prediction reporting format).

BIOWIN 2, 3 and 6-results are assessed in combination according to ECHA-guidance on Information requirements and Chemical Safety Assessment, part R11 (ECHA, European Chemicals Agency, 2012c).

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<sup>13</sup> SMILES = Simplified Molecular Input Line Entry Specification

<sup>14</sup> <http://www.oecd.org/env/ehs/risk-assessment/theoecdqsartoolbox.htm>

According to this guidance, for combinations of BIOWIN 2 and 3 ( $< 0.5$  and  $< 2.2$ , respectively) or BIOWIN 6 and 3 ( $< 0.5$  and  $< 2.2$ , respectively) indicating persistence, compounds are judged as *persistent* according to REACH for screening purposes. This method has been already applied for prioritisation of low production volume substances under REACH regarding PBT criteria by the Environment Agency UK (Brooke and Burns, 2009) and for prioritisation of semipolar polycyclic aromatic compounds (Schwarz, et al., 2014). However, as the REACH guidance is slightly imprecise in giving the limit for BIOWIN 3-results as  $< 2.2$  (“months or longer”), the cut-off-value as given in the BIOWIN 3 documentation for two decimal places ( $\leq 2.25$ ) for the time range “months or longer” is taken.

**Thus, evaluating the numerical output of BIOWIN 2, 3, and 6,**

→ compounds with numerical output for

- BIOWIN 2  $< 0.5$  and
- BIOWIN 3  $\leq 2.25$

and / or

- BIOWIN 3  $\leq 2.25$  and
- BIOWIN 6  $< 0.5$

**are regarded as *persistent* within the concept and must further be assessed for mobility.**

→ compounds with numerical output above these thresholds are regarded as *not P* in water and **no further action is required** within PMT assessment.

#### 2.1.4 Summary and discussion on persistence

In this project we provide a methodology to identify *persistent*, *mobile* and *toxic* substances (PMT substances) in raw water, as occurrence of such substances should be avoided. The focus is on substances in the regulatory framework of REACH. Accordingly, the identification of substance-specific (PMT) properties should be linked to information as provided under REACH regulation and guidance.

We addressed:

- parameters determining persistence,
- existing testing guidelines on persistence-linked parameters of substances,
- data availability under REACH,
- qualification of persistence parameters as generated with REACH exposure assessment tools (EUSES/TRA),
- definition and handling of persistence in former related projects and scientific literature

We further discriminated persistence in surface and in groundwater and we provided demarcations for aspects of persistence not covered in this project.

With this background, we developed a methodology for persistence assessment as a tiered approach in section 2.1.3.

Persistence of a substance is defined according to half-lives in different environmental compartments, most often water, sediment and soil. Most relevant will be the compartment specific degradation rates for those compartments to which the respective chemical will preferentially distribute due to its physicochemical properties. It is evident that a substance may be regarded as persistent in one of the compartments and, at the

same time, may not fulfil the persistence criteria for another compartment. For freshwater cut-off criteria for persistence according to REACH Annex XIII are DegT50 >40 days (PBT substances) or > 60 days (vPvB substances).

Data necessary for estimating persistence of chemicals will often be available. Already for low tonnages (1-10 t/year), for organic compounds ready biodegradability tests (OECD 301 A-F and OECD 310) are mandatory. For higher tonnages additional tests are requested, depending on the outcome of the “ready-test” and solubility in water. These are the test on hydrolysis as a function of pH (OECD 111) and/or simulation tests on biodegradation in surface water, sediment and soil (OECD 309, 307 and 308, respectively). Further screening-type tests other than ready biodegradability tests may be available which can be used in persistency assessment according to REACH guidance part R.11 (PBT/vPvB assessment), such as “enhanced ready biodegradability tests” and “tests on inherent biodegradability (OECD 302B and C). Detailed guidance on interpretation and combination of tests is provided in the REACH-guidance document R.7B in combination with R.11.

Rather, we outlined that most important are degradation events in sewage treatment plants, followed by degradation in surface waters and soil. In this respect biodegradation and hydrolysis are crucial. With regard to biodegradation, if a chemical is *ultimately biodegraded*, it is *completely metabolized to CO<sub>2</sub> and water* (aerobic biodegradation).

Screening tests on ready (OECD 301 tests and OECD 310) and inherent (OECD 302 tests) biodegradability generally assess ultimate biodegradability in that either O<sub>2</sub>-consumption or CO<sub>2</sub>-production is compared to theoretical values deduced from structure (or chemical oxygen demand)<sup>15</sup>. Higher tier tests simulating e.g. biodegradation in surface water (OECD 309) or soil (OECD 307) may assess both, ultimate and primary biodegradation. Often these tests are restricted to primary biodegradation if radioactively labelled materials are not available and specific analytics for parent compounds are applied. *Primary biodegradation* – like hydrolysis – leads to *degradation products (transformation products)* which may or may not (rapidly) be biodegraded. Due to oxidation events playing a major role for degradation or the nature of hydrolysis, transformation products most often are more polar than the parent and may therefore be of higher mobility in water. However, while some information on transformation products will be available from hydrolysis tests or simulation tests, in effect identification is mostly restricted to very basic information and definite identification of compounds is lacking.

In case screening test results are used for exposure assessment under REACH, half-lives for surface water, soil and sediment are derived from so-called translation tables. It is demonstrated that the results of the translation tables do not fit well to test results and persistence assessments based on criteria given in REACH guidance document R.11 (ECHA, European Chemicals Agency, 2012c). Thus, persistence assessment in this work is based on REACH Annex XIII criteria where half-lives are determined directly from the tests. With regard to screening tests rather than using half-lives determined from translation tables we apply criteria given in REACH guidance document R.11 (ECHA, European Chemicals Agency, 2012c).

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<sup>15</sup> Note that OECD 301 A (DOC Die-Away) and 301 E (Modified OECD Screening) relate to dissolved organic carbon. These tests are inappropriate for highly adsorptive compounds and generally require an adsorption control incubation in parallel for adsorbing compounds.

Preceding projects on raw water relevance (IfW, 2010; 2011) postulated, that for industrial chemicals found in drinking water the relevant contamination pathway would be the one from sewage to surface waters, while other pathways and especially the sludge to field pathway could be disregarded. In spite of this, according to IfW-approach the highest weight is assigned to (anaerobic) degradation data with regard to media influencing groundwater (soil) or bank storage water (sediment) concentrations of chemicals. Further, anaerobic degradation events are important only for the lower sediment layers, the groundwater and anaerobic digestion of sewage sludge. The IfW-approach does not consider that most important degradation pathways for surface water concentrations are aerobic.

Depending on the  $\text{DegT}_{50}$  derived for a substance from degradation data, an index is derived in the IfW-approach. This index is directly added to the indexes connected to mobility, i.e. no separate assessment of persistence is performed. This approach has the draw back that an a priori exclusion of rapidly biodegradable substances is not possible. Rather, given a high mobility the mobility score may mask biodegradability.

Götz et al. (2010) addressed aquatic micro-contaminants for monitoring in Switzerland. In this regard degradation is assessed. Relying on screening data on biodegradability only, fortified by data on hydrolysis and – given that those data were not available – QSAR screening, a classification for persistence independent from mobility was performed allowing for targeted assessment of those compounds predicted to be highly or moderately persistent *and* predicted to partition into surface waters.

The persistence evaluation scheme as proposed in this project (section 2.1.3) is based on both, importance of test results (screening tests with information on ultimate biodegradability preferred over results on primary degradability) but also on common data availability under REACH. Within the tier P1-assessment, successively data from ready biodegradability tests in the narrow sense, enhanced ready biodegradability tests, and finally tests on inherent biodegradability are evaluated. Corresponding to REACH requirements, tier P2-assessment evaluates tests on hydrolysis as a function of pH. In case of inconclusive results in regard to persistence up to then and also in case of positive hydrolysis results (concern for transformation products) the tier P3-assessment utilizes data from simulation tests on degradation in surface waters to conclude on persistence. In the final step (tier P4), for compounds with only non-guideline tests on biodegradability (often difficult to evaluate) or compounds having these tests in addition to not more than a negative ready tests and / or negative test on hydrolysis, in tier P4a the persistence assessment performed within REACH PBT assessment is adopted, if qualified (taking into account these non-guideline tests) and conclusive. If it is not possible to resort on REACH PBT assessment and data are restricted to ready biodegradability tests (with pass levels failed) and / or negative data on hydrolysis, in tier P4b these compounds are additionally assessed by QSAR for persistence using BIOWIN modules according to REACH guidance R.11 (ECHA, European Chemicals Agency, 2012c). This is because of the stringency of tests on ready biodegradability, with a negative result not necessarily demonstrating persistence. Thus, if QSAR predicts degradability in contrast to the ready-test result, this prediction overwrites a negative test on ready biodegradability. The flowchart below (Figure 2) summarizes the decision process. However, some details and additional options are eliminated in the flowchart for reasons of clarity.

With regard to media, we restrict our assessment on sewage treatment plants as well as surface water (data from biodegradation screening tests, tests on hydrolysis as well as simulation tests on surface water indicative for degradation potential). While concentrations in the water phase are separately assessed in the sediment simulation test (OECD 308), it cannot easily be decided whether a decline in concentration is caused by degradation or rather adsorption to sediment particulate matter what causes the necessity of an expert judgement. Therefore, tests on degradation in sediments are not considered here. Bank storage water

is not considered on its own but - for simplification and as a worst case - regarded as a special form of surface water. Also, as potential for raw water contamination is the focus here with soil exposure being only secondary to sewage treatment plant degradation (by application of sewage sludge on fields) soil specific degradation is not assessed. Importance of transformation products is recognized and – whenever these may be a concern in certain tests, alerts are given during assessment of persistence – but, given limited information available under REACH no detailed guidance on treatment of transformation products can be given at this stage.

Finally, OECD-guidelines on biodegradation tests are generally accepted. However, all these tests do not foresee tests at different pH values. It cannot be excluded therefore, that at environmentally relevant pH values differing from the ones in the test guidelines biodegradation efficacy may be positively or negatively affected. The same holds true for temperature dependence of degradation events or differences in eutrophication status of natural waters.



## 2.2 Mobility assessment

### 2.2.1 Data availability under REACH

This chapter gives an overview on data requirements related to mobility for registrations under REACH, i.e. data that normally should be available for registered substances dependent on their tonnage level. Readers not familiar with properties determining mobility (i.e. especially adsorption) are encouraged first to read section 2.2.2, chapter *Background to adsorption and distribution*, and then to return to this chapter.

Data necessary for estimating mobility of chemicals which will be available under REACH depending on the tonnage level valid for the registration are summarized in Table 7.

The most essential data are generally present for all registered compounds, i.e. already at the lowest tonnage level (1-10 t/year). These are water solubility and vapour pressure, from which Henry's law constant can be calculated together with the partition coefficient n-octanol/water ( $K_{ow}$ ). These are the minimum physicochemical input parameters needed for exposure estimation under REACH using EUSES or TRA (see section 2.2.3, Exposure estimation with ECETOC TRA).

Table 7: Data requirements under REACH in regard to parameters determining mobility

1-10 t/year (Annex VII)	$\geq 10$ t/year, data additionally required (Annex VIII)	$\geq 100$ t/year, data additionally required (Annex IX)
Water solubility Needs not to be determined if - the substance easily hydrolyses ( $t_{1/2} < 12$ h) - the substance is prone to oxidation in water	Adsorption/desorption screening Needs not to be determined if - $\log K_{ow} < 3$ - the substance and its relevant degradation products decompose rapidly	Dissociation constant ( $pK_a$ )
Vapour pressure Needs not to be determined for - gases - solids (melting point $> 300^\circ\text{C}$ ) - unstable substances decomposing below boiling point	- estimation methods are appropriate Is essential for - substances ionisable at environmentally relevant pH range - surfactants	Further information on adsorption/desorption depending on the results of the study required in Annex VIII Needs not to be determined if - $\log K_{ow} < 3$ - the substance and its relevant degradation products decompose rapidly
n-octanol/water partition coefficient Needs not to be determined for - inorganic substances - unstable, surface active or reactive substances (calculated value required) - insoluble in water or octanol or not available in pure form (calculated value required)		

Water solubility and vapour pressure determine the partitioning between water and air ( $K_{air-water}$ , dimensionless Henry's law constant, see background section 2.2.2), while  $K_{ow}$  is an approximate measure for partitioning between water and organic material (especially lipids, only to a certain degree organic carbon of the solids compartment). In turn, from  $K_{ow}$  and  $K_{air-water}$   $K_{oct-air}$  can be calculated (see background section 2.2.2).

From  $K_{OW}$   $K_{OC}$  may be calculated from quantitative structure-property relationships (QSPR). By regression analysis a simple equation was derived, which is however only valid for neutral, hydrophobic (non-polar) substances for which sorption is governed only by unspecific dispersion interactions (Schüürmann, et al., 2007):

$$K_{OC} = 0.41 * K_{OW} \quad (5)$$

To include further determinants of adsorption especially involving polar groups, compound class specific regression equations based on  $\log K_{OW}$  were derived (for reference, see e.g EC, 2003; Lyman, et al., 1990). Meanwhile, calculation methods based on chemical structure alone yield often better results, especially for certain substance types (Meylan, et al., 1992; Schüürmann, et al., 2006; Schüürmann, et al., 2007). Both basic methods are implemented in freely available software packages: KOCWIN within US-EPA EPI suite 4.11<sup>16</sup> implementing as structure based method the one published by Meylan et al. (according to Meylan, et al., 1992) besides a  $\log K_{OW}$ -based approach using chemical class or fragment specific correction factors; and ChemProp software (available from Helmholtz Centre For Environmental Research<sup>17</sup>), implementing (besides other methods) as a structure based method the one published by Schüürmann et al. (2006).

For substances produced or imported at a tonnage level  $\geq 10$  t/a experimentally determined values for  $K_{OC}$  may be available.

OECD test guideline 121 (Estimation of  $K_{OC}$  using High Performance Liquid Chromatography) is a screening test method. It was developed for neutral compounds and according to REACH guidance on information requirements and chemical safety assessment, chapter R.7a may also be used for weak acids (negatively charged upon ionisation) and bases (positively charged upon ionisation) if buffer systems of appropriate pH range are used. A further requirement is that a pH must be used were at least 10% of the test compound must be ionised. Further, two tests must be performed in this case, one with the non-ionised and one with the ionised form of the substance using appropriate buffer solutions. However, the applicable pH range is very narrow (pH 5.5 to 7.5) and thus cannot span the environmentally relevant range (pH 5 to 9). Further, due to the column matrix being neutral, at least for soil with its – in most instances - surplus of negative charge  $K_{OC}$  will be overestimated for negatively charged compounds (repulsion in soil) and severely underestimated for positively charged substances (strong binding to negatively charged residues in soil). Therefore, regarding adsorption to soil, this method is actually not appropriate for determining  $K_{OC}$  for ionisable compounds.

Following OECD test guideline 106 (Adsorption-Desorption using a batch equilibrium method)  $K_{OC}$  may experimentally be determined for both, compounds acting as acids (negatively charged due to ionisation, i.e. proton release) and bases (proton binding from solution), zwitterionic compounds and of course for non-ionisable compounds. Using natural soils covering a wide range of soil properties (including pH) for determination of adsorption and desorption kinetics makes this the most reliable currently available standardized method for determination of  $K_{OC}$  for all compound types.

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<sup>16</sup> <http://www.epa.gov/oppt/exposure/pubs/episuite.htm>

<sup>17</sup> <http://www.ufz.de/index.php?en=6738>

## 2.2.2 Parameters determining mobility

### Background to adsorption and distribution

Mobility may be defined generically as “the tendency for a chemical to move in the environment” (US-EPA, 2012)<sup>18</sup>. Mobility of a substance is therefore associated with the potential for relocation from one environmental compartment to another. The degree of mobility inversely depends on the degree of “net adsorption” to particulate matter, where net adsorption takes into account both, adsorption and desorption processes over time. Mobility in the water cycle is quantified mainly by the “Soil Organic Carbon-Water Partitioning Coefficient” ( $K_{oc}$ ) of a chemical (which will be demonstrated below).

Leaving behind organisms, on the highest hierarchy environmental compartments are the water phase, air and solids, the latter summarizing particulates in the water column, sediment, sludge (sewage treatment plants) and soil. For non-polar organic substances, the organic material fraction of solids is most important for partitioning and thus partitioning between the three phases water, air and solids (organic material) may be approximated for this compound group by the following partitioning coefficients (Boethling, R. S., et al., 2004):

- partition coefficient air / water ( $K_{air-water}$ );  $K_{air-water}$  is the dimensionless Henry’s law constant.
- partition coefficient octanol / water ( $K_{ow}$ ), with octanol being a surrogate for the lipid phase of organisms (not considered here) and organic matter content of solids, and
- partition coefficient octanol / air ( $K_{oct-air}$ ), which is equal to the ratio of the former two

While this is of course an oversimplification, from these interdependencies it becomes clear that for example a non-polar organic compound with  $\log K_{ow} > 3$  will partition preferentially to (organic) solids. At the same time, the higher the associated dimensionless Henry’s law constant ( $K_{air-water}$ , measure for evaporation from water), the higher the evaporation from the fraction bound to organic solids (soil) will be (i.e. the lower  $K_{oct-air}$ , being equal to  $K_{ow}/K_{air-water}$ ). Thus, especially at higher temperatures, the compound may be mobilized from soil to the air compartment. Temperature dependence is due to the fact that Henry’s law constant is highly temperature dependent.

Thus, a highly mobile substance may be distributed within the air compartment as well as the aquatic compartment (surface waters, groundwaters), the ratio being dependent on  $K_{air-water}$ . Conversely, at equilibrium an immobile substance is predominantly bound to the solids fraction, where distribution is much more limited (e.g. distribution via sewage sludge to agricultural land or mobilisation of sediments by flood events).

Thus, mobility is easier to define via the opposite, the degree of immobility, i.e. adsorption / desorption behaviour of a substance.  $K_{ow}$  is a very approximate measure of distribution potential to solids (organic matter) and only valid for non-polar organic compounds. Experimentally and valid also for polar compounds, from the ratio of adsorption equilibrium (ads.equ.) concentrations of the compound fraction bound to solids (s;  $\mu\text{g/g}$ ) and the fraction in aqueous solution (aq;  $\mu\text{g/cm}^3$ ) the distribution coefficient  $K_d$  can be calculated:

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<sup>18</sup> [www.epa.gov/dfe/pubs/tools/ctsa/ch5/mod5-3.pdf](http://www.epa.gov/dfe/pubs/tools/ctsa/ch5/mod5-3.pdf)

$$K_d = C_s(\text{ads.equ.})/C_{\text{aq}}(\text{ads.equ.}) \text{ [L/kg]} \quad (1)$$

The distribution coefficient  $K_d$  generally is specific only for the medium used in the equilibrium experiment.  $K_d$  is a function of the molecular structure of the compound in solution, the solution as well as properties of the solids phase, e.g. ionic strength, pH, organic carbon content, type and content of clay minerals, the surface area of solid particles and their size (Boethling, R. S., et al., 2004).  $K_d$  covers sorption in general which is due to adsorption onto surfaces and absorption due to penetration into the volume of the sorbent (Schüürmann, et al., 2007). Mostly adsorption and absorption cannot be treated separately and generally the term adsorption also includes sorption phenomena based on absorption. Sorption (adsorption) is thus not solely an intrinsic property of the respective chemical but rather determined by the types of interactions between the chemical given and constituent parts of its surrounding solid and liquid (ionic strength, pH) phase.

From the soil liquid phase neutral organic compounds adsorb to soil particles via several weak intermolecular forces, depending (beyond others) on the particular functional groups and thus the degree of polarity: Most important are hydrogen bonds. Positively polarized hydrogen atoms of e.g. OH- and NH<sub>2</sub>-functional groups of organic molecules may interact with e.g. negatively polarized oxygen present on the surface of clay minerals or carbonyl groups of organic matter. Vice versa, OH- functional groups are present on the surface of clay minerals as well as organic matter of the soil (humic substances) enabling hydrogen bonding. Also stable charge-transfer complexes may be formed. Electron donors are easily ionisable compounds like aromatic hydrocarbons, compounds with free electron pairs (alcohols, amines, ethers), or polar molecules (e.g. alkyl halogenides), while acceptors are mostly neutral molecules having an appropriate LUMO (lowest unoccupied molecular orbital), e.g. aromatic hydrocarbons with NO<sub>2</sub> substituents (Haberer and Böttcher, 1996). The actual binding strength of neutral organic molecules is thus governed by multiple factors and may be approximated by  $K_{\text{OW}}$  alone only very roughly.

Alkaline organic compounds tend to bind protons and thus acquire a positive charge rendering them highly polar. The protonated fraction depends on the pH of the medium and the  $pK_a$ <sup>19</sup> of the ionisable compound: At  $pK_a = \text{pH}$ , 50% of the molecules will be in their ionized state, i.e. positively charged. Strong bases have high  $pK_a$ -values. The fraction of the neutral species for monovalent bases at a given pH can be estimated according to the Henderson-Hasselbach equation (Franco and Trapp, 2008):

$$\text{neutral fraction (bases)} = (1 + 10^{pK_a - \text{pH}})^{-1} \quad (2)$$

While the neutral fraction may be regarded as neutral organic molecule (for which  $K_{\text{oc}}$ -values may generally readily be estimated), distribution constants for dissociated fractions (i.e. the cationic molecules) are at present hardly predictable and experimental data are mandatory under REACH (see below). However, generally valid is, that positively charged compounds comprising also ionisable organic molecules generally sorb strongly. This is due to the fact that soil in general has a surplus of negative charge and acts as a cation exchanger.

Acidic organic compounds release protons in solution and thus acquire a negative charge, rendering them highly polar. Being repulsed by the predominantly negatively charged soil functional groups, anionic

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<sup>19</sup> The  $pK_a$  is a measure for the strength of an acid or a base. The lower it is, the stronger an acid, the higher it is, the stronger a base.  
 $pK_a = -\log\left(\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}\right) \text{ 1/mol}$

compounds sorb very poorly to soil. The higher the soil pH the higher the negative net charge of the solid phase and above approximately pH 8 generally no adsorption is observed at all (Haberer and Böttcher, 1996). The negatively charged fraction of organic acids depends on the pH of the medium and the  $pK_a$  of the ionisable compound: At  $pK_a = pH$ , 50% of the molecules will be in their ionized state, i.e. negatively charged. Strong acids have low  $pK_a$ -values. The fraction of the neutral species for monovalent acids can be estimated according to the Henderson-Hasselbach equation (Franco and Trapp, 2008):

$$\text{neutral fraction (acids)} = (1 + 10^{pH-pK_a})^{-1} \quad (3)$$

Due to the different types of solid matter (soil composition, sediments, sewage sludge), determined  $K_d$ -values can vary by up to three orders of magnitude (McCall, et al., 1981). For (neutral) organic chemicals  $K_d$  values measured in different soils generally turned out to vary proportionately to the fraction of organic carbon contained in the respective soils. Normalizing  $K_d$  values to organic carbon (OC) content leads to much less variation (20 to 50%) due to organic matter being the most important determinant for sorption of organic molecules (Gustafson, 1989; McCall, et al., 1981; Schüürmann, et al., 2007):

$$K_{OC} = K_d/f_{oc} = K_d * 100 / \%OC \quad (4)$$

$f_{oc}$  is the weight fraction of organic carbon. Often, soils have an OC content between 1.5%-2%, but there is considerable variability.

Thus a measure for adsorption is obtained which is largely independent on the soil type and which may also be used for estimation of sorption to sediment or sewage sludge. Exceptions to this are ionizing organic compounds. Their partitioning behaviour is not well correlated to organic carbon content of soil as besides binding to the organic carbon fraction adsorption is e.g. also determined by binding of positively charged compounds to negatively charged clay minerals (see above). Nonetheless, to have a comparable measure for adsorption it is reasonable also for these compounds to normalize to organic carbon and this is generally done (OECD, 2000). Gustafson (1989) proposes for these substances rather to determine an arithmetic mean  $K_d$  for relevant soils for which adsorption had been measured and to divide this by a typical mean organic carbon content for agricultural soils.

## Surface water

### *Conclusions from REACH and EUSES/TRA calculations, respectively*

As already indicated in the background section on adsorption and distribution (section 2.2.2), a substance will preferentially partition into surface water if

- adsorption to organic matter (particulates, sludge, sediment) is low (low  $K_{oc}$ , see above, or low  $K_{OW}$  as a surrogate value) and
- Henry's law constant is low and
- there is a minimum water solubility.

Water solubility is not the decisive criterion. Rather, the ratio between vapour pressure and water solubility (i.e. Henry's law constant) is. Due to  $K_{OW}$  being not independent from water solubility, decreasing water solubility implies for most neutral organic chemicals increasing  $K_{OW}$  (see e.g. Chiou, et al., 1977). Thus, water solubility is indirectly quantitatively incorporated while considering the two decisive criteria, Henry's law constant and  $K_{OW}$  (preferably  $K_{oc}$ ).

From Table 8 this relationship becomes obvious. The table was taken from Guidance on IR & CSA, Chapter R.16, Annex R.16-3 (ECHA, European Chemicals Agency, 2012e) and quantifies in a banding approach

partitioning of chemicals to the aquatic phase of sewage treatment plants under the assumption that biodegradation rate is zero. Thus, fractions not found in the water phase will partition into the other two compartments, namely sludge (with  $K_{OC}$  being the most important determining parameter) and air (with Henry's law constant being most important in this respect). Background for data presented in Table 8 is the EUSES/TRA model and associated assumptions for sewage treatment plants (for further details, see section 2.2.3, Exposure estimation with ECETOC TRA). Please notice that for actual calculations in EUSES/TRA calculations are performed using continuous values for the parameters and instead of  $K_{OW}$   $K_{OC}$  is used (calculated or experimental).

From the categorized data of Table 8, a significant effect of Henry's law constant becomes obvious only at values for  $\log H$  somewhere between 1 and 2 (10 and 100 Pa·m<sup>3</sup>/mol at 12°C, respectively) and above, driving a relevant fraction into the air compartment. On the other hand,  $\log K_{OW}$  leads to a significant reduction of the water phase fraction only at values somewhere between  $\log K_{OW}$  of 4 to 5 and higher.

**Table 8: Sewage treatment plants - partitioning of chemicals to the water phase depending on their Henry's law constant (at 12°C) and their  $\log K_{ow}$ . Biodegradation is assumed to be zero. Table taken from REACH guidance document R.16 and modified. Shaded area: predominantly partitioning to surface water**

		log H									
% to water		-4	-3	-2	-1	0	1	2	3	4	5
log Kow	0	100	100	100	100	98	85	36	9	5	5
	1	100	100	100	100	98	85	36	9	5	5
	2	99	99	99	99	97	84	36	9	5	5
	3	96	96	96	96	94	82	35	8	5	5
	4	79	79	79	79	77	68	30	8	5	4
	5	39	39	39	39	39	35	19	6	4	4
	6	15	15	15	15	15	14	11	6	4	4

While water solubility is not the decisive parameter driving partitioning of chemicals, it is nonetheless reasonable to introduce a lower cut-off limit, as there are substances of very low water solubility and at the same time low vapour pressure ( $H$  will be low) being even of low solubility in octanol (e.g. certain pigments). To exclude compounds like this from considerations regarding mobility in surface water, a cut-off value for water solubility, at or below which raw water mobility can safely be excluded for ground as well as surface waters, of  $\leq 150 \mu\text{g/L}$  is proposed (see chapter 2.2.3, section *Water solubility cut-off*, for rationale).

### ***Conclusions from other projects and literature evaluation***

In this section, approaches followed in preceding projects or published in the literature are summarized shortly and conclusions are drawn, if and to what degree these might be integrated into the current project.

#### ***Approach by IfW***

Preceding projects on raw water relevance (IfW, 2010; 2011) postulated, that for industrial chemicals found in drinking water the relevant contamination pathway would be the one from sewage to surface waters, while other pathways and especially the sludge to field pathway could be disregarded (IfW, 2011). While not any supporting proofs for this assumption are provided, the screening model focusses on the contamination pathway by effluents only.

The screening assessment considers the following substance specific properties:

- water solubility (7 classes)
- log  $K_{OW}$  (7 classes)
- DegT<sub>50</sub><sup>20</sup> in days (biodegradation, 7 classes).

The classification system is outlined in Table 9. The class number corresponds to the index points assigned for this property class. The total index is derived by simple summation over the allocated index points for all three property classes.

Table 9: Indexing system for raw water as being *pervious*<sup>21</sup> according to (IfW, 2011)

Index Property	1	2	3	4	5	6	7
S [mg/L]	$x < 1$	$1 < x < 10$	$10 < x < 100$	$100 < x < 1,000$	$1,000 < x < 10,000$	$10,000 < x < 100,000$	$100,000 < x$
log $K_{ow}$	$x > 5$	$5 > x > 4$	$4 > x > 3$	$3 > x > 2$	$2 > x > 1$	$1 > x > 0$	$0 > x$
DegT <sub>50</sub> [d]	$x < 10$	$10 < x < 40$	$40 < x < 60$	$60 < x < 120$	$120 < x < 180$	$180 < x < 400$	$400 < x$

This indexing scheme has the following draw-backs:

- Water solubility is given overly much weight, while this parameter actually has a low relevance for surface water distribution of chemicals (see sections above).
- log  $K_{OW}$  is used for screening and the index given for this property is simply added to the index for water solubility. As outlined above, log  $K_{OW}$  correlates inversely with water solubility for most non-charged organic chemicals (see also Figure 3). Adding indices is only valid for independent physicochemical properties. The addition of the index for water solubility and log  $K_{OW}$  thus results in an overly high total index while being of no or low discriminatory value regarding raw water contamination potential.
- $K_{OW}$  is a good estimate for the partition coefficient lipids-water for organisms and thus bioaccumulation potential. It correlates however only weakly with partitioning to the solids compartment. Even calculated values for  $K_{OC}$  are preferable over  $K_{OW}$  to characterize partitioning behaviour of substances.
- The Henry's law constant, being besides  $K_{OC}$  the most important property determining environmental distribution, is not considered at all.
- Biodegradation half-life is directly included into the index, while biodegradability could be used as a largely independent criterion to exclude rapidly biodegradable substances right away from the start. Particularly, as data on ready biodegradability are in principle available for all compounds registered under REACH (see section 2.1.2), while data on  $K_{OC}$  are not.

In conclusion, because of the outlined draw-backs of this approach we propose a profoundly different one to decide on raw water mobility (see especially section 2.2.3).

<sup>20</sup> In this source designated as DT<sub>50</sub>

<sup>21</sup> IfW called this "drinking water relevance" in their project.



Density Sediment,  $\rho_{\text{Sed}}$   
 Density Particles,  $\rho_{\text{p}}$

Thus at this stage, biodegradation is not assessed and only partitioning to the water phase is modelled. For ease and comparability, the three example substances of section 2.2.3 (Exposure estimation with ECETOC TRA), compounds 1, 10 and 13 are used in the following exemplary calculations. Substance 1 is of high water solubility, low Henry's law constant ( $1.47 \text{ Pa}\cdot\text{m}^3/\text{mol}$ ) and low  $\log K_{\text{OW}}$  (-0.24). Substances 10 and 13 have  $\log K_{\text{OW}}$  values above 4 (4.48 and 4.38), water solubilities in the 10 mg/L range and low ( $5.28 \text{ Pa}\cdot\text{m}^3/\text{mol}$ ) and high ( $767 \text{ Pa}\cdot\text{m}^3/\text{mol}$ ) Henry's law constants, respectively. For these examples, the following per cent values for  $\phi_{\text{water}}$  are resulting, which are compared with the approximate values derived from the banding approach of Table 8 above (simple read-out with the given values for  $\log K_{\text{OW}}$  and Henry's law constants):

- Substance 1:  $\phi_{\text{water}}$  89% (Götz et al.) versus 98%
- Substance 10:  $\phi_{\text{water}}$  50% (Götz et al.) versus 35% to 68% ( $\log K_{\text{OW}}$  4.48)
- Substance 13:  $\phi_{\text{water}}$  1.5% (Götz et al.) versus 6% to 8% ( $\log K_{\text{OW}}$  4.38)

In spite of the differences that

- $K_{\text{OC}}$  is used in the model according to Götz et al. (2010) instead of  $K_{\text{OW}}$  for the banding approach applied for Table 8 and
- that parameters used correspond to a Swiss lake rather than a sewage treatment plant,

while keeping in mind the inaccuracy associated with banding approaches in general, the overall agreement is very good as a very similar methodology is applied (see section 2.2.3, Exposure estimation with ECETOC TRA) for details on methodology used in EUSES/TRA sewage treatment plant modelling).

However, while the full EUSES/TRA (banding approach of Table 8 sewage treatment plant only) also considers the sludge to groundwater pathway (see section 2.2.3, Exposure estimation with ECETOC TRA), this is not the case in the model of Götz et al. (2010). Thus, while both assessments agree for substance 1 to partition in relevant amounts to surface water, according to EUSES/TRA the relevant water compartment for compounds 10 and 13 is groundwater. But again, both models agree with substance 13 to partition in significant amounts to air and thus compared to compound 10 raw water mobility of compound 13 would be assumed to be lower than that of compound 10 by both models.

Concluding from the approach of Götz et al. (2010) and the similar (but more sophisticated) approach followed for exposure assessments under REACH, fate models including the different environmentally relevant compartments are probably best suited to judge on the raw water mobility of chemicals.

## Groundwater

### *Conclusions from REACH and EUSES/TRA calculations, respectively*

The groundwater compartment is assessed in REACH not directly, however while performing detailed exposure estimations including the exposure assessment of "man via the environment" required only for classified substances of higher tonnage levels ( $\geq 100 \text{ t/a}$ ) or generally for substances produced or imported at  $\geq 1000 \text{ t/a}$  (for details see section 2.6.2). In this section, also a detailed description of input values, algorithms applied and results obtained can be found. Groundwater concentration is calculated within EUSES in the course of assessing the "drinking water pathway". This estimation is associated with the

following assumptions and observations, deduced from calculations performed within section 2.2.3 (Exposure estimation with ECETOC TRA):

- By far the most relevant exposure of soil is from sewage sludge applied on agricultural land. This holds true even for substances with high Henry's law constant and thus high  $K_{\text{air-water}}$  which are prone to partition into the air compartment and may deposit again on soil.
- Exposure of agricultural land by sewage sludge is integrated over a 10 years period in the model, such that very high concentrations may accumulate over time for substances with significant sludge adsorption (e.g.  $\log K_{\text{OC}} > 2.7$  as deduced from the classification scheme according to McCall et al. (1981), defining the "medium mobility class" as  $K_{\text{OC}}$  between 150 to 500, and above this upper boundary (corresponding to a log-value of 2.7) compounds are further classified to be of low mobility, slightly mobile or immobile).
- Due to increasing sludge adsorption with increasing  $K_{\text{OC}}$  and concomitant accumulation on fields over the 10 year period concentration of such height may accumulate that even with relatively high partition coefficients soil/water ( $K_{\text{sw}}$ ) resulting pore water concentrations may be much higher than calculated concentrations for surface water for the same compounds.
- As a simplification, calculated pore water concentrations are taken directly as groundwater concentration in EUSES/TRA. As a result, with increasing  $K_{\text{OC}}$  substances become more and more relevant for groundwater while surface water relevance is decreasing. However, as outlined in section 2.2.3, at approximately  $\log K_{\text{OC}}$  of 3.0 a maximum for groundwater concentration is reached and a further increase of  $\log K_{\text{OC}}$  leads to a decrease in estimated groundwater concentration.
- Water solubility was found to play a very minor role in the whole process apart from being one crucial parameter for Henry's law constant (together with vapour pressure) determining partitioning to air relevant especially for the eliminated fraction in sewage treatment plants.

Concluding from the parameters investigated and observations made in the examples elaborated in section 2.2.3 (Exposure estimation with ECETOC TRA), neither low water solubility nor high adsorption to soil may serve as the sole parameters to exclude mobility to groundwater.

### ***Conclusions from other projects and literature evaluation***

#### *Approach by IfW*

As outlined above, preceding projects on raw water relevance (IfW, 2010; 2011) postulated, that for industrial chemicals found in drinking water the relevant contamination pathway would be the one from sewage to surface waters, while other pathways and especially the sludge to field pathway could be disregarded (IfW, 2011). Therefore, groundwater specific pathways were not accounted for in these projects.

#### *Approach by Gustafson*

Gustafson (1989) investigated several physicochemical factors in addition to half-life in soil influencing leachability of pesticides to groundwater. Leachability of a pesticide is defined here as "...that when used in a normal agricultural manner under conditions conducive to movement, it moves down through the soil in quantities sufficient to be detected in nearby wells of proper construction. Areas with direct connection between the surface and saturated zones, e.g. agriculture drainage wells or sink holes, are excluded in this definition." The Starting point of this examination was a list of 44 pesticides compiled by California Department of Food and Agriculture (CDFA). This list is characterized by a consistent set of physicochemical properties and a consistent classification of these pesticides as

- known contaminants of groundwater (leachers)
- known non-contaminants (non-leachers)
- transition pesticides with conflicting evidence in regard to leachability to groundwater

excluding from this classification “point-source contamination events”. For 22 pesticides of the list values for both  $K_{OC}$  and  $t_{1/2}$  in soil had been collected by CDFA. In addition, for most of the total list of 44 pesticides values for water solubility were available. The  $t_{1/2}$  for soil [days] is defined by the author as the “average time it takes, in the field, for soil residues of the parent molecule to decline by 50%.” Gustafson plotted these 22 pesticides defined as leachers and non-leachers as dots according to their  $\log K_{OC}$  (abscissa, spanning a range between approximately  $\log K_{OC}$  of 1.2 to 5.3) and their  $\log t_{1/2}$  soil (ordinate, spanning a range between approximately  $\log t_{1/2}$  [d] of 0.6 to 4.6). Leachers occupied the left and upper portions of the figure, representing pesticides more mobile and more persistent in soil, as Gustafson points out. Due to the curved nature of the borderline between leachers and non-leachers a hyperbolic function was derived discriminating between both groups, called Groundwater Ubiquity Score (GUS):

$$GUS = \log_{10}(t_{1/2}^{soil}) \times (4 - \log_{10}(K_{oc})) \quad (6)$$

Based on a sensitivity analysis, a transition zone between leachers ( $GUS > 2.8$ ) and non-leachers ( $GUS < 1.8$ ) was defined, centred on actual separation point of  $GUS = 2.3$ . The author suggests the following interpretation:

Compounds within the leachers zone or transition zone would require further investigations proving their safeness in regard to groundwater, whereas compounds of the non-leachers zone could be excluded from further examinations. This GUS methodology proved to be superior compared to other screening schemes based on strict cut-off criteria which are not able to follow the curved nature of the borderline between leachers and non-leachers.

In a second step Gustafson examined if other physicochemical properties would improve separation between leachers and non-leachers. Water solubility could not separate leachers from non-leachers. In fact, leachers are found within a water solubility range of 0.3 mg/L and 269 g/L, non-leachers in a range of 0.002 mg/L and 6.2 g/L. Also  $\log K_{OW}$  proved to be not appropriate to discriminate between leachers and non-leachers. According to Gustafson, this is not surprising, as “the octanol/water partition coefficient, while an excellent model for sorption in biological membranes, is not chemically representative of the soil-water system, and no particularly strong correlation with leachability would be expected.” As a last physicochemical property, volatility as a function of Henry’s law constant,  $K_{OC}$  and molecular weight could be disproved to be of any use for separating leaching from non-leaching pesticides.

In the last part of the examination Gustafson successfully evaluated the GUS index based classification on monitoring data using results from well-water monitoring programs.

Using GUS formula (equation 6) with a score of 1.8 for non-leachers and a  $\log(t_{1/2}^{soil})$  of 5 (100,000 days i.e. 274 years, i.e. no biodegradation in soil), a  $\log K_{OC}$  of 3.64 results above which even for non-biodegradable compounds a potential for groundwater contamination could safely be excluded.

According to another model of the same author (cited in the described work) including dispersion and diffusion, plotting  $\log K_{OC}$  (abscissa) against  $\log t_{1/2}^{soil}$  results in curved lines, each line representing a certain per cent of chemical (between 2 and 100% ) leached below 1 metre. From this model, the curve for 2% leaching approximates asymptotically a very similar  $\log K_{OC}$  of about 3.65 with increasing persistence, corroborating the assumption from above that chemicals with  $\log K_{OC}$  above 3.64 could be regarded as safe for groundwater independent from their biodegradability.

### Retardation factor approach

Considerations according to Haberer and Böttcher (1996) implying retardation factors due to adsorption to soil result in similar conclusions:

Regarding soil as a chromatography column, adsorption on soil of a chemical will lead to its retardation compared to passive migration within the water current passing through the soil. The retardation factor can be calculated according to the following formula:

$$R = 1 + (\text{RHOSolid}/\text{Fair}_{\text{soil}}) * K_d,$$

where

- RHOSolid is the density of the solid phase in [ $\text{kg}_{\text{solid}} / \text{m}^3_{\text{solid}}$ ], per default 2500 (REACH guidance R. 16),
- Fair<sub>soil</sub> is the volume fraction air in soil in [ $\text{m}^3 \text{air} / \text{m}^3 \text{soil}$ ] (porosity), per default 0.2 (REACH guidance R. 16),
- and  $K_d$  the distribution coefficient for adsorption [ $\text{L}/\text{kg}$ ], which can be calculated from  $K_{OC}$  by multiplication with the fraction of organic carbon in soil (0.02 per default according to REACH guidance R.16)

Thus, using these default values, R can be calculated if a value for  $K_{OC}$  is available.

Migration of water through soil is dependent on both, the type of soil as well as the water potential. The water potential (German: *Wasserspannung*) is the negative pressure exerted by the opposing forces of gravity and capillary forces. At a water potential of 300 cm water column (= hPa), gravity and water potential (acting in opposite directions) are at equilibrium, i.e. percolation will be approximately zero. Water potential is close to zero when a soil is close to saturation and migration of water will be fastest under saturation conditions. At water saturation, which is not typical for agricultural soils, sandy soils have the highest hydraulic conductivity (approximately  $10^{-4}$  m/s). This declines however sharply with increasing water tension. Under environmentally relevant conditions, water potential is usually between  $10^2$  to  $10^4$  cm water column (=hPa), i.e. the soil is *not* saturated. According to Haberer and Böttcher (1996), silty soils have the highest hydraulic conductivity under these circumstances. Thus, taking a water potential of  $10^2$  cm water column and the soil type with the highest hydraulic conductivity (silty soil), this corresponds to a hydraulic conductivity between  $10^{-7}$  and  $10^{-8}$  m/s. Therefore, as a conservative approach hydraulic conductivity is assumed to be even higher by a factor of 10 (i.e. between  $10^{-6}$  and  $10^{-7}$  m/s). Thus, for the following calculations a *hydraulic conductivity of  $5 * 10^{-7}$  m/s is assumed.*

Results from a soil column experiment for the herbicide Terbutylazin (CAS: 5915-41-3) described in Haberer and Böttcher (1996) very well demonstrate the applicability of the estimation approach outlined above. In this case however, migration was assessed under *saturated* conditions with a flow rate of 4 mm/d (approximately  $3 * 10^{-6}$  m/s; and a column length of 26 cm). The concentration peak in the percolate was at day 105, quantification was possible starting from day 43. Thus, under these experimental conditions 165 to 400 days (peak of concentration) would be needed for 1 m of migration through the soil. In comparison, using the formulas and default values given above with an experimental log  $K_{OC}$  of 2.32 (available via KOCWIN of US-EPA's EPI Suite from the SRC-DB) and the experimental hydraulic conductivity of  $3 * 10^{-6}$  m/s (saturated conditions), a retardation factor R of 53.2 can be calculated which leads to a calculated migration of 1.78 m/a or 205.4 days needed to migrate 1 meter. This fits very well to the experimental value.

As pointed out above, according to the GUS formula (equation 6) by Gustafson (1989) for non-leachers (score of 1.8) and no biodegradation in soil ( $\log(t_{1/2}^{\text{soil}})$  of 5), a  $\log K_{OC}$  of 3.64 results such that chemicals with values above this could be regarded as safe for groundwater. Rounding this up to a value of  $\log K_{OC}$  of 3.7 and using this with the formulas and default values given above (hydraulic conductivity of  $5 \cdot 10^{-7}$  m/s), it can be approximated that the chemical will migrate 1.26 cm/a, i.e. approximately 80 years would be needed to move 1 m into the soil under the conservative assumption for hydraulic conductivity. The following exemplary calculations using input parameter as outlined above illustrate the effect of  $K_{OC}$  on the migration potential to groundwater:

- $\log K_{OC}$  3.3: R= 500; 32 years needed to move 1 m into the soil;
- $\log K_{OC}$  3.7: R= 1254; 80 years needed to move 1 m into the soil;
- $\log K_{OC}$  4.0: R= 2501; 159 years needed to move 1 m into the soil;
- $\log K_{OC}$  4.5: R= 7907; 501 years needed to move 1 m into the soil;
- $\log K_{OC}$  5.0: R= 25001; 1586 years needed to move 1 m into the soil;

### Other classifications of mobility based on $K_{OC}$

According to the California Department of Pesticide Regulation (DPR) Screening methodology ([http://www.pesticideinfo.org/Docs/ref\\_regulatoryCA.html#CAGroundWater](http://www.pesticideinfo.org/Docs/ref_regulatoryCA.html#CAGroundWater)) pesticide active ingredients are placed on the list of potential leachers if their  $K_{OC}$  is below 1900 L/kg, i.e.  $\log K_{OC} < 3.28$  and their aerobic soil half-life is above 610 days (one of several possible combinations of properties).

Classification of mobility was performed by McCall et al. (1981). Accordingly, compounds are classified as slightly mobile with  $K_{OC}$  between 2000 and 5000 ( $\log K_{OC}$  between 3.3 and 3.7) and immobile if their  $K_{OC}$  is above 5000 ( $\log K_{OC} \geq 3.7$ ).

### Conclusions

From other studies, a  $\log K_{OC}$  of 3.7 is derived at and above of which compounds may be safely regarded to have no relevant potential for contaminating groundwater, independently from their biodegradability. Note that an even higher cut-off is finally used when we define “mobility” within the PMT assessment (see section 2.2.3). With relation to the retardation factor approach, it depends if a duration of 80 years or still longer durations needed to move 1 meter into soil are regarded as safe. In any case, methodology used within EUSES/TRA for compounds with high adsorption potential is considered to be very conservative.

In addition, from data presented by Gustafson (1989) grouping leachers and non-leachers according to their water solubility, the lowest water solubility found for leachers was 300  $\mu\text{g/L}$  (for Naled). This indicates that *below* this value leaching into groundwater will not be probable (see chapter 2.2.3, section *Water solubility cut-off* for rationale for cut-off).

## Bank storage water

Bank storage water originates from surface water. It percolates through sediment and adjacent river banks where it is gathered for drinking water treatment. While dedicated models were developed for assessment of bank storage water (Scheytt, et al., 2011), for simplification and as a worst case, bank storage water may be regarded as a special form of surface water:

Also for bank storage water, most relevant are chemicals of low adsorption potential. This is, because sediment and adjacent river banks provide additional sorbent and chemicals concentration will decrease dependent on their respective partition coefficients (the higher their  $K_{oc}$ , the lower their concentration in bank storage water will be).

Thus, bank storage water will not be considered as source of raw water on its own, rather it will be taken as a special form of surface water, which may be regarded a reasonable worst case.

## Transformation products

Transformation products or metabolites may be formed by hydrolysis or primary biodegradation events. While mineralisation (formation of  $CO_2$ ), if complete, will lead to complete disappearance of the compound, disappearance of the parent by hydrolysis or primary biodegradation leads to transformation products, which most often are of higher polarity than the parent (ECHA, European Chemicals Agency, 2013) and thus may be expected often to be more mobile in the water phase. Most often however transformation products are not clearly identified and thus detailed assessment will not be possible in most cases.

### 2.2.3 Mobility assessment in this project

The objective here is to define parameter for mobility, which are

- inherent to the substance in question depending essentially on its physico-chemical properties and
- independent of environmental half-lives and
- independent of emission scenarios.

As pointed out in section 2.2.2 mobility with regard to raw water is a complex interplay of partitioning processes governed mainly by  $K_{OC}$  and volatility. If relevance for surface water decreases due to adsorption, relevance for groundwater via the sludge to soil pathway is expected to increase. Thus, it may not be possible to define simple cut-off criteria, at least not without more sophisticated considerations.

We follow therefore an approach to perform purely exemplary exposure estimations according to REACH guidance document R.16 using ECETOC TRA software to work out how the two parameters regarded as decisive,  $K_{OC}$  and volatility, will influence raw water concentration, and to check whether other parameters regarded as less important (water solubility,  $K_{OW}$ ) are indeed rated as being of less predictive power. In ECETOC TRA (the same is true for EUSES software) raw water concentration (called “drinking water” concentration within this tool) is defined as the maximum of annual average PEC surface water (reduced by a purification factor) and PEC groundwater. The following sections describe methodology and results of this approach aiming at defining cut-off criteria for mobility.

A first cut-off, however, is related to water solubility. A solubility benchmark should be provided, below which no further consideration of other physicochemical parameters is necessary.

### Water solubility cut-off

As pointed out in section 2.2.2, water solubility is no decisive criterion determining whether a substance is *pervious* in raw water. Nonetheless, it is plausible that a minimum water solubility is required below which a certain compound may be regarded of no (or low) concern because of negligible environmental exposure.

There exist no universally valid and applicable definition for categories of water solubility and no cut-offs without ambiguity.

Certain organic pigments may for example fall into the class of low concern, being highly insoluble in water and often at the same time of very low solubility in octanol. Given a density higher than water, they would be expected to partition by gravity to the solid phase and to reside there essentially unaltered.

To exclude these and similar compound groups, a water solubility cut-off of

150 µg/L

is introduced, at or below which a substance is not regarded to be *pervious* to ground - or surface water. This criterion therefor can be included into an early tier of mobility assessment (tier M1).

From data presented by Gustafson (1989) grouping leachers and non-leachers into groundwater according to their water solubility (see section 2.2.2, Groundwater), the lowest water solubility found for leachers was 300 µg/L (for Naled). This indicates that below this value leaching into groundwater will not be probable.

To support this, we selected all model compounds used for the ECETOC TRA calculations below (see section 2.2.3) with a water solubility of 300 µg/L or less (13 out of 65 compounds). All but 2 had log  $K_{OC}$  values higher than the cut-off for mobility of 4.5 (as defined later on in this chapter, see section *Determination of cut-off values for K<sub>OC</sub> to conclude on mobility*). The remaining 2 compounds had – while below the cut-off - also high values for log  $K_{OC}$  (3.85 and 4.34), still indicating very low mobility (see section 2.2.2, Groundwater). Moreover, according to TRA model, for all these compounds with water solubilities of  $\leq 300$  µg/L the groundwater pathway is the more relevant compared to surface water. From this it may be concluded that the solubility value derived from Gustafson (1989) for groundwater may be sufficiently protective also for surface water.

Due to the fact that one pesticide with a water solubility of 300 µg/L (Naled) was actually detected in groundwater, we applied a factor of 2 on this value, in order to maintain some margin of safety. Thus we decided on a cut-off value of 150 µg/L at or below which raw water mobility can safely be excluded for ground as well as surface waters. The size of this value is thus in between the definition of “poorly soluble in water” ( $< 1$  mg/L) of e.g. EC (2003) or ECHA (2012a) and the specification of “very low water solubility” (“in the low µg/L range”, not further specified, of ECHA (2012a)).

### Modelling approach for confirming $K_{OC}$ as decisive parameter for mobility

$K_{OC}$  was concluded to be the decisive parameter for mobility based on an evaluation of scientific literature in section 2.2.2. Current exposure estimation under REACH implicitly takes into account mobility to model environmental partitioning. In order to confirm importance of  $K_{OC}$  for the mobility aspect implicitly assessed within environmental exposure modelling under REACH, a modelling approach using an accepted software tool under REACH, namely ECETOC TRA (version: 3.0), was used.

In order to make it clear as to why we followed such an approach, and as to how it was actually performed, and finally as to how one should interpret its results, we first of all have to give an introduction into the basic

model assumptions implemented in environmental exposure modules of ECETOC TRA most relevant to raw water.

### ***Exposure estimation with ECETOC TRA***

Basic aspects of environmental exposure estimation as implemented in EUSES and ECETOC TRA (targeted risk assessment) software used under REACH are described in the Guidance IR & CSA, Chapter R.16 (ECHA, European Chemicals Agency, 2012e), which largely builds on the older Technical Guidance Document (EC, 2003). Both software tools (based on the same models and algorithms) also calculate a concentration of the chemical in drinking water (subsequently used for risk characterisation). However, some specific aspects are not fully explained in these documents. This is especially true for the algorithm deriving the concentration of a substance in drinking water, which is only described in detail in the respective EUSES background report (RIVM, 2004).

The procedure of environmental exposure estimation can broadly be divided in the following steps (ECHA, European Chemicals Agency, 2012e):

- Step 1: release estimation
- Step 2: partitioning and degradation
- Step 3: exposure and intake estimation

Each of these steps is dependent on input parameters and specific algorithms applied. The following section tries to identify key parameters for the three steps and will run an example along with the more theoretical description to illustrate calculations and impacts of the parameters. The example relates to the manufacture of chemical and only the data most relevant to follow the “drinking water pathway” will be discussed. Only the local assessment is followed here and no uses are included (i.e. the regional compartment is only “filled” from the manufacture assessed).

#### **Step 1: release estimation**

The key input parameters for the release estimation, together with data availability and the specific data for the example, are shown in the following table (Table 10):

Table 10: Key input parameters and data availability for step 1: release estimation

Parameter		Available from	Example
Tonnage (t/a)	T	Registrant's data	100,000
Fraction of EU tonnage to region	F	Defaults (EUSES, TRA)	1 (default)
Emission days	ED	ECHA (2012e), spERC, A/B tables	300
Fraction main local source	F <sub>main</sub>		1 (default)
Amount used locally (kg/d)	Q	Calculated: $T \times 1000 \times F \times F_{\text{main}} / ED$	333,333
Release factor	RF	ERC (ECHA, European Chemicals Agency, 2012e), spERC, A/B tables (EC, 2003), OECD-ESD (see e.g. OECD, 2009; OECD, 2011)	0.06 (ERC1)
Release rate (kg/d)	RR	Calculated: $Q \times RF$	20,000

\* This is also taken as the rate of STP influent rate

Many of these input parameters are interdependent. For example, the number of release days depends on the tonnage and the value of 300 d applies to tonnages > 10,000 t/a for manufacture. If, for example, the tonnage manufactured is only 5,000 t/a, the number of release days is 100. ECHA (2012e) states that – by default – it is assumed that the total tonnage manufactured and used industrially is processed by a single site and this represents the worst case approach included in an ERC-based assessment for industrial uses. However, both the spERC-based approach and the A/B tables (EC, 2003) apply fractions main local source depending on the tonnage. If, for example, more than 25,000 t/a of a basic chemical are manufactured, this is not considered to take place at a single site.

In addition, the specific values for the release factor are independent of any other input parameter in the ERC-based approach. In contrast, the spERC-based approach, the A/B tables (EC, 2003) as well as the OECD Emission Scenario Documents (ESDs) apply release factors differentiated by the physico-chemical properties of the substance to be assessed. For example, the release factor for emissions to waste water depends on the water solubility of the substance, while the release factor for emissions to air depends on the vapour pressure of the substance. Some of these other approaches also differentiate by technological processes (e.g. “wet” vs. “dry”) and the type of technological function of the substance under evaluation. For example, the release factors for plasticisers during polymer processing are differentiated by the physico-chemical properties and by type of processing, such as calendaring, extrusion, injection moulding and spread coating (OECD, 2009). The A/B tables also apply release factors differentiated by the tonnage in some cases; the rationale being that companies manufacturing/using large amounts of a substance will have technologically advanced processes with less release.

All these factors can have a large impact on the release rate (in kg/d) and all subsequent calculations. In the example above, for example, the release factor for waste water according to the A/B tables would be 0.003 rather than 0.06 (factor 20) due to the large tonnage produced according to the A/B tables. If the substance manufactured is a poorly soluble solvent (water solubility: 1-10 mg/L), the release factor in the corresponding spERC would be 0.00003 (difference: factor 2,000).

The release rate is divided by the STP discharge rate, resulting in the concentration of the chemical in the stream entering the STP. Within the STP, the substance will be degraded and will partition between different environmental compartments. These processes largely depend on the physico-chemical properties of the substance under evaluation and its liability to biodegradation, processes covered in the next step.

## **Step 2: partitioning and degradation**

The key input parameters for this step, together with data availability and the specific data for the example, are shown in the following table (Table 11). Note that only those parameters that are critical in the pathways relevant here are described.

The calculations shown refer to two pathways, which are compared in the final exposure estimation.

Table 11: Key input parameters, parameters calculated and data availability for step 2: partitioning and degradation

Parameter		Available from	Example
STP influent concentration (mg/L)	INF	Calculated: RR/DR (see Table 10 for RR and below for DR)	10,000
Molecular weight (g/mol)	MW	Available from structure	58.08
Water solubility (mg/L)	WS	IUCLID (REACH Annex VII)	1,000,000
Vapour pressure (Pa)	VP	IUCLID (REACH Annex VII)	53,000
Log $K_{ow}$	$K_{ow}$	IUCLID (REACH Annex VII)	-0,24
$K_{oc}$ (L/kg)	$K_{oc}$	IUCLID (REACH Annex VIII) If not available, derived by QSAR from log $K_{ow}$ in EUSES/TRA	1.5
Biodegradation test result	DEG	IUCLID (REACH Annex VII)	Readily biodegradable
Henry constant (Pa x $m^3/mol$ )**	HC	Calculated: $VP \times MW / WS$	3,08(1.47)
Surface water pathway			
STP discharge rate ( $m^3/d$ )*	DR	Default (EUSES, TRA)	2000
Fraction released to STP effluent	$F_{eff}$	Calculated in software(EUSES/TRA); can also be approximated from Appendix R.16-3 in ECHA (2012e) with log HC, log $K_{ow}$ and biodegradability test result	0.1245
STP Effluent concentration (mg/L)	EFF	Calculated: $INF \times F_{eff}$	1,245
Dilution factor	DF	Default in R.16, EUSES and TRA for rivers	10
Concentration in local surface water, annual average, dissolved (mg/L)	$C_{sw}$	Calculated: $EFF / DF * ED / 365$ ED from Table 10	102
Purification factor, maximum	$F_{pur}$	Calculated in software(EUSES/TRA); can also be calculated from HC, log $K_{ow}$ and biodegradability test result (i.e. half-life) according to EUSES background report (RIVM, 2004)	1
Concentration in local surface water abstracted for drinking water (mg/L)	$C_{swdw}$	Calculated: $C_{sw} \times F_{pur}$	102
Sludge-groundwater pathway			
Fraction released to sludge	$F_{slge}$	Calculated in software(EUSES/TRA); can also be approximated from Appendix R.16-3 in ECHA (2012e) with log HC, log $K_{ow}$ and biodegradability test result	0.000142

Parameter		Available from	Example
Sludge production rate (kg/d)	$R_{slge}$	Default in R.16, EUSES and TRA	710
Concentration (initial) in dry sludge (mg/kg) ***	$C_{slge}$	Calculated: $RR \times F_{slge} * 1,000,000 / R_{slge}$ RR taken from Table 10	4,000
PEClocal soil (mg/kg) ***	$PEC_{ls}$	Software output (EUSES/TRA)	0.874
Soil-water partitioning coefficient ( $m^3/m^3$ )	$K_{sw}$	Software output (EUSES/TRA)	0.245
Bulk density of soil ( $kg/m^3$ )	RHO	Default in R.16, EUSES and TRA	1,700
PEClocalsoil porewater (mg/L) ***	$PEC_{pw}$	Calculated: $(PEC_{ls} * RHO) / (K_{sw} * 1000)$	6.06
Concentration in local groundwater (mg/L)	$C_{gw}$	Calculated: = $PEC_{pw}$	6.06

\* This is also taken as the rate of STP influent rate.

\*\* The value in parenthesis is the one used in the software, which calculates the Henry constant from vapour pressure and water solubility at environmental temperatures (21,100 Pa and 832000 mg/L, respectively).

\*\*\* The final estimation of the concentration in soil is quite complex, since it also involves deposition from the atmosphere and considers accumulation from sludge application over time. In addition, removal from soil by processes such as volatilisation and biodegradation are accounted for. These processes, however, are by and large driven by the parameters provided in the table above (namely the biodegradation test result and Henry constant).

The values given for soil refer to agricultural soil, which is taken as the basis for the calculation of the concentration in groundwater.

It is quite obvious that the first pathway, in which drinking water is simply abstracted from surface water, is mathematically easy to follow. Only two values must be taken from the software employed:

- the fraction released to STP effluent ( $F_{eff}$ ) and
- the maximum purification factors ( $F_{pur}$ ), i.e. the maximum of the two values derived for a) open reservoirs and b) dune recharge from surface water.

These values, however, can be easily looked up in the Guidance IR & CSA, Chapter R.16 ( $F_{eff}$ ) or the EUSES background report (RIVM, 2004) for  $F_{pur}$ . In both cases, the underlying input are Henry constant,  $\log K_{ow}$  and the biodegradation test result.

The second pathway, in which the concentration of the substance in groundwater is estimated from the concentration in soil is much more complex and involves several different partitioning and degradation processes. Several partitioning coefficients are calculated in the software (EUSES or TRA) and many of the parameters given in Table 11 enter these calculations at many different levels. For example, a change in the water solubility affects the Henry constant, which alters the fractions released to the different compartments (relevant to both pathways). However, in the sludge-groundwater pathway the Henry constant also has an

impact e.g. on the volatilisation from soil and thus determines the concentration in soil that serves as the basis to estimate the concentration in groundwater.

As a consequence, the impact of individual parameters is not easily assessed but rather requires a full assessment using available software models, with EUSES and ECTOC TRA being generally used in the context of REACH.

It is also critically important to use valid data for the input. For example, calculation of the Henry constant from the water solubility and the vapour pressure may result in unreliable values for substance miscible in water (as the one taken here as an example) and this parameter should be measured experimentally using an appropriate method (ECHA, European Chemicals Agency, 2012e; 2013). Similarly,  $\log K_{OW}$  is difficult to determine for a variety of substances, such as poorly soluble, volatile, surface active or ionisable compounds (ECHA, European Chemicals Agency, 2013). For example, very high  $\log K_{OW}$  values are regularly estimated for substances that are poorly soluble in water. As a consequence, a high adsorption to solids is predicted which has a large impact on partitioning in the environment. In some cases, these substances are also poorly soluble in octanol, resulting in much lower  $\log K_{OW}$  values and ultimately a lower adsorption to solids.

While the various interactions and pathways in the software models are complex, the initial behaviour in the STP in dependence of the physico-chemical properties as well as the biodegradation test result can be visualised quite easily. Using the simplified percentages given in the Guidance IR & CSA, Chapter R.16, Annex R.16-3 (ECHA, European Chemicals Agency, 2012e), the emissions from the STP to the relevant environmental compartments as well as the fraction degraded (depending on the biodegradation test result), can be presented.

The following figures (Figure 4) shows the relative emissions directed to the various compartments plotted against the  $\log K_{OW}$  for two different values of the Henry's law constant:  $1 \text{ Pa} \times \text{m}^3/\text{mol}$  (solid symbols) and  $100 \text{ Pa} \times \text{m}^3/\text{mol}$  (open symbols), respectively. The figures show the two extremes in terms of biodegradation, with the top figure displaying the values for readily biodegradable substances and the bottom figure showing the respective curves for substances that are not biodegradable (substances that are e.g. inherently biodegradable are in between these extremes). These figures show the following:

- The sludge-groundwater pathway is practically not affected by input parameters other than  $K_{OC}$  (derived from  $\log K_{OW}$  within the software, which is shown in the figure's x-axis). It becomes more important with increasing  $\log K_{OW}$  values (i.e. increasing  $K_{OC}$ ) and is primarily relevant (relative emission of 20% or more) at  $\log K_{OW}$  values  $> 4$ . With increasing emissions to sludge, the relative emissions to all other compartments, including air, decrease. This is an important finding since the concentration of the substance in soil (from which the one in groundwater is derived) is determined both by sludge application and deposition from air. The sludge-groundwater pathway – with respect to relative emissions from the STP – is only somewhat affected by biodegradation (upper vs. lower chart). For example, the relative emission to sludge at  $\log K_{OW} = 5$  is 60% for a substance that is not biodegradable and 45% for a readily biodegradable substance. While biodegradation thus results in a somewhat lower emission to sludge, the relative fraction of 45% is still substantial.

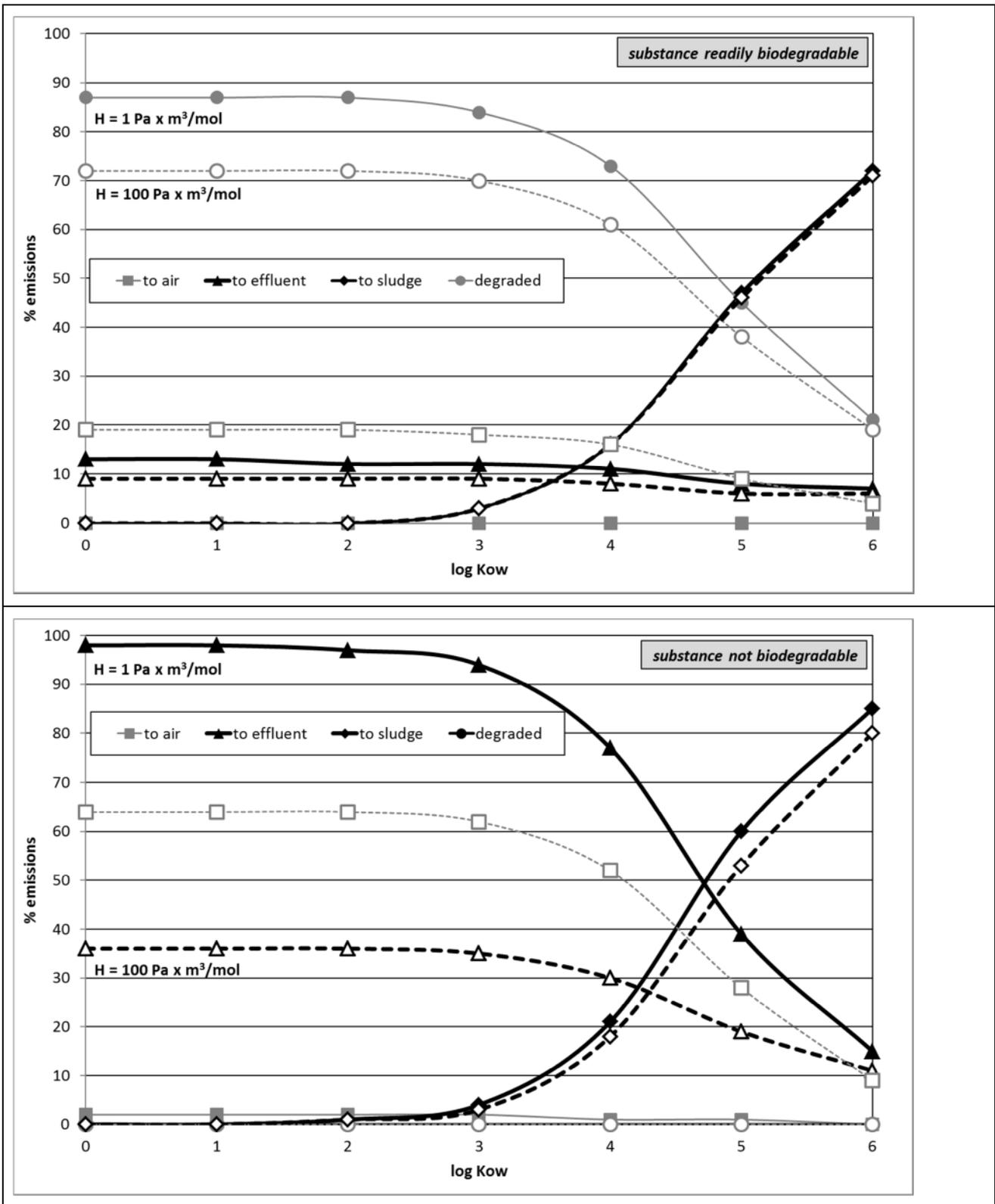


Figure 4: Relative emissions from the STP directed to the various compartments depending on the physico-chemical properties: readily biodegradable (top) and not biodegradable (bottom) substances. Two different values of the Henry's law constant are presented:  $1 \text{ Pa} \times \text{m}^3/\text{mol}$  (solid symbols) and  $100 \text{ Pa} \times \text{m}^3/\text{mol}$  (open symbols)

- The STP effluent-surface water pathway, in contrast, is much more dependent on biodegradation, but also shows a stronger impact of the Henry's law constant (i.e. the water solubility and vapour pressure from which the Henry's law constant is calculated). If the substance is readily biodegradable, biodegradation and – at higher log  $K_{OW}$  values – adsorption to sludge are the most important pathways. Emissions to air and to the effluent are always below 20%, no matter what the log  $K_{OW}$  value is. It is also interesting to note that the relative emissions to effluent are about 3-4 times higher than those to sludge up to log  $K_{OW}$  values of about 3.

If the substance is not degraded, however, more than 95% are emitted to the effluent and/or air at log  $K_{OW}$  values  $\leq 3$ , with the relative share of each compartment being defined by the Henry's law constant (up to 95% of all emission are to air at log  $K_{OW} < 3$  and Henry's law constant  $\geq 10,000 \text{ Pa} \times \text{m}^3/\text{mol}$ ; not shown in Figure 4). For substances with higher log  $K_{OW}$  values, adsorption (i.e. emissions to sludge) gains in importance and the relative contribution of emissions to air and effluent decreases. For these substances (e.g. log  $K_{OW} = 5$ ), there is a slightly lower emission to sludge at higher Henry's law constants, because emissions to air are still substantial.

It is important to realise that these figures only relate to emissions from the STP. Modelling the concentration in soil, which is relevant for the groundwater pathway, involves several partitioning and degradation events and is not only dependent on the amount emitted to sludge, but also on deposition from air. As indicated above, the overall calculation of the concentration in drinking water is therefore complex.

### Step 3: exposure and intake estimation

The key input parameters for this step were derived in step 2. The final exposure estimation in step 3 simply involves taking the maximum value from the two values calculated above, i.e. the concentration resulting from surface water abstraction and the concentration in groundwater.

Table 12: Key input parameters, parameters calculated and data availability for step 3: exposure estimation

Parameter		Available from	Example
Concentration in local surface water abstracted for drinking water (mg/L)	$C_{swdw}$	From Table 11	102
Concentration in local groundwater	$C_{gw}$	From Table 11	6.06
Concentration in drinking water (mg/L)	$C_{dw}$	Calculated: maximum of $C_{swdw}$ and $C_{gw}$	102
Drinking water consumption (L/d)	DWC	Default in R.16, EUSES and TRA	2
Body weight (kg)	BW	Default in EUSES and TRA	70
Daily intake via drinking water (mg/kg bw/d)	DOSE	Calculated: $C_{dw} * \text{DWC} / \text{BW}$	2.91

These calculations (see Table 12) show that there is no additional critical input for calculating the concentration in drinking water needed. For dose calculation, both TRA and EUSES apply a body weight of 70 kg. This appears to be somewhat in contradiction to consumer exposure estimation, where the body

weight of females (taken as 60 kg) is typically applied, e.g. in the ECETOC TRA consumer tool as well as according to Guidance IR & CSA, Chapter R. 15 (ECHA, European Chemicals Agency, 2012d).

In summary, it is clear that the parameters influencing the release estimation as well as partitioning and degradation are of critical importance. While the release estimation can be followed easily in terms of the mathematics underlying it, the partitioning and degradation modules are more complex and a full assessment is required to evaluate the impact of individual parameters.

### **Delineating parameter impacts**

As indicated above, both step 1 and step 3 involve relatively simple calculations that can easily be performed manually. In contrast, more complex calculations are performed in step 2. It is worth mentioning that the basic input data for these calculations (molecular weight, vapour pressure, water solubility, log  $K_{OW}$  and biodegradation test result) are available for all substances that need to be registered (i.e. >1 t/a according to REACH Annex VII).  $K_{OC}$  is the only parameter that needs to be determined at tonnages > 10 t/a (REACH Annex VIII), but this parameter can be calculated from log  $K_{OW}$  with QSAR models within EUSES and ECETOC TRA, if no experimental value is available. The respective QSAR models are differentiated by chemical class and usually yield sufficiently reliable values (although exceptions exist).

In order to analyse the impact of different parameters in more detail, three substances with different physico-chemical properties and different biodegradation test results were assessed using ECETOC TRA (v.3, 2012). The exposure scenario was the same as the one described in step 1 above (manufacturing, ERC1, 100,000 t/a). Therefore, the concentration of the substance in the STP influent is the same and the differences observed are solely due to the differences in degradation and partitioning within and after the STP.

The underlying assumptions for the release estimate are Tier 1 with default values, leading to extremely high releases to waste water of 20 tons per day, equalling 10,000 mg/L in the STP influent (see step 1 above). As a consequence, the values shown below should not be interpreted in absolute terms, but only in relative terms between the three substances.

“**Substance 1**” is miscible in water (WS set to 1,000 g/L) with a high vapour pressure. Despite the high vapour pressure, the Henry’s law constant is low due to the extreme water solubility. The substance is readily biodegradable and does not adsorb to solids. This is the substance shown in steps 1-3 above.

“**Substance 10**”, in contrast, only shows a comparatively low water solubility of 6 mg/L and a low vapour pressure. The Henry’s law constant is 4-times higher than for “substance 1” (primarily due to the low water solubility), but is still comparatively low. More important, however, is the high log  $K_{ow}$ , the strong tendency to adsorb to solids and the lower degree of biodegradation. This substance is mentioned in the context of polar persistent pollutants (see e.g. Loos, et al., 2010).

“**Substance 13**” also has a high tendency to adsorb to solids (based on the high  $K_{oc}$ ) and is biodegradable, but failing the 10-day window. The main difference, however, is its high Henry’s law constant, indicating high volatility.

All input data were retrieved from publicly available sources. While they have been checked for consistency, an in-depth evaluation of the input data was not within the scope of this analysis. It is also not required, since the primary focus is on demonstrating the impacts of the different parameters and not so much the actual values.

Table 13: Summary of the input and results for two exemplary substances

Parameter	Substance no.		
	1	10	13
MW	58.08	220.34	134.11
VP [Pa]	53,000	0.3	141
WS [mg/L]	1,000,000	6.0	11.8
log K <sub>ow</sub>	-0.24	4.48	4.38
Biodegradation test result*	R	I	R-f
K <sub>oc</sub> [L/kg] - data-based	1.50	5,360	2,500
Henry's law constant [Pa x m <sup>3</sup> / mol] - calculated**	1.47	5.28	767
PEC local groundwater [mg/L]	6.00	791	49
PEC local surface water, AA, dissolved [mg/L]	102	302	55
F <sub>pur</sub>	1.0	0.5	0.25
Modified PEC local surface water, AA, dissolved [mg/L]	102	151	14
PEC local drinking water [mg/L]	102	791	49
<b>Background: interim results for releases from STP</b>			
Percentage released to air	0.57%	3.6%	60%
Percentage released to sludge	0.0142%	35%	17%
Percentage degraded	87%	25%	16%
Percentage removal	87.5%	63%	93%
Percentage released to effluent (F <sub>eff</sub> -> step 2 above)	12.5%	37%	7%

Note: For substance 10 and 13, calculated PECs are above the water solubility. Again, this is due to the extremely high release assumed and further shows that these values should not be interpreted in absolute terms.

\* Substance 1: readily biodegradable; substance 10: inherently biodegradable, fulfilling criteria; substance 13: readily biodegradable, failing 10-d window.

\*\* This is the actual value used in ECETOC TRA, which is about 50% of the value calculated from VP and WS at room temperature, since the Henry's law constant is estimated in the software for environmental temperature (12 °C).

The comparison of the three substances (see table above) reveals several interesting aspects:

- While “substance 10” is much less soluble in water, the modelled concentration both in groundwater and surface water is higher than the one for “substance 1”. This finding is due to the fact that “substance 1” is readily biodegradable, resulting – with the physic-chemical properties of the substance – in a removal in the STP of 87.5%, which is almost completely due to biodegradation. The removal of “substance 10” is lower (63%), resulting in a higher concentration in the STP effluent and, as a direct consequence, to a higher concentration in the surface water prior to the application of the purification factor (F<sub>pur</sub>). This relationship is directly proportional, with the difference in PEC local surface water (302 mg/L / 102 mg/L = 2.96) being identical to the one for the STP release to effluent (37% / 12.5% = 2.96). “Substance

13” shows an even higher removal (93%) in the STP, which, however, is primarily due to its high volatility, resulting in 60% of the emissions being directed to air. As a consequence, relative emissions to the STP effluent are lower than for “substance 1” (7% vs. 12.5%) and, again, this directly translates into lower concentrations in the surface water.

- A comparison of the three substances reveals the impact of  $K_{OW}$  and the volatility (Henry’s law constant) on the purification factor. “Substance 1” is miscible in water and therefore shows a low volatility from water despite its high vapour pressure. It also has a low  $K_{OW}$  and therefore does not adsorb to particles in the aqueous phase. This substance thus remains in the water and the purification factor is 1, i.e. no reduction in the surface water concentration. The other two substances are expected to adsorb to solids (which are assumed to be removed during abstraction of surface water for drinking water) and therefore the purification factor is 0.5. “Substance 13”, in addition, shows a high volatility with an additional factor of 0.5, resulting in an overall purification factor of 0.25. In the case of “substance 13”, the initial PEC surface water was higher than the PEC groundwater (55 vs. 49 mg/L). However, both the adsorption to particles and the volatilisation from the water lead to a reduction of the surface water concentration relevant for drinking water abstraction to one fourth, i.e. 14 mg/L. As a consequence, groundwater becomes the compartment determining the concentration in drinking water. Full details on calculation of the purification factor are contained in the EUSES background report (RIVM, 2004), but not in the Guidance IR & CSA, Chapter R.16 (ECHA, European Chemicals Agency, 2012e).
- Another difference between “substance 1” on the one hand and “substance 10” and “substance 13” on the other hand, however, is evident in the case of groundwater, in which the concentrations of “substance 13” and “substance 10” are about one and two orders of magnitude higher than the one of “substance 1”. This is a direct consequence of the higher  $K_{OC}$  values for these substances that lead to larger fractions (35% and 17%, respectively) being adsorbed to sludge in the STP. Since the EUSES/TRA default assumes that this sludge is applied to soil, the groundwater concentration becomes very high. In fact, if sludge application to soil is prevented (this can be set within the software and, of course, has to be communicated in the exposure scenario), the concentration of “substance 10” in groundwater declines from 791 mg/l to 0.371 mg/L (details not shown). This testifies to the fact that sludge application – rather than deposition from air – is the primary pathway leading to increased groundwater concentrations.
- The lower concentration of “substance 13” in groundwater compared to “substance 10” is the result of several factors. First, due to the much higher volatility of “substance 13”, a higher fraction is emitted to air from the STP, leading to 2-times lower emissions to sludge. This difference is directly represented by the initial concentration in soil after sludge application, which is 2-times lower for “substance 13” than for “substance 10” (Table 14). Second, “substance 13” shows a higher degree of biodegradation and volatilisation, leading to much less accumulation of the substance over the 10-year period considered in the software for the pathway “sludge-to-soil”. The lower biodegradation rate of “substance 10” is worsened by its high  $K_{oc}$ , which increases its half-life in soil (see also the methodology details in ECHA (2012e) and RIVM (2004) for these aspects).
- The higher fractions of emissions to sludge for “substance 10” and “substance 13” (35% and 17%, respectively) compared to “substance 1” (0.0142%) directly translate into different concentrations in soil at the beginning of the sludge application. For the example of “substance 10” vs. “substance 1”, the difference in relative emissions of  $(35\% / 0.0142\%) = 2,465$  is equal to the different initial concentrations in soil (factor 2450, see the following table; slight differences due to rounding). Since accumulation of the substance applied with sludge over 10 years is considered (see above), this leads to

even higher values after this period, also because the substance is much less biodegradable than “substance 1” (factor almost 86,000). However, the high  $K_{OC}$  initially responsible for the high relative emission to sludge also results in a stronger adsorption to soil particles, resulting in a lower partitioning to pore water. In the underlying mathematics, the concentration in the soil is divided by the soil-water partition coefficient ( $K_{sw}$ ; see step 2 above), which largely depends on  $K_{OC}$  (at least for all substances that are not extremely volatile). Since  $K_{OC}$  is higher for “substance 10” than for “substance 1”, the large difference between “substance 10” and “substance 1” in the soil concentration is reduced to a factor of about  $(85,698 * 0.00152 =) 130$ . Since the concentration in pore water is set as the concentration in groundwater, this is also the factor by which the groundwater concentrations modelled differ. The same basically applies for “substance 13”, although to a lesser extent for reasons discussed above. In the case of “substance 13”, it is also interesting to see that the difference in concentrations in soil after the 10-years period of sludge application (factor 35, Table 14) is not represented in the difference in concentrations in groundwater (factor only 16). This is entirely due to the fact that “substance 13” leaches more easily to groundwater than “substance 10” due to its lower  $K_{oc}$ .

- As already mentioned above, “substance 13” is highly volatile and 60% of the emissions from the STP are to air. Nonetheless, deposition only plays a negligible role in comparison to sludge application. For this substance the concentration in agricultural soil due to sludge application is about three orders of magnitude higher than the respective concentration due to deposition. It must also be taken into account that the high volatility also has an impact on the concentration in soil, since evaporative losses are considered here as well.

Table 14: Comparison of the three exemplary substances in the sludge-groundwater pathway

	Substance no.			Factors difference S10:S1 - S13:S1 - S10:S13
	1	10	13	
Concentration in agricultural soil due to sludge in first year at t=0 [kg/kg wt.w]	0.00000527	0.0129	0.00644	2,450 - 1220 - 2
Concentration in agricultural soil, averaged over 180 days [kg/kg wt.w]	0.000000874	0.0749	0.00218	85,698 - 2,500 - 35
RHsoil (bulk density), default [kg wtw/m3]	1,700	1,700	1,700	Not applicable
Ksoil-water [m3/m3]	0.245	161	75	0.00152 - 0.00327 - 0.466*
PEC local groundwater [mg/L]	6.0	791	49	130 - 8.2 - 16

\* Reciprocal values, e.g.  $1/(161/0.245)$

- Ultimately then, the difference in the  $K_{OC}$  by a factor of  $(5360 / 1.5 =) 3,573$  and the poorer biodegradability of “substance 10” compared to “substance 1” translate in a difference in terms of the groundwater concentration by a factor of “only” 130.

From the analysis of the impact of physical-chemical substance properties on the predicted groundwater concentration presented above, it appears that the water solubility itself does not have a large impact on the partitioning events and the concentrations in drinking water. Rather, the results from biodegradation tests, the  $K_{OC}$  (or the  $K_{ow}$ , if no  $K_{OC}$  value is available) and – at least in relation to emissions from the STP – the volatility (Henry’s law constant) determine much of the fate of the chemical. In the case of the latter, a high water solubility leads to low volatilisation potential, thus directing more of the substance to the STP effluent. But again, this fraction is very much dependent on the biodegradation and the  $K_{OC}$  value of the substance to be assessed.

When the three substances used in the assessment above are assumed to be present in soil at identical concentration (e.g. 1 mg/kg wt.w), then the concentration in groundwater follows the relative leachability, i.e. the substances with substantially higher  $K_{OC}$  values (“substance 10” and “substance 13”) have a much lower concentration in groundwater than “substance 1” (Table 20). This finding underlines the importance of  $K_{OC}$  in partitioning within the STP and accumulation of the substance in soil. In other words, the high  $K_{OC}$  values for “substance 10” and “substance 13” (together with the biodegradation test result) are responsible for the high concentrations of these substances in groundwater, despite the fact that the high  $K_{OC}$  values impede leaching of these substances to groundwater.

**Table 15: Comparison of the three exemplary substances in the sludge-groundwater pathway assuming initially identical concentrations in soil**

	Substance no.		
	1	10	13
Set concentration in agricultural soil, averaged over 180 days [kg/kg wt.w]*	0.000001	0.000001	0.000001
$RHO_{soil}$ (bulk density), default [kg wt.w/m <sup>3</sup> ]	1,700	1,700	1,700
$K_{soil-water}$ [m <sup>3</sup> /m <sup>3</sup> ]	0.245	161	75
PEC <sub>local groundwater</sub> [mg/L]	6.9	0.011	0.023

\* Set to 1 mg/kg wt.w

As indicated above, the importance of  $K_{OC}$  is manifold: first, it is decisive for the extent that a substance is adsorbed to sludge; second,  $K_{OC}$  determines the extent of adsorption to solids in soil, preventing leaching of the substance to groundwater; finally,  $K_{OC}$  also has an impact on the biodegradation rate in what is essentially a banding approach. Thus, the half-lives in soil for the different biodegradation test results (e.g. 30 d for a substance that is readily biodegradable and has a  $K_{OC}$  value of 5,000 L/kg or lower) are multiplied with 10, if the  $K_{OC}$  value is between 5,000 and 50,000 and are multiplied with 100, if  $K_{OC}$  values are between 50,000 and 500,000 (see also the methodology details in ECHA (2012e) and RIVM (2004)).

Overall, this evaluation shows that the input values for the release estimation in step 1 are of major importance. For step 2, i.e. partitioning and degradation, the water solubility itself appears to be of less importance and  $K_{ow}/K_{oc}$ , volatility and biodegradation define much of the environmental fate. This finding has also been made by others. For example, Verdonck et al. (2005) identified biodegradation,  $\log K_{OW}$  and the vapour pressure as key input values (vapour pressure was used instead of the Henry’s law constant in the EUSES model then available).

### ***Application of ECETOC TRA modelling to define mobility***

In order to analyse the mobility aspect – as assessed in current exposure estimation under REACH – in more detail, ECETOC TRA modelling for a relatively large number of substances already registered under REACH was performed using a default scenario. This modelling approach includes the following key aspects:

- Default scenario: an identical release pattern is assumed, leading to an identical concentration of each substance in the STP influent. Any influence of the use of a substance is therefore excluded.
- Physico-chemical and environmental fate data: these were retrieved via eChemPortal from ECHA CHEM, focussing on experimental data with a reliability of 1 or 2 (to avoid e.g. questionable calculated values for  $K_{oc}$ ).
- Exclusion of biodegradation: biodegradation forms the basis of the persistence assessment and is excluded in the modelling that aims to analyse the mobility term. Removal processes in the STP (i.e. reducing the discharge into surface water) therefore only include emission to air (driven by Henry's law constant, itself a function of vapour pressure, water solubility and molecular weight) and adsorption to sludge (driven by  $K_{oc}$ ), the latter increasing the importance of the soil-groundwater pathway.

This section describes the approach taken in the ECETOC TRA modelling.

#### **Default scenario**

The default scenario chosen represents the manufacture of 100,000 t/a of a substance with the Environmental Release Category (ERC) 1. This ERC assumes a high release to wastewater of 6% of the amount manufactured per day (100,000 t/a / 300 d/a), resulting in a release of 20,000 kg/d. With the default assumption of an STP discharge rate of 2,000 m<sup>3</sup>/d, this leads to a concentration of the substance in the STP influent of 10,000 mg/L. This concentration is extremely high and – even if a high removal of e.g. 90% from the STP (by biodegradation, evaporation and/or adsorption to sludge) is assumed – leads to concentrations in the STP (1,000 mg/L) that will be higher than most PNECs derived for this compartment. However, this is a default scenario to be used under REACH (see e.g. ECHA, European Chemicals Agency, 2012e), as implemented in ECETOC TRA. In this context, it is worth noting that the corresponding release factor under the previous EU risk assessment procedures (EC, 2003) was more differentiated (e.g. by tonnage, type of process or water solubility, depending on the industrial category) and was 20-times lower (0.3%) for the production of basic chemicals at the tonnage of 100,000 t/a used here.

The purpose of the evaluation presented here, however, is to gain an understanding of the impact of the physico-chemical properties of a substance on the concentrations estimated to be present in groundwater and surface water (and, ultimately, drinking water). Since these concentrations show a linear relationship with the concentration in the STP influent, the absolute values are irrelevant. If, for example, the concentration in the STP influent is 100-times lower, then the concentration in drinking water estimated by ECETOC TRA will also be 100-times lower.

As a consequence, the evaluation reported here *does not present absolute concentrations*, but rather *the fraction of the STP influent concentration* that is estimated to be present in either surface water or groundwater. This is an important point to remember and ultimately points to the fact that the default scenario is entirely artificial.

### Physico-chemical and environmental fate input data

The property search function of eChemPortal (<http://www.echemportal.org>) was used to search for relevant input data. While this function allows searching four different databases with property data, ECHA CHEM is the most important source in terms of substances and data points covered.

Initially, very broad searches identified many hits per endpoint, which, however, included many hits for the same study, e.g. the same data from different dossiers, the same data presented in different units or vapour pressures for different temperatures (20 °C, 70 °C, 150 °C etc.). For the latter, this is not unusual, since the vapour pressure is often experimentally determined at higher temperatures and vapour pressures at 20-25 °C are then calculated by regression with Antoine constants. The following printscreen (Table 16) shows an example for which six hits were retrieved for the vapour pressure that all relate to the same study (two different temperatures given, reported in three different dossiers).

Table 16: Printscreen of an example of retrieved vapour pressure data in the initial search

Year	Testing	Guideline	GLP	Vapour pressure	at
1992	according	other guideline: Annex V, A3	yes	0.47 Pa	20 °C
1992	according	other guideline: Annex V, A3	yes	7980 Pa	180 °C
1992	according	other guideline: Annex V, A3	yes	0.47 Pa	20 °C
1992	according	other guideline: Annex V, A3	yes	7980 Pa	180 °C
1992	according	other guideline: Annex V, A3	yes	0.47 Pa	20 °C
1992	according	other guideline: Annex V, A3	yes	7980 Pa	180 °C

Another problem associated with the broad searches is that data in different units (e.g. mm Hg, mbar and Pa for the vapour pressure) are obtained that would require manual conversion into an identical unit, since units are included in the value field.

With these problems in mind, the final searches were more limited by:

- restricting vapour pressure data to temperatures < 30°C
- restricting data to the main unit (given in the help file for eChemPortal) for the specific endpoint.

For some key endpoints, namely adsorption, different entries are possible (e.g.  $K_{oc}$ ,  $\log K_{oc}$ ,  $K_d$ ) and no limitation was performed to retain as many data as possible. In addition, biodegradation data were retrieved to retain the option of including this information in future analyses.

With this limited search strategy and for different combinations of endpoints, i.e. retrieving only substances with data fulfilling the search criteria for all endpoints, the following number of hits is retrieved (Table 17):

Table 17: Number of hits for endpoint combinations from eChemPortal property search

Parameter*	Number of hits
WS and VP	4,147
ADS and WS and VP	1,843
BIO and ADS and WS and VP	2,035
$K_{ow}$ and BIO and ADS and WS and VP	1,349
DC and $K_{ow}$ and BIO and ADS and WS and VP	112
DC and BIO and ADS and WS and VP	149

\* ADS: Adsorption (i.e.  $K_d$ ,  $K_{oc}$  or  $\log K_{oc}$ ), BIO: Biodegradation data (screening tests); DC: Dissociation constant,  $K_{ow}$ :  $K_{ow}$  or  $\log K_{ow}$ ; VP: Vapour pressure, WS: Water solubility

Note that the number of hits is much greater than the number of substances covered. As a consequence, adding the dissociation constant reduces the number of hits to an extent that results in too few substances being covered. Even when excluding  $K_{ow}$ , the number of hits is too low (the 149 hits actually only relate to 10 substances). This is due to the low number of hits for the dissociation constant alone (491). It can be speculated that many dossiers waived this endpoint due to a lack of an ionisable functional group in the molecule, which is in agreement with the integrated testing strategy for this endpoint (ECHA, European Chemicals Agency, 2013).

In some cases, data extraction for adsorption only yielded  $K_d$  values. The dossier was then consulted and  $K_{oc}$  values for these substances taken from the dossier (usually reported in the executive summary or other free text fields in the dossier).

In the final evaluation step, the following hits were removed:

- Hits with no substance identification number: unclear substance identification
- Hits for members of a category: to avoid double counting of identical values
- Hits from read across endpoint study records: to avoid double counting
- Hits with obviously identical values for the same substance: these are believed to come from different dossiers, but reflect the result of the same study

When more than one value remained per substance and parameters, the most reliable value was selected based on several descriptors such as the reliability score, GLP and other endpoint-specific data. In some cases (although very few), several valid values remained in the evaluation and the arithmetic mean (AM) was calculated. In addition, the following evaluation of ambiguous or complex data was performed:

- Ranges: the AM was calculated, provided that the maximum did not differ by more than a factor of 2 from the minimum.
- Limit values: values presented as “<” or “>” were taken as the closest number with one significant figure less. For example, a value reported as “<1.32” was taken as 1.3 and a value reported as “>5.5” was taken as 6. For all values reported as “≤” or “≥”, the exact value was chosen (e.g. “≤ 1.1” → = 1.1).
- Biodegradation data: generally, the interpretation in the endpoint study record was followed, but several data had to be assessed manually on the basis of the persistence criteria developed in section 2.1.3 (e.g. because the interpretation was “inherently biodegradable” without indication of fulfilment of specific criteria).

Data evaluated were experimental data with a reliability of 1 or 2 with only very few exceptions (e.g. estimated vapour pressures are acceptable for substances with a melting point between 200 and 300 °C according to REACH Annex VII).

Table 18: Descriptive statistics for the sample used in ECETOC TRA modelling

	MW (g/mol)	log K <sub>oc</sub>	WS (mg/L)	VP (Pa)	HLC (Pa m <sup>3</sup> /mol)	log K <sub>ow</sub>	P/Not P
N	64	64	64	64	64	64	64
AM	315	3.67	75,198	340	6,249	3.13	P: 55% Not P: 45%
Median	293	3.23	36.1	0.00145	0.0168	2.80	
25 <sup>th</sup> perc.	193	1.76	0.475	0.0000142	0.000094	0.678	
75 <sup>th</sup> perc.	391	5.69	2,298	1.35	6.8	5.43	
MIN	76	-0.320	7.00E-08	1.00E-10	3.65E-13	-3.87	
MAX	781	10.2	910,000	7,263	266,000	17.0	

\* HLC: Henry's law constant (calculated from molecular weight, water solubility and vapour pressure at 20-25 °C); P: Persistent; VP: Vapour pressure, WS: Water solubility

The molecular weight of a substance is not accessible in eChemPortal and is – in fact – not reported in ECHA CHEM. For mono-constituent substances, the molecular weight was researched using the CAS or EC number from publicly available sources. In some cases, it was calculated from the structural or molecular formula provided in the dossier. For UVCB substances (e.g. with varying chain length), matters are more complicated and the molecular weight of the main constituent had to be estimated. This makes the molecular weight somewhat uncertain. As a consequence, UBA was asked to retrieve molecular weights for these substances directly from the respective CSRs. The evaluation resulted in 64 substances that entered ECETOC TRA modelling. Their physico-chemical and fate data are summarised in Table 18.

The Henry's law constant is only presented to show the range of values in the sample. The value is automatically calculated in ECETOC TRA for the environmental temperature (default 12 °C).

The data show that the sample covers a very wide range and even the “middle fifty” (25<sup>th</sup>-75<sup>th</sup> percentiles) spans several orders of magnitude (except, of course, for the molecular weight). These data suggest that there is no obvious bias in the sample towards extreme physico-chemical or environmental fate properties.

With regard to persistence, it turned out that 55% of the substances were actually *persistent*, 45% were not. It has to be emphasized here, that nonetheless persistence was assumed for *all* compounds of the set in the modelling approach with ECETOC TRA as described above (biodegradation rate of zero assumed in calculation).

### Running the model

The input data for all 64 substances were entered into ECETOC TRA, except for the biodegradation test result. The latter parameter was set to “not biodegradable”, since the purpose of this exercise was to analyse the impact of physico-chemical properties on the mobility, while biodegradation enters the persistence assessment.

The following values (Table 19) were extracted from ECETOC TRA or calculated externally on the basis of those taken from the software (note that raw water as defined here is essentially identical to “drinking water” as used in ECETOC TRA or ECHA Guidance (ECHA, European Chemicals Agency, 2012e)):

Table 19: Data calculated by ECETOC TRA and used for further analyses

Parameter	Remark
Annual average local PEC in surface water (dissolved)	Taken from ECETOC TRA; both are multiplied externally to give the concentration in surface water relevant for drinking water
Purification factor ( $F_{pur}$ )	
Local concentration in surface water	Calculated externally from the above
Local PEC in groundwater	Taken from ECETOC TRA
Local concentration in drinking water	Taken from ECETOC TRA; can be checked with values calculated externally (i.e. maximum of surface water vs. groundwater concentrations)
Removal in STP (fraction)	Retrieved for additional analyses
Local total daily intake for humans	Retrieved for additional analyses

### Results of TRA calculations – conclusions on mobility parameters

#### *Concentration in surface water and groundwater as a function of water solubility*

For all 64 model compounds, for which ECETOC TRA calculations were performed, water solubilities were retrieved from ECHA CHEM. The range of water solubility for these compounds spans 13 orders of magnitude, from below  $10^{-7}$  mg/L to  $10^6$  mg/L. Thus it was interesting to analyse if a correlation exists between water solubility and the fraction of STP influent concentration estimated for surface water and groundwater, respectively, by ECETOC TRA.

Results are given in Figure 5 for both, surface water concentration and groundwater concentration. Surface water concentration is given without application of the purification factor applied by ECETOC TRA for calculation of actual raw water concentration (called drinking water within the software). The purification factor models removal of the dissolved fraction of a substance from surface water due to degradation, adsorption and volatilisation. As described in RIVM (2004) in more detail, a simple banding approach is applied in relation to biodegradation rates,  $\log K_{OW}$  (for adsorption) and HLC (for volatilisation).

The data in Figure 5 clearly show that if there is any correlation between the concentration in surface water or groundwater and water solubility, it is very weak and of no predictive value. Comparing the three data pairs at the utmost left side of the graph (compounds of the set with the three lowest water solubilities), concentration differences for surface and groundwater between the second most insoluble compound (2) and the first (1) and third (3) most insoluble compounds are considerable.

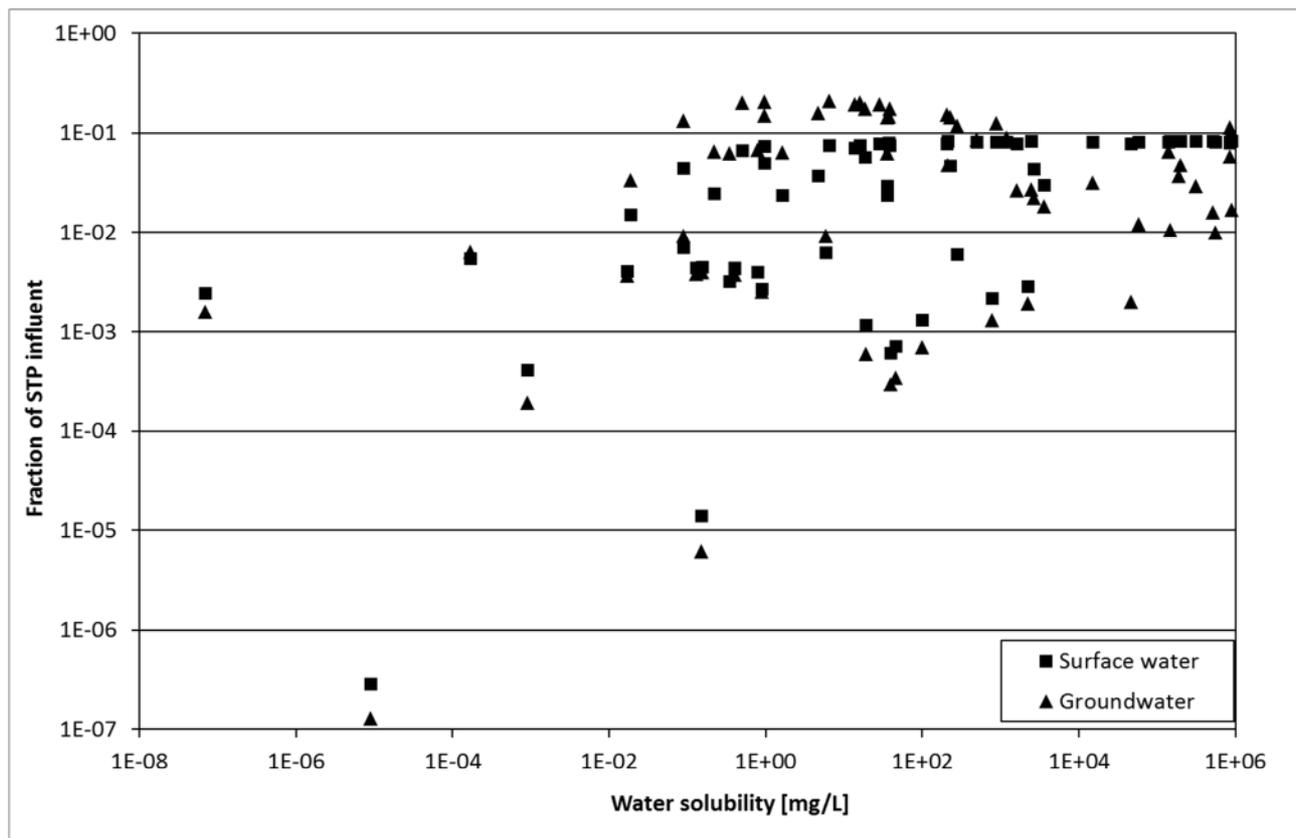


Figure 5: Fraction of STP influent in surface water (no purification factor) and groundwater as a function of water solubility

We therefore had a closer look on their physicochemical properties, from which HLC and  $\log K_{OC}$  are given below besides their water solubilities:

- (1): Water solubility  $7 \times 10^{-8}$  mg/L, HLC 260.7 Pa m<sup>3</sup>/mol and  $\log K_{OC} = 6.08$
- (2): Water solubility  $9 \times 10^{-6}$  mg/L, HLC 0.93 Pa m<sup>3</sup>/mol and  $\log K_{OC} = 10.18$
- (3): Water solubility  $1.7 \times 10^{-4}$  mg/L, HLC 134.0 Pa m<sup>3</sup>/mol and  $\log K_{OC} = 5.46$

In result, for these compounds neither water solubility nor HLC correlate with concentrations for surface and groundwater, but  $\log K_{OC}$  does. For HLC, those compounds which would be assumed to have a higher tendency of getting lost to the atmosphere in the STP are the ones with actually much higher concentrations for surface and groundwater in comparison to compound (2) with a very low HLC.

#### *Concentration in surface water and groundwater as a function of Henry's Law Constant (HLC)*

For all 64 model compounds, for which ECETOC TRA calculations were performed, water solubilities and vapour pressures were retrieved from ECHA CHEM, such that HLC could be calculated. The range of HLCs for these compounds spans 17 orders of magnitude, from around  $10^{-12}$  Pa m<sup>3</sup>/mol to  $10^5$  Pa m<sup>3</sup>/mol. Note that these values were calculated outside the software for temperatures of 20-25 °C (i.e. the temperatures for which water solubility and vapour pressure are usually reported) for the presentation below, while ECETOC TRA actually calculates HLC for an environmental temperature of 12 °C and this value was used in all calculations. The fraction of the STP influent concentration estimated by ECETOC TRA for surface water and groundwater, respectively, is plotted over the HLC in the following figure (Figure 6).

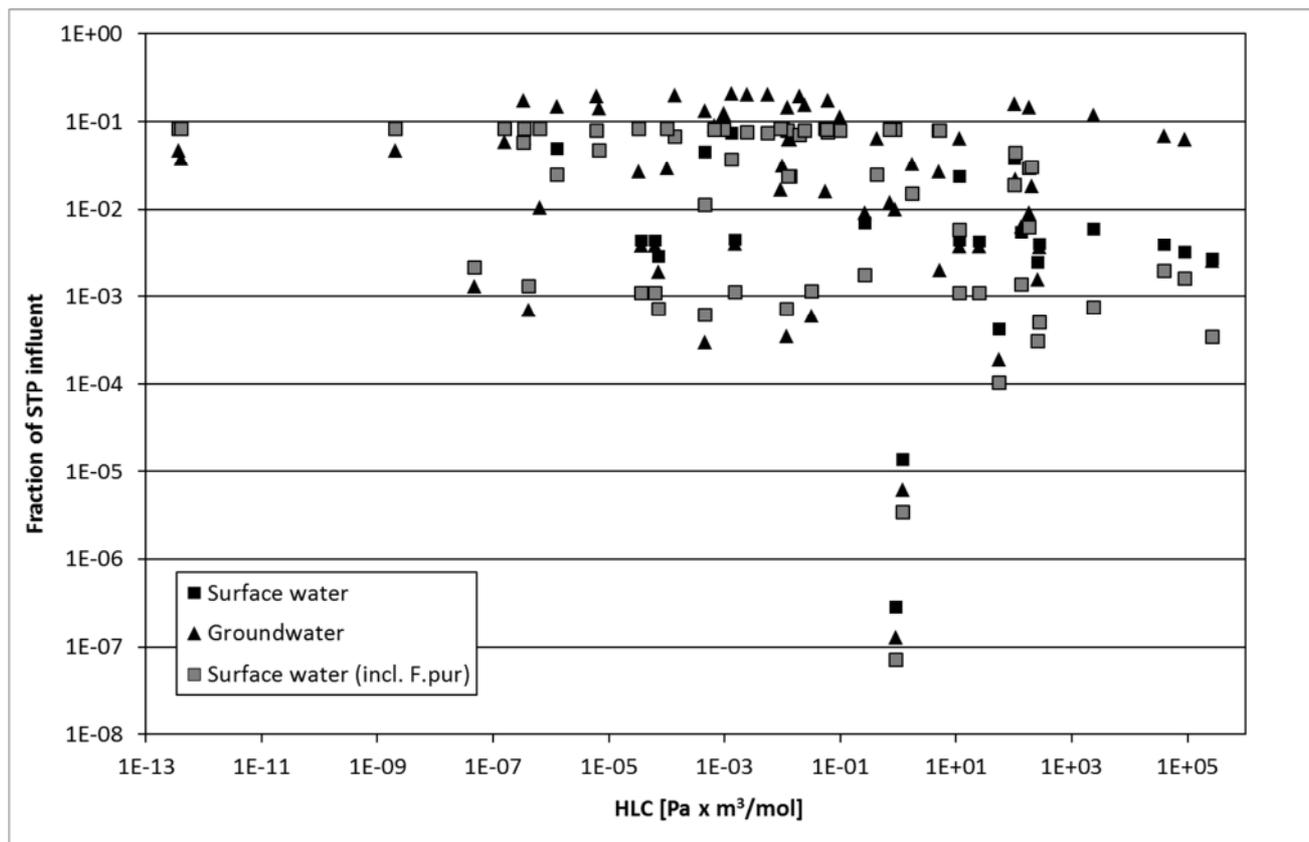


Figure 6: Fraction of STP influent in surface water (with and without purification factor) and groundwater as a function of HLC (at around 20°C)

For the calculation of raw water concentrations from surface water concentrations, a *purification factor* ( $F_{\text{pur}}$ ) is applied both in EUSES and ECETOC TRA that considers volatilisation (HLC), adsorption to particulates ( $K_{\text{OW}}$ ) and biodegradation (per default no biodegradation, thus not relevant here). Details on the *purification factor* can be found in section 2.2.3 (Exposure estimation with ECETOC TRA) and Table 20. Due to HLC being one determinant of the size of  $F_{\text{pur}}$ , also surface water concentration after reduction by  $F_{\text{pur}}$  (grey shaded squares) are given in Figure 6. From the plot of Figure 6 it becomes clear that there is no obvious correlation between surface water or groundwater concentration and HLC. Also, significant volatilisation could be expected only from HLC of around 50 Pa m<sup>3</sup>/mol (at 12°C) and higher (see section 2.2.2, Table 8), which translates approximately to around 100 Pa m<sup>3</sup>/mol at higher temperatures of around 20-25°C shown in Figure 6. Indeed, above HLC of around 100 there is indication of a slight decrease in surface water concentrations with increasing HLC. As exemplified for the compounds with the fourth, third and second highest HLC, very high HLC may shift importance from surface water to groundwater. This holds true, however, only if  $K_{\text{OC}}$  is not very high (see chapter below on the influence of  $K_{\text{OC}}$ ). For example, the compound with the highest HLC of the set has a high log  $K_{\text{OC}}$  of 5.81 and the concentrations in surface water (without purification factor) and groundwater are identical (in fact, the symbol for groundwater is hidden behind the one for surface water in the figure above). Thus, overall HLC seems to have no major predictive impact on mobility with regard to raw water concentrations. The data, however, indicate that at high values for HLC, the surface water concentration is slightly reduced as would be expected from physicochemical properties.

*Concentration in surface water and groundwater as a function of  $K_{OW}$  and – alternatively – of  $K_{OC}$*

For all 64 model compounds, for which TRA calculations were performed, values for  $\log K_{OW}$  and  $\log K_{OC}$  were retrieved from ECHA CHEM. The range of  $K_{OW}$  and  $K_{OC}$  spans 20 and 10 orders of magnitude, respectively, for this set of compounds. Thus, very diverse properties are covered.

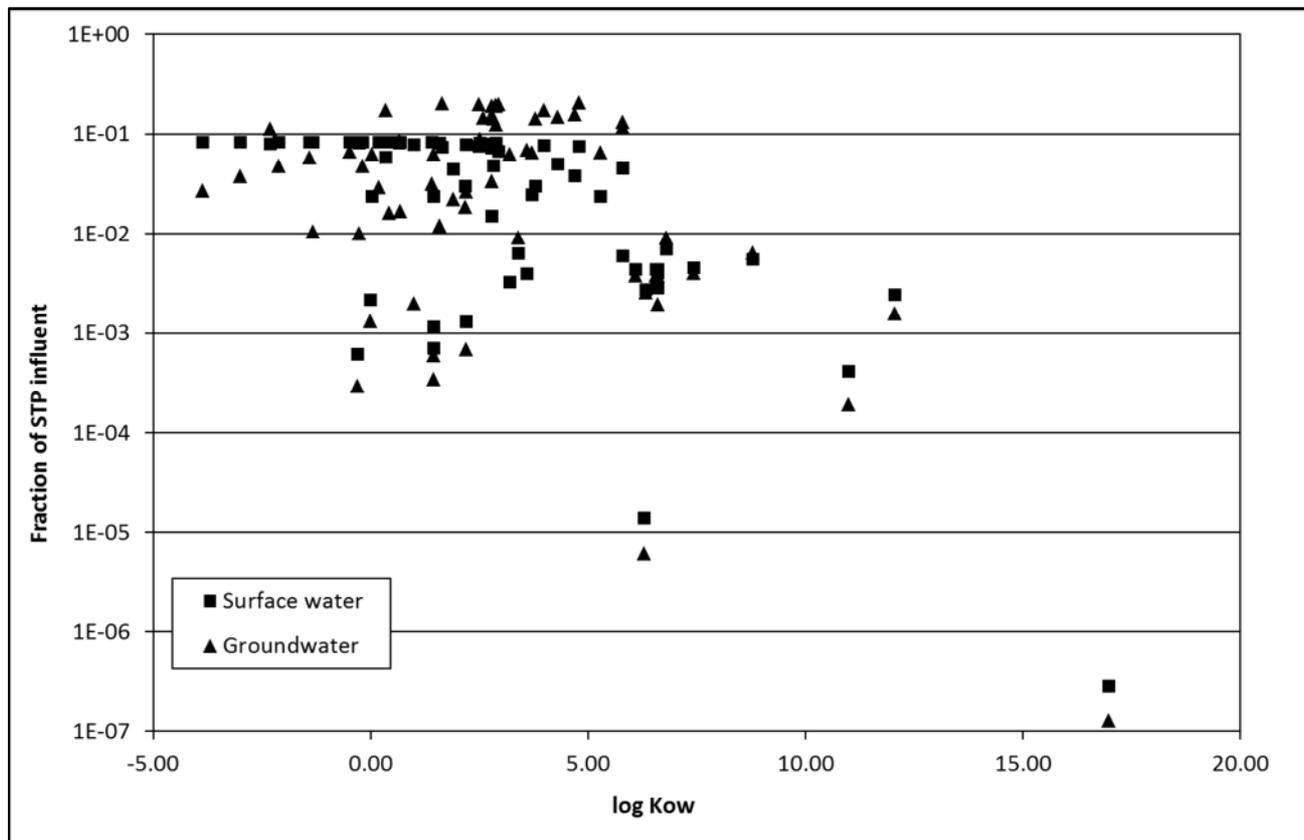


Figure 7: Fraction of STP influent in surface water (with and wo purification factor) and groundwater as a function of  $\log K_{OW}$

Earlier projects used  $\log K_{OW}$  as a substitute for  $\log K_{OC}$  to estimate the mobility in water (IfW, 2010; 2011). Thus it was interesting to compare results for plotting surface water and groundwater concentrations for the 64 compounds a) as a function of  $\log K_{OW}$  (Figure 7) and b) as a function of  $\log K_{OC}$  (Figure 8).

Comparing results of Figure 7 and Figure 8 it becomes obvious that – while there is some similarity in the patterns (as expected) – only  $\log K_{OC}$  correctly predicts the processes important for concentrations in groundwater: a) increasing concentrations up to a certain value (around 3.0) due to increasing concentrations in soil and, as a consequence, porewater; b) at higher  $\log K_{OC}$  values, the stronger adsorption outweighs increasing soil concentrations and concentrations in porewater (identical to groundwater in EUSES/ECETOC TRA) decline. However,  $\log K_{OW}$  has a relatively large influence on the *purification factor* ( $F_{pur}$ ) (compared to HLC) and thus on the surface water concentration at  $\log K_{OW} > 4.0$  and even more at  $\log K_{OW}$  values  $> 5.0$  (banding approach for  $F_{pur}$ , see Table 20). HLC, in contrast, has some but not a very high impact on the observed spread for surface water concentrations caused by  $F_{pur}$ .

The impact of  $\log K_{OW}$  on  $F_{pur}$ , however, is solely due to the fact that EUSES/ECETOC TRA employs this parameter as an indicator of adsorption onto particles. This could well be substituted with  $\log K_{OC}$ , which is a better parameter of adsorption processes.

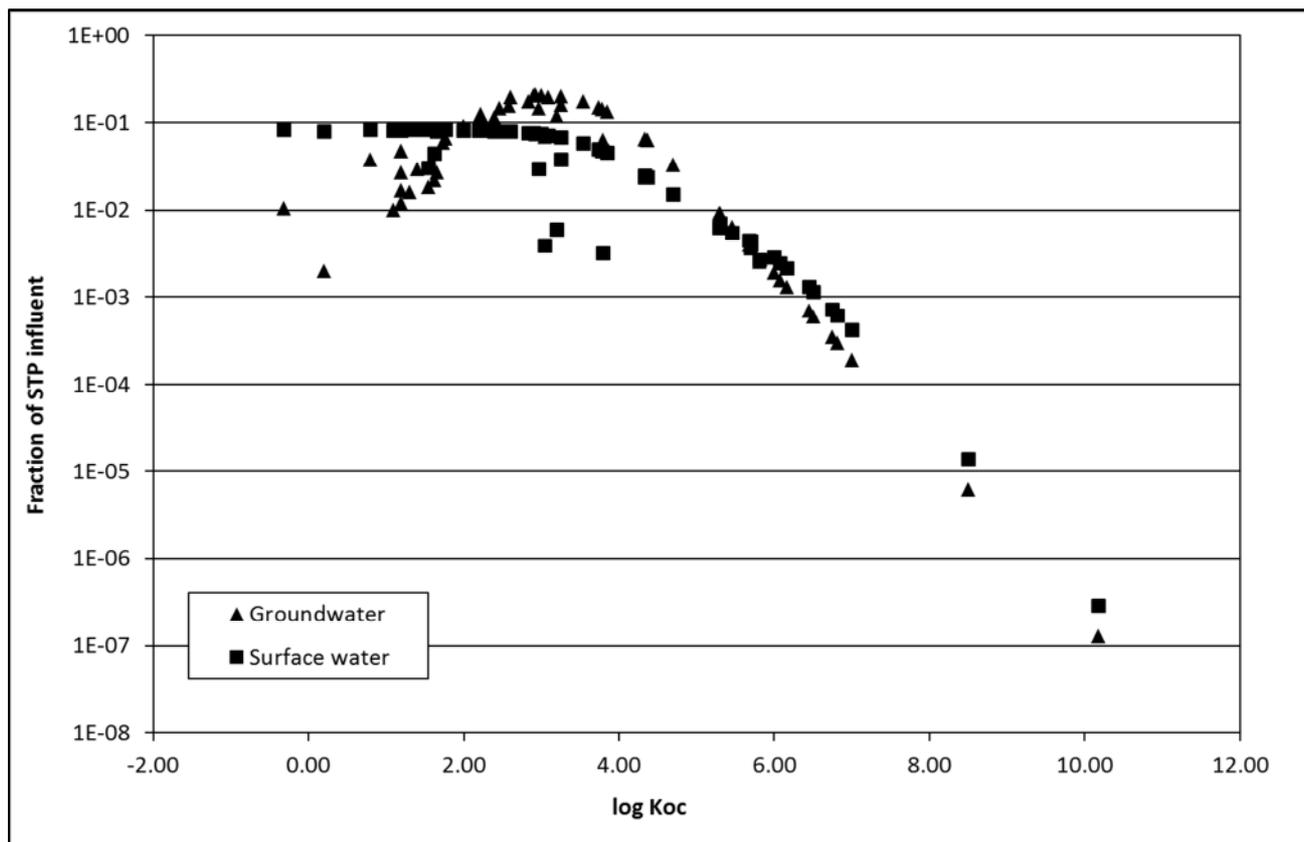


Figure 8: Fraction of STP influent in surface water (wo purification factor) and groundwater as a function of  $\log K_{OC}$

Overall,  $K_{OC}$  must clearly be regarded as the key parameter for mobility, while  $K_{OW}$  may at best be regarded as indicative, but does not describe all of the processes considered relevant. Water solubility and HLC, in contrast, are clearly not key parameters, but HLC may have some mitigating effect for surface water concentrations at high values (see above and discussion in the following section).

#### *Determination of cut-off values for $K_{OC}$ to conclude on mobility*

From the preceding sections, it became clear that  $K_{OC}$  must be regarded as the by far most relevant parameter for mobility of chemicals in surface water and groundwater. Because ECETOC TRA includes the application of a purification factor ( $F_{pur}$ , derived in a banding approach from parameters HLC,  $\log K_{OW}$  and biodegradability) for the concentration in surface water used as raw water, only values including  $F_{pur}$  are given for surface water in Figure 9. The following can be observed from plotting surface water and groundwater concentrations (expressed as fraction of STP influent concentration) against  $\log K_{OC}$  (Figure 9):

#### Surface water:

The surface water concentration is relatively constant for low  $\log K_{OC}$  values up to a value of about 2.4 with about 8% of STP influent concentration. At higher  $\log K_{OC}$  values, the surface water concentration declines with ever increasing slope until a nearly constant decline is reached at about  $\log K_{OC}$  of 4.5.

#### Groundwater:

Groundwater concentrations are below surface water concentrations at very low  $\log K_{OC}$  values and steadily increase with increasing  $K_{OC}$  up to a maximum value at about  $\log K_{OC}$  of 3.0 corresponding to approximately

20% of STP influent concentration. The intersection with surface water concentration (approximately equal concentration) is at a log  $K_{OC}$  of about 2.4. At higher log  $K_{OC}$  values, groundwater concentrations decline with ever increasing slope until a nearly constant decline is reached at about log  $K_{OC}$  of 4.5.

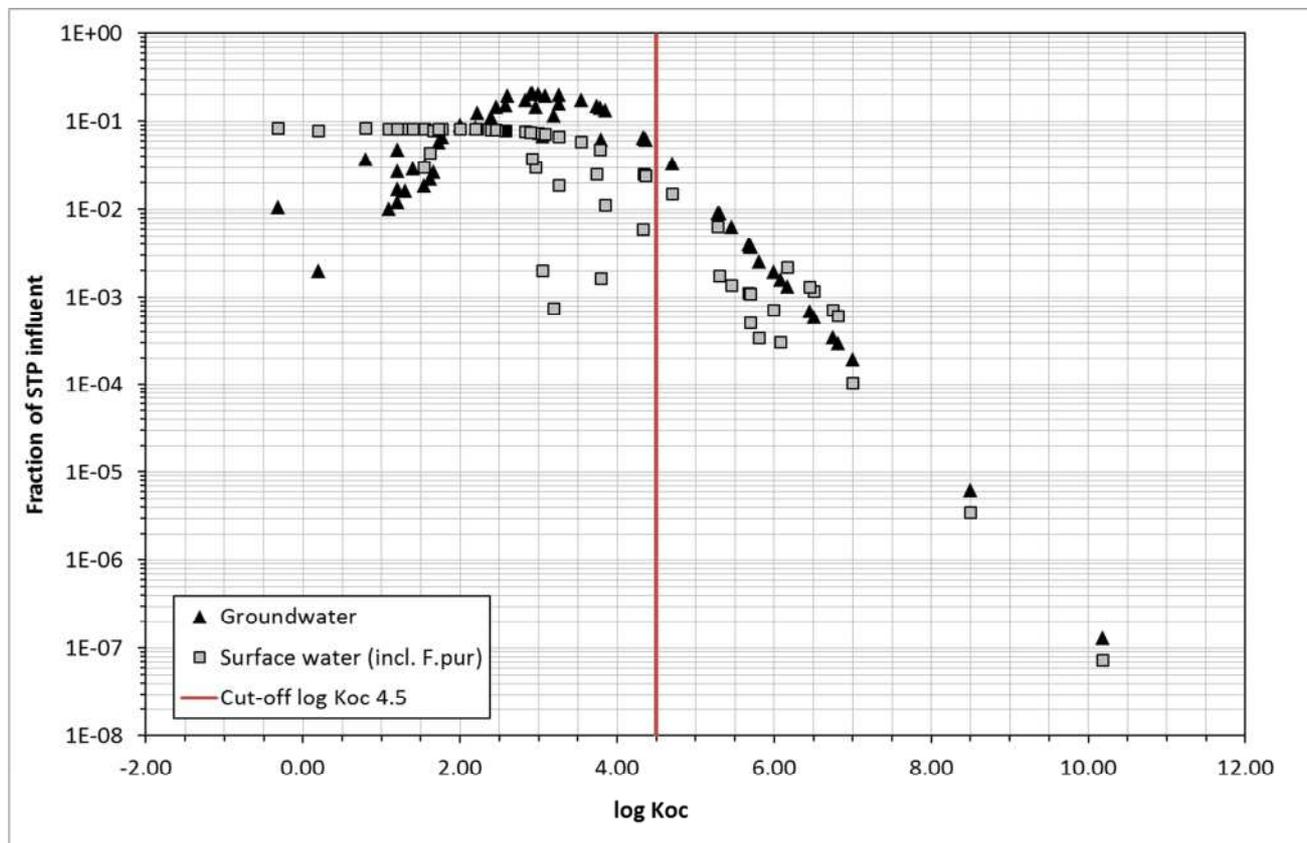


Figure 9: Fraction of STP influent in surface water (including purification factor) and groundwater as a function of log  $K_{OC}$  - proposed cut-off of log  $K_{OC}$  of < 4.5 for mobility.

The more pronounced scattering of the surface water curve is due to the influence of HLC and log  $K_{OW}$ : If either of these or even both are high, this results in a correspondingly higher removal from the STP (HLC and log  $K_{OC}$ ) as well as a higher purification factor  $F_{pur}$  (HLC and log  $K_{OW}$ ). As the latter follows a relatively crude banding approach (no effect:  $F_{pur}=1$  up to log  $K_{OW}=4.0$  and HLC of 100 Pa m<sup>3</sup>/mol at 12°C (approximately 210-250 Pa m<sup>3</sup>/mol at 20-25°C)), this implies overestimation of surface water concentrations especially for those compounds close to the banding limits or above the limit of the highest band (see Table 20 for details on banding approach).

It further leads to overestimations of surface water concentrations for those compounds for which log  $K_{OW}$  is no appropriate descriptor of adsorption behaviour. This is the case for 19% of the set of 64 compounds analysed. For these compounds, log  $K_{OW}$  is  $\leq 4$  while log  $K_{OC}$  is  $> 3.7$ . It was pointed out in section 2.2.2, Groundwater that compounds with a log  $K_{OC} > 3.7$  may be regarded as immobile or at least highly adsorptive. As regards HLC, while it may indeed reduce surface water concentration (much less pronounced for groundwater), its impact is comparably low relative to log  $K_{OC}$ . Therefore, we conclude from the data that it is justified to relate parameters defining mobility solely to log  $K_{OC}$ , disregarding the influence of HLC.

Table 20: Purification factor  $F_{pur}$  - banding approach used in EUSES / TRA according to RIVM (2004)

	A: Factor due to $\log K_{ow}$			B: Factor due to HLC at 12°C [Pa m <sup>3</sup> /mol]	
	≤4	4-5	>5	≤100	>100
$F_{pur} = A*B$	1	1/2	1/4	1	1/2

With regard to surface water concentrations, there are further factors, resulting most probably in a considerable overestimation of surface water concentrations. According to EC (2003), the default dilution factor of 10 used for exposure estimation is a conservative value even at low flow for substances used in the chemical industry. With a higher actual dilution, surface water concentrations will be lower. In addition, as explained below for groundwater, actual adsorption as a function of  $K_{OC}$  to solids is underestimated (conservative approach). This may possibly also be the case for sludge adsorption in sewage treatment plants, which would lead to overestimation of surface water concentrations. Finally, in these model calculations (n= 64 compounds) biodegradation was set to zero. This will seldom be the case even for substances classified as P according to the concept outlined in section 2.1.3.

As regards groundwater concentrations, 88% of compounds with a  $\log K_{OC}$  above 2.4 (38 out of 43) have a higher predicted concentration in groundwater than in surface water and thus, in EUSES/TRA, the groundwater concentration will be set as the raw water concentration (called “drinking water” in the software). The basic shape of the curve for groundwater (see Figure 9) was expected, as the sludge to field pathway gains importance with increasing  $\log K_{OC}$ , leading to the increase of groundwater concentrations in the left part of the curve. Then, with increasing  $\log K_{OC}$  equilibrium is shifted more and more to the bound state, until compounds may be essentially regarded as immobile. This opposing trend is reflected by the shape of the curve for the groundwater concentration, going through a maximum value at  $\log K_{OC}$  of about 3.0. However, according to data gained from pesticides (see section 2.2.2, Groundwater), compounds with  $\log K_{OC}$  values above 3.7 may be regarded as immobile, i.e. not reaching the groundwater to a measurable extent. This is corroborated using an independent model (not restricted to pesticides) derived from chromatography and implying retardation factors on the flow rate of water in non-saturated soils. Under conservative assumptions regarding the flow rate of water in soil a  $\log K_{OC}$  of 3.7 and 4.5 would translate into a duration of 80 and 501 years, respectively, needed to move 1 meter into the soil. Thus, most probably the oversimplification of setting the concentration in soil porewater as equal to the concentration in groundwater leads to a dramatic overestimation of groundwater concentrations. This is corroborated by the two example substances for which monitoring data for both, groundwater and surface water, are available (diuron and nonylphenol, see Figure 10 below): For both compounds actual groundwater concentrations were pronouncedly lower (by a factor 15 to 50) than surface water concentration. In contrast, estimated groundwater concentrations were by a factor of 2.5 (diuron) and 6 (nonylphenol) higher than estimated surface water concentrations.

Thus, a cut-off for mobility based on  $\log K_{OC}$  for determination of PMT compounds is identified. This cut-off may hold true in a strict sense to *persistent* compounds only, as due to the methodological approach our results on mobility may not be independent from persistence. This is accounted for in the following subsumption specifying the cut-off :

*Persistent* compounds are regarded as *mobile* in water, if their  $\log K_{OC}$  is < 4.5 and their water solubility is above a minimum value (> 150 µg/L).

The following section summarizes arguments for the above conclusion (see also Figure 9):

- Assuming that general tendencies are reflected by the curves for surface water and groundwater rather than absolute values, both surface and groundwater concentrations reach a constant steep decline at a log  $K_{OC}$  4.5 and above. Thus, this value corresponds to a point on the curve for groundwater sufficiently far away from the turning point (maximum) at log  $K_{OC}$  3.0. Also for surface water, the relatively constant course of the curve at low log  $K_{OC}$  is clearly replaced by a steep decline at a log  $K_{OC}$  of 4.5 and higher.
- Data for pesticides support the proposed cut-off value. For example, according to the California Department of Pesticide Regulation, pesticides are regarded as potential leachers to groundwater only at log  $K_{OC}$  of  $< 3.28^{22}$ . Immobility at log  $K_{OC} \geq 3.7$  is supported by the GUS concept by Gustafson (1989) and the mobility classification by McCall et al. (1981). The retardation factor approach with conservative assumptions for flow rate of water in non-saturated soil leads to a duration of 501 years necessary to move 1 meter into soil at log  $K_{OC}$  of 4.5 (see chapter 2.2.2, section Groundwater and discussion above). Concluding from these data, the proposed cut-off for mobility of log  $K_{OC} < 4.5$  must be regarded as conservative.
- With regard to surface water, concentrations may be assumed to be very low at high sludge adsorption implicit in a log  $K_{OC}$  of 4.5 and higher. The value of approximately 2% of STP influent concentration estimated by ECETOC TRA most probably represents a significant overestimation due to several conservative assumptions pointed out above.
- The EUSES background report (RIVM, 2004) rates the conservatism of estimations for different parameters. For “drinking water” (corresponding to definition of raw water in this report and being equal to the highest value of estimates for both, groundwater and surface water) the report states that estimation represents a worst case scenario. Thus, the fraction of the STP influent concentration reported above for groundwater and surface water at the cut-off level of log  $K_{OC}$  4.5 must not be taken literally.
- Note that the derived criterion for mobility applies to single molecules, only. Detergent-like behavior, i.e. formation of micellar aggregates, is not accounted for. Supramolecular assemblies may behave pronouncedly different compared to single molecules.

The suggested cut-off of log  $K_{OC} < 4.5$  for mobility in raw water (surface and groundwater) corresponds approximately to the lower 35<sup>th</sup> percentile (i.e. raw water concentration of 4.5% of STP influent) of the sample of 64 substances. With regard to the set of 64 model compounds this means that compounds with raw water concentration of about 4.5% of STP influent and lower would be discarded as being not *mobile*. 65% of the 64 model compounds would be regarded as *mobile* with raw water concentrations between approximately 4.8% to 20% (peak for groundwater) of the STP influent concentration.

To compare predicted concentrations in surface water and groundwater with measured values from monitoring programs, data from Loos et al. for polar organic persistent pollutants in river water (2009) and groundwater (2010) complemented by monitoring data from IOW/INERIS (2009) on priority substances within the context of the Water Framework Directive were reviewed. Data found for four relevant compounds were added to the plot of Figure 10. Diuron, DEHP and Triclosan were already within the set of

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<sup>22</sup> [http://www.pesticideinfo.org/Docs/ref\\_regulatoryCA.html#CAGroundWater](http://www.pesticideinfo.org/Docs/ref_regulatoryCA.html#CAGroundWater)

64 compounds used for model calculations. However, the log  $K_{OC}$  value as reported by ECHA-CHEM (key study) and used as input for model calculations was 2.92 (from HPLC screening method). Reviewing the data, another valid study summary (non-key) is available, where  $K_{OC}$  was determined by batch equilibrium with sewage sludge suspended solids with a log-value of 4.7. It is questionable, though, if this result can be translated 1:1 to soil. With both studies having their limitations, the arithmetic mean of both  $K_{OC}$  values was taken (4.4) and the resulting data point added to the plot. The later (see section 4.2) identified result for mean log  $K_{OC}$  from a batch equilibrium test with 2 soils of 4.18 (Karnjanapiboonwong, et al., 2010) corroborates this approach. Nonylphenol was not included in the sample, but input data could be retrieved. The corresponding ECETOC TRA calculations were performed separately and data were added to the plot of Figure 10, giving a total of 66 compounds (double-count for Tricolosan, due to different log  $K_{OC}$  values as explained).

For diuron (log  $K_{OC}$  2.6) the 90<sup>th</sup> percentile of groundwater concentrations was 3 ng/L (maximum value found 279 ng/L, frequency 28.7%), the corresponding value for nonylphenol (log  $K_{OC}$  3.7) was 39 ng/L (maximum value found 3850 ng/L, frequency 11.0%), both determined from 164 samples (Loos, et al., 2010). The values for surface water (90<sup>th</sup> percentile) determined by Loos et al. (n= 122; 2009) for diuron and nonylphenol were 115 ng/L (maximum value found 864 ng/L, frequency 70.0%) and 268 ng/L (maximum value found 4489 ng/L, frequency 29.0%), respectively and thus considerably higher than groundwater concentrations. Surface water concentrations for both compounds are essentially corroborated by the values reported within the context of the Water Framework Directive (IOW/INERIS, 2009). Concluding from screening tests according to the P assessment outlined above, diuron is *persistent* and nonylphenol inherently biodegradable.

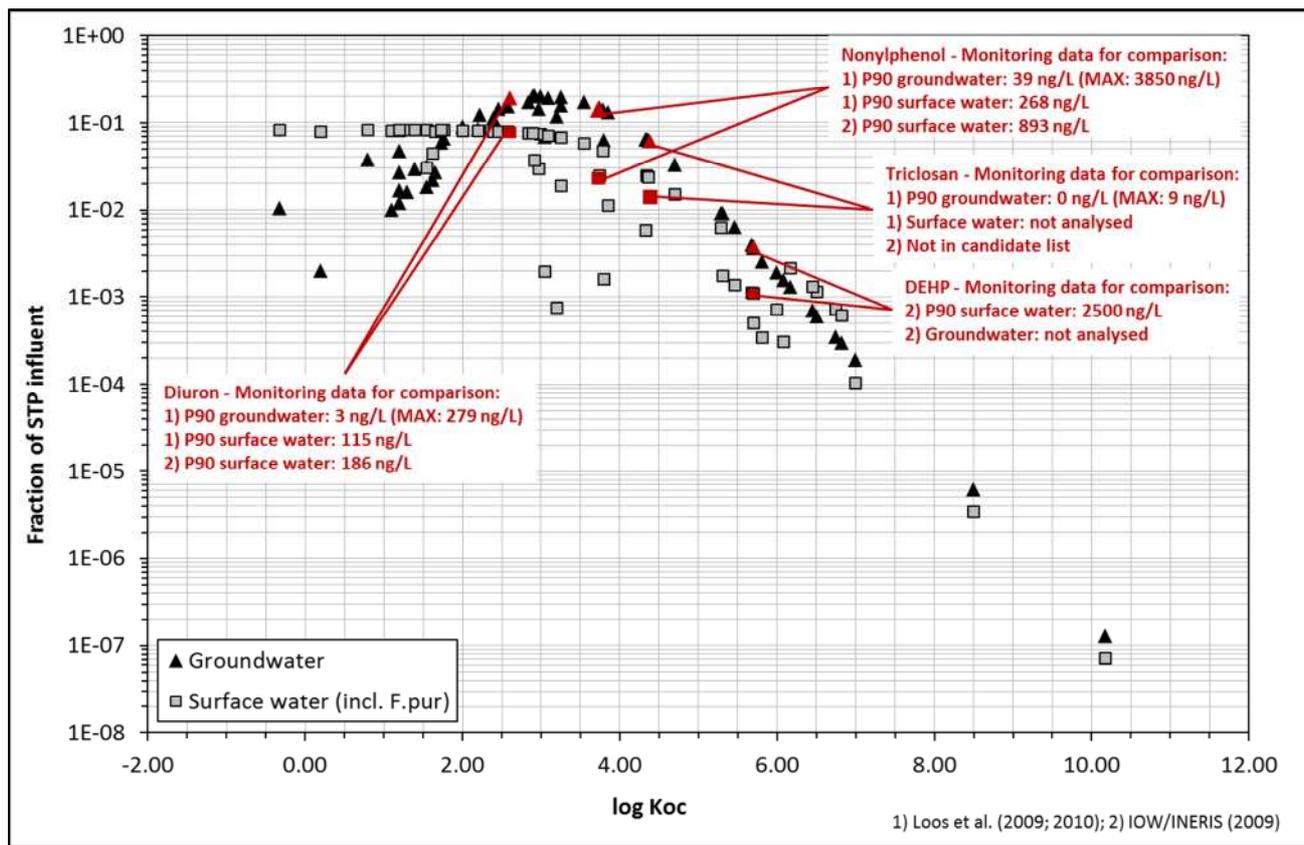


Figure 10: Fraction of STP influent in surface water (including purification factor) and groundwater as a function of  $\log K_{oc}$

Thus, for the two compounds diuron and nonylphenol, predicted values for groundwater (19.3% and 14.1% of STP influent, respectively) were higher than for surface water (7.8% and 2.3% of STP influent, respectively) while measured concentrations were higher in surface water<sup>23,24,25</sup>. This corroborates the assumption stated above that groundwater concentrations are overestimated even more than surface water concentrations by ECETOC TRA/EUSES.

Another compound with monitoring data is Triclosan.  $\log K_{oc}$  of this compound is considerably higher (4.38) and indeed environmental concentrations in water seem to be much lower. No data on surface water are reported by Loos et al. (2009). In contrast to the other substances, triclosan was not a candidate in the monitoring-based ranking for priority substances under the Water Framework Directive (IOW/INERIS, 2009), possibly indicating a low occurrence in surface water. A more detailed analysis of monitoring data in

<sup>23</sup> Similar concentrations as reported in figure 9 for nonylphenol (groundwater) are documented in literature:

<http://www.hindawi.com/journals/tswj/2002/394274/abs/> (visited July, 10, 2013)

<sup>24</sup> Similar concentrations as reported in figure 9 for nonylphenol (surface water) are documented in literature:

<http://www.socopse.se/download/18.3cd20f1b1243376c1168000577/1256019490924/SR+Nonylphenols.pdf> (visited July, 10, 2013)

<sup>25</sup> Identical observations on diuron regarding the ratio from surface water to groundwater were reported in literature:

<http://www.ncbi.nlm.nih.gov/pubmed/12549556> (visited July, 10, 2013)

section 4.2.6 demonstrates that Triclosan occurs in surface waters, however predominantly in low concentrations. In groundwater, the 90<sup>th</sup> percentile was 0, the maximum concentration found was 9 ng/L and the frequency of detection (n= 164) was 1.8% (Loos, et al., 2010). Concluding from screening tests according to the P assessment outlined above, triclosan is *persistent*. Due to its everyday use in many products (e.g. detergents and cosmetics), a widespread exposure must be assumed. Thus, the low concentrations found for triclosan in groundwater and mostly also in surface water (see section 4.2.6) are in support of the suggested cut-off of  $\log K_{OC} < 4.5$  for mobility in raw water<sup>26</sup>.

For the third compound, DEHP, no sufficiently qualified reports on monitoring data for groundwater were found. Due to its high  $\log K_{OC}$  of 5.7 contamination of groundwater is assumed to be highly unlikely. However, the 90<sup>th</sup> percentile for surface water reported within the context of the Water Framework Directive prioritisation (IOW/INERIS, 2009) is high compared to the other substances (2.5 µg/L). However, there are three arguments to give this result/example not too much weight:

1. DEHP is produced at very high tonnages and due to its widespread distribution in articles exceptionally high exposure may be superimposing inherent mobility properties.
2. In France (origin of many analytical data for DEHP in surface water), the reliability of the data has been seriously questioned by a French governmental agency: “En eau, des phtalates sont quantifiés mais associés à de forts doutes analytiques. ... Contamination possible des échantillons par le matériel de prélèvement et d'analyse”<sup>27</sup> (i.e. contamination from sampling equipment is considered a possibility).
3. For DEHP it may be assumed that this substances deviates in behaviour from substances currently covered in this project: single molecules may aggregate to build up a colloid structure (micelles). This may significantly change environmental fate properties and explain some occurrence in ground and surface water (ECB, 2008).

Thus, the few monitoring data on surface and groundwater concentrations available for compounds close to the identified cut-off of  $\log K_{OC} < 4.5$  for mobility in raw water essentially support this approach or are at least not strong enough or explained by exceptions (DEHP) to put it into question.

### Systematic Mobility Assessment

Before an assessment of mobility, persistence must have been assessed. As outlined in section 2.2.3, in order to determine a cut-off for mobility (in terms of  $\log K_{OC}$ ) persistence was assumed. The cut-off for mobility ( $\log K_{OC} < 4.5$ ) is therefore only valid for *persistent* compounds. If a substance was determined not to be *persistent* beforehand, it does not fulfil a necessary property of a PMT substance, and no assessment of mobility or toxicity is needed.

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<sup>26</sup> U.S. EPA comments on Trichlosan: “Considering the low probability of triclosan being released into household wastewater and surface waters from EPA-regulated antimicrobial uses, the Agency also concluded that chronic aquatic risks are unlikely originating from consumer uses of triclosan-treated plastic and textile items. Therefore, the Agency can reasonably conclude that the antimicrobial uses of triclosan (e.g., triclosan-treated plastic and textile items in households) are unlikely to contribute significant quantities of triclosan into household wastewater and eventually in surface water.”

[http://www.epa.gov/oppsrrd1/REDS/factsheets/triclosan\\_fs.htm](http://www.epa.gov/oppsrrd1/REDS/factsheets/triclosan_fs.htm) (visited July, 10, 2013)

<sup>27</sup> <http://www.developpement-durable.gouv.fr/IMG/bilan%20pres%20mico%20.pdf> (visited July, 10, 2013)

Further, substance type evaluation and – directly related to this – the applicability domain of the PMT assessment methodology is closely related to the mobility assessment (especially with regard to a possible potential for ionisation) and must therefore be preceding the latter. Therefore, assessment of a relevant ionisation potential is explained here in detail and other aspects of applicability are shortly outlined here and specified in more detail in section 2.5.1. Naturally, it is beneficial to check the applicability domain already before assessment of persistence.

Substance types being currently out of the applicability domain of the assessment or which rather may be assessed under certain conditions, only (see section 2.5.1 for details):

The following compounds are excluded right away:

- Inorganic/organometallic compounds
- UVCBs (substances with unknown or variable composition, complex reaction products or biological materials)
- Multi-constituent substances
- Surface active compounds (detergent-like properties)

Transition metal complexes with organic ligands can be evaluated only if experimental data on biodegradability (only the organic constituents may be assessed) and adsorption are available (QSAR not applicable; see section 2.5.1). Similarly, toxicity assessment must be based on experimental values only, as e.g. CRAMER classification based on Toxtree<sup>28</sup> will neither be possible (also here, SMILES codes are the prerequisite for application of the respective decision tree structure).

For salts dissociating upon solution in water, each constituent has to be assessed separately: Due to environmental distribution and partitioning as well as buffer effects, anions and cations of soluble salts will distribute separately. An example for this is diphosphoric acid, compd. with piperazine (66034-17-1). Here the anion is inorganic (i.e. not in the scope of the assessment), while the cation (piperazine) is relevant (basic amine). In the assessment tool developed in this project (see section 3), by user dialogue the substance type is determined and in such case corresponding advice is given.

In this tool (see section 3), by user dialog it is further determined if the substance is ionic, zwitterionic or ionisable in the environmentally most relevant pH range (pH 6-8). According to REACH guidance on Information Requirements and Chemical Safety Assessment, Chapter R.7a (page 58), the environmentally relevant pH range is broader, namely from pH 5 to pH 9. For assessment of mobility we narrow this range to pH 6 to pH 8, which likely will prevail in surface waters and agricultural areas. Thus, while dissociation may still be relevant for certain habitats of more extreme pH, restricting the assessment to the most relevant pH range of pH 6-8 is a compromise between taking account of environmentally relevant physico-chemical properties and keeping the applicability domain for assessment as broad as possible<sup>29</sup>.

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<sup>28</sup> [http://ihcp.jrc.ec.europa.eu/our\\_labs/computational\\_toxicology/qsar\\_tools/toxtree](http://ihcp.jrc.ec.europa.eu/our_labs/computational_toxicology/qsar_tools/toxtree)

<sup>29</sup> For ionisable substances, only  $K_{OC}$  values are accepted which were experimentally determined using the batch equilibrium method. As those values are lacking for many substances, defining ionisability in a very strict sense (e.g. pH 5 to 9, dissociation degree less than 10%) would lead to a considerable number of substances which currently could not be evaluated for PMT properties because a suitable  $K_{OC}$  value is missing.

Within the tool, the user is given advice how to assess ionisability (i.e. acting as an acid or base) in the specified pH range. Because determination of ionisability is of high importance for evaluation of data on water solubility and adsorption, it is described here in more detail.

Basically, ionisability (pH range 6-8) is determined by the size of  $pK_a$  values: A substance is determined to be ionisable, if the  $pK_a$  for acidic functionality  $<8.5$  and/or  $pK_a$  for alkaline functionality  $>5.5$ . This corresponds to a dissociation degree of  $< 24\%$  for the pH range 6-8. In case experimentally determined  $pK_a$  value are not available or the user does not know if these values refer to acidic or alkaline functionality, the user is requested to use the “[ACE and JChem acidity and basicity calculator](#)”, with a SMILES code for the substance derived from e.g. [ChemIDplus](#). A pronounced benefit of this tool is the nomenclature of resulting  $pK_a$  -estimates: A  $pK_a$  is called

- $pK_a$  if it is associated with **acidic functionality** of a compound, while it is called
- $pK_b$  (deviating from the scientific definition  $pK_a + pK_b = 14$  at room temperature) when referring to **alkaline functionality**.

Because it can be very difficult to judge from structure if a compound will act as acid or base (in fact, both can be true at the same time for zwitterionic substances), this is exactly what is needed here for assessment of the ionisation potential.

Taking as an example ethanolamine (CAS: 141-43-5), the SMILES code provided by [ChemIDplus](#) is **C(CO)N** which may simply be copied into the clipboard. Assessing then the “[ACE and JChem acidity and basicity calculator](#)” in “**JChem.**” mode (eventual security warnings must be ignored<sup>30</sup>), by activating the paste button the structure will be drawn (and eventually may easily be edited: This may be necessary for a salt of an acid to obtain the  $pK_a$  value for the carboxylic acid group: the counter ion has to be eliminated using the eraser function and the carboxylic acid group be neutralized using the right mouse button menu to add a proton)<sup>31</sup>. By clicking on the button “View pKas” a table opens with the following information:

Table 21: *ACE acidity and basicity calculator* (JChem.-mode) output using ethanolamine as an example

Atom	$pK_a$	$pK_b$
C1	35.7	
C2	35.7	
O3	15.6	-2.5
N4	34.8	9.6

<sup>30</sup> A current Java version must be installed in the web-browser used. Java settings can be modified using the [Java control panel](#) (system settings / Java): In the security folder, the web address of the ACE tool can be added to the exceptions field to avoid problems with security settings.

<sup>31</sup> The same applies to [salts from compounds acting as bases](#), like e.g. butylamine hydrochloride (SMILES: [Cl-].CCCC[NH3+]).

*The molecular  $pK_a$  values: 15.6 (atom 3), 34.8 (atom 4), 35.7 (atom 1).*

*The molecular  $pK_b$  values: 9.6 (atom 4), -2.5 (atom 3).*

The lowest “molecular  $pK_a$ ” as well as the highest “molecular  $pK_b$ ” as given within the text below the tabular output have to be considered here. It is important to remember that  $pK_a$  for a basic functional group is referred to as  $pK_b$  using the ACE and JChem acidity and basicity calculator. The given example would be evaluated the following way:

1. Potential acidity (acting as acid): This is regarded to be relevant if  $pK_a$  is in the most common range of environmental pH (6-8). At  $pK_a = \text{pH}$ , 50% of the compound would be dissociated and the acidic property would be relevant. If  $pK_a \geq \text{pH} + 0.5$ , less than 24% would be dissociated. As the highest pH considered here is 8, a  $pK_a \geq 8.5$  is considered not to be relevant for the current assessment. Thus, for the example above (ethanolamine) no relevant acidic dissociation behaviour can be expected.
2. Potential basicity (alkaline functionality): This will only be relevant if  $pK_b$  is in the most common range of environmental pH (6-8). At  $pK_b = \text{pH}$ , 50% of the compound would be protonated and the alkaline functionality would be relevant. If  $pK_b \leq \text{pH} - 0.5$ , less than 24% would be protonated. As the lowest pH considered here is 6, a  $pK_b \leq 5.5$  is considered not to be relevant for the current assessment. Thus, for the example above (ethanolamine) the alkaline functionality will be relevant due to a calculated  $pK_b$  of 9.6.

Further on, generally compounds with a water solubility of  $\leq 150 \mu\text{g/L}$  are assessed as not M due to the low water solubility, potential for raw water contamination is very low. However, for ionisable compounds with a water solubility of lower than or equal to the cut-off ( $150 \mu\text{g/L}$ ), it is important at what pH the water solubility was determined. Ionisation leads to a significant increase in polarity and thus water solubility. Water solubility would be underestimated if determined at a pH at which predominantly the non-ionised form of an ionisable compound was present. Therefore, in the PMT assessment tool (see section 3) the user is asked to provide the pH the water solubility was determined at. Taking into consideration the environmentally relevant pH range of 5-9, and the lowest  $pK_a$  as well as highest  $pK_b$  entered by the user beforehand, the tool evaluates if the solubility is valid; or rather a possibly higher solubility could have been obtained if an appropriate pH value would have been chosen. Generally, for appropriate determination of water solubility, for compounds acting as bases pH should be lower than  $pK_a$  for solubility testing (within the range 5-9), whilst for compounds acting as acids, pH for solubility testing should be higher than  $pK_a$  (within the range 5-9). In case the pH-value for determination of water solubility was not chosen appropriately, or in case a pH value was not reported within the experimental data set associated with water solubility determination, the water solubility cut-off is invalid, i.e. the compound must be treated as if it would have a water solubility above  $150 \mu\text{g/L}$ .

The information on the substance type (ionisable or not within pH 6-8) must be considered for evaluation of data on mobility (adsorption/desorption). Therefore, in the tool described in section 3 this information is carried forward to the actual mobility evaluation module.

As outlined in section 2.2.2,  $K_{OC}$  was determined as the relevant determinant for mobility in raw water. Details on determination of  $K_{OC}$  are also given in this section, but are shortly summarized here, taking account of the applicability of each method with regard to substance properties (especially ionisation potential):

OECD test guideline 106: Adsorption-Desorption using a batch equilibrium method

For all compounds (ionic, zwitterionic and non-ionisable) this is the most reliable currently available standardized method for determination of  $K_{OC}$ .

OECD test guideline 121: Estimation of  $K_{OC}$  using High Performance Liquid Chromatography

This is a screening test method. It was developed for neutral compounds and its use for ionisable substances is severely limited. We advise against this method for ionisable compounds out of the following reasons: Due to the column matrix being neutral, at least for soil with its surplus of negative charge  $K_{OC}$  will be overestimated in most instances for negatively charged compounds and severely underestimated for positively charged substances.

Calculated:

$K_{OC}$  may be calculated for organic, non-charged molecules with reasonable accuracy. Meanwhile, calculation methods for  $K_{OC}$  based on chemical structure alone yield often better results than regression based on  $\log K_{OW}$ , especially for certain substance types. Structure based methods are implemented in freely available software packages, e.g.:

1. KOCWIN within US-EPA [EPI suite](#): Molecular connectivity index method (MCI) according to Meylan et al., 1992
2. ChemProp software (available from [Helmholtz Centre For Environmental Research](#)), implementing as a structure based method the one published by Schüürmann et al. (2006).

If both, an experimentally determined value for  $K_{OC}$  and (a) calculated value(s) are available, the experimental value should be preferred if determined in a reliable study. If no reliable experimentally determined values are available, for non-ionisable compounds a value calculated from structure may be preferable if within the applicability domain of the QSAR model.

Thus, while non-ionisable organic compounds can be evaluated independently from the way  $K_{OC}$  was determined, for ionisable compounds (within pH range 6 to 8) a  $K_{OC}$  value determined by the batch equilibrium method is generally needed. If this value is lacking, the ionisable compound cannot currently be assessed by this methodology. It must be mentioned here that European REACH regulation in conjunction with REACH guidance document R.7a (ECHA, European Chemical Agency, 2014) requires experimentally determined values for  $K_{OC}$  for ionisable compounds at a tonnage level of  $\geq 10$  t/a. OECD test guideline 121 (Estimation of  $K_{OC}$  using High Performance Liquid Chromatography) is a screening test method only and not suitable for ionisable chemicals.

With an appropriately determined experimental value available, also ionic, zwitterionic and ionisable substances may be fully assessed for mobility. If several, equally reliable values for  $K_{OC}$  are available – which is often the case as values for different soils are usually determined in studies according to OECD 106 (batch equilibrium test) – the most relevant should be selected. If it is not obvious which of several determined  $K_{OC}$  values for different soils is the most relevant, the geometric mean value should be chosen, which is equivalent to the arithmetic mean of the log-values.

The final mobility assessment is straight forward: *Persistent* compounds with  $\log K_{OC} < 4.5$  are regarded to be *mobile* (assignment of M property), while *persistent* compounds with  $\log K_{OC} \geq 4.5$  are not. A  $\log K_{OC}$  below 4.5 indicates a mobility sufficiently high to leach into groundwater from field applications (e.g. sewage sludge) within a longer time frame or to be of relevance for surface water by entering from sewage treatment plant effluents. At this stage, the substance would have been determined to be *persistent* and *mobile* (PM). The assessment should be continued with Exposure Evaluation Tier 2 (E2) to determine if

environmental exposure is assumed to be potentially relevant (then, also assessment of toxicity is required, see section 2.3) or not. Thus, if relevant releases to the environment can be excluded, an evaluation of toxicity will not be necessary.

In case the substance in question was determined to be immobile with regard to raw water contamination, no further assessment is required because one necessary property for a PMT substance, namely mobility, is not fulfilled.

#### 2.2.4 Summary and discussion on mobility

In this project we provide a methodology to identify *persistent, mobile* and *toxic* substances (PMT substances) in raw water, as occurrence of such substances should be avoided. The focus is on substances in the regulatory framework of REACH. Accordingly, the identification of substance-specific (PMT) properties should be linked to information as provided under REACH regulation and guidances.

Sections 2.2.1 to 2.2.3 of this report specifically relate to mobility. In these sections we addressed:

- parameters determining mobility,
- data availability under REACH and existing testing guidelines on adsorption-desorption,
- qualification of mobility parameters as generated with REACH exposure assessment tools (EUSES/TRA),
- definition and handling of mobility in former related projects and scientific literature.

We further discriminated mobility in surface and in groundwater and we provided demarcations for aspects of mobility not covered in this project.

With this background, we developed a methodology for mobility assessment in section 2.2.3.

Mobility is defined as “the tendency for a chemical to move in the environment” (US-EPA, 2012)<sup>32</sup> and is therefore associated with the potential for relocation from one environmental compartment to another. The degree of mobility is determined by a complex interplay of substance specific physico-chemical properties and the environment (media and their composition, temperature). We give an outline of the interdependencies of Henry’s law constant (dimensionless partition coefficient air / water), the partition coefficient octanol / water ( $K_{OW}$ ), the partition coefficient octanol / air ( $K_{oct-air}$ ), the distribution coefficient for adsorption ( $K_d$ ) and the organic carbon normalised adsorption coefficient ( $K_{OC}$ ) of a chemical. Different binding mechanisms of chemicals on soils and pH dependence of binding by ionisable compounds (acting as acids or bases) are explained. We conclude that the degree of mobility in raw water inversely depends on the degree of “net adsorption” to particulate matter, where net adsorption takes into account both, adsorption and desorption processes over time. Thereby, mobility in the water cycle is quantified mainly by the  $K_{OC}$  of a chemical.

Within REACH, availability of data associated with mobility will often be restricted to log  $K_{OW}$ , which however is not appropriate to estimate adsorption for ionisable compounds. For the latter, OECD 106 (Adsorption-Desorption using a batch equilibrium method) is the appropriate testing guideline for

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<sup>32</sup> [www.epa.gov/dfe/pubs/tools/ctsa/ch5/mod5-3.pdf](http://www.epa.gov/dfe/pubs/tools/ctsa/ch5/mod5-3.pdf)

determining adsorption to soil. OECD 121 (Estimation of  $K_{OC}$  using High Performance Liquid Chromatography) is a screening-type test which actually should be applied for neutral compounds only. REACH allows for calculation of  $K_{OC}$  for neutral compounds lacking experimentally determined values for  $K_{OC}$ .  $K_{OC}$  may be calculated for most neutral organic compounds with sufficient accuracy from  $\log K_{OW}$  or by methods based on chemical structure alone, the latter often yielding better results, especially for certain substance types.

Using REACH exposure assessment tools (EUSES/TRA) and corresponding background material, mobility parameters were qualified. With regard to surface water, concentration will be high if adsorption to organic matter (particulates, sludge, sediment) is low (low  $K_{OC}$ , or low  $K_{OW}$  as a surrogate value) and Henry's law constant is low and there is a minimum water solubility. It is obvious however, that water solubility is not the decisive criterion, rather, the ratio between vapour pressure and water solubility (i.e. Henry's law constant) is. Due to  $K_{OW}$  being not independent from water solubility, decreasing water solubility implies for most neutral organic chemicals increasing  $K_{OW}$  (see e.g. Chiou et al., 1977). Thus, water solubility is indirectly quantitatively incorporated while considering the two decisive criteria, Henry's law constant and  $K_{OW}$  (preferably  $K_{OC}$ ). A significant effect of Henry's law constant ( $H$ ) becomes obvious however only at values for  $\log H$  somewhere between 1 and 2 (10 and 100 Pa·m<sup>3</sup>/mol at 12°C, respectively) and above, driving a relevant fraction into the air compartment. On the other hand,  $\log K_{OW}$  (as a surrogate for  $K_{OC}$ ) leads to a significant reduction of the water phase fraction only at values somewhere between  $\log K_{OW}$  of 4 to 5 and higher. A chemical's concentration in groundwater is calculated within EUSES/TRA in the course of assessing the "drinking water pathway" (human via the environment). The most important pathway for soil exposure (and concomitant exposure of groundwater by leaching of chemicals through soil) is the application of sewage sludge to field. This holds true even for substances with high Henry's law constant where deposition from air to soil might be important but obviously has no relevant impact. With increasing  $K_{OC}$  the fraction of chemical bound to sewage sludge and thus the amount deposited on agricultural fields increases, implying accumulation over the years. Correspondingly, soil pore water concentration taken as a measure for groundwater concentration by EUSES/TRA increases with increasing  $K_{OC}$ , leading to a shift in partitioning from surface water to groundwater up to a maximum value (see below). Again, water solubility was found to play a very minor role in the whole process apart from being one crucial parameter for Henry's law constant (together with vapour pressure) determining partitioning to air relevant especially for the eliminated compound fraction in sewage treatment plants.

In a preceding work aimed to establish screening parameters for substances with raw water relevance, IfW (IfW, 2010; 2011) developed an integrative scoring system for drinking (raw) water relevance. The work was however focussing on surface water only, integrating degradation time (DegT50),  $\log K_{OW}$  and water solubility. Main weaknesses of this approach are that two properties closely linked to one another ( $K_{OW}$  and water solubility) are scored independently ("double-weighting") and further, that an independent criterion (persistence) with a potential for exclusion of *non-persistent* compounds right away from the start is integrated in an overall score. A further approach is outlined focussing on surface water (Götz, et al., 2010) using a simple Mackay-type model with four compartments (water, air, sediment, and suspended particles) for distribution modelling and was assessed to be leading to similar results like EUSES/TRA in respect to surface water.

Regarding groundwater, Gustafson (1989) investigated several physicochemical factors in addition to half-life in soil influencing leachability of pesticides to groundwater and found  $K_{OC}$  (besides DegT50 in soil) the only determinant allowing for separation of "leaching" pesticides from "non-leaching" ones. He derived a formula integrating DegT50 and  $K_{OC}$ , allowing for determination of a  $K_{OC}$  for *persistent* compounds at and

above which leaching of pesticides to groundwater can be excluded with reasonable confidence (approximately  $\log K_{OC} \geq 3.7$ ). A further and complementary approach is considered, outlined by Haberer and Böttcher (1996). Retardation factors are implied which slow down the passive flow rate of chemicals with water through non-saturated soils because of chemical adsorption onto soil. Using this approach with conservative assumptions for the flow rate of water through soil, a  $\log K_{OC}$  of 3.7 and 4.5 may be assigned a time period of 80 and 159 years, respectively, needed for a (*persistent*) chemical to move 1 m into the soil.

With  $K_{OC}$  being the principal parameter for mobility in the water phase, it was still ambiguous how to define cut-off criteria given the shift in partitioning from surface to groundwater (via sludge to field pathway) with increasing  $K_{OC}$ . To this end, within this project targeted exemplary exposure estimations using defined artificial input parameters were performed for 64 compounds with reliable physico-chemical and environmental fate data retrieved via eChemPortal from ECHA CHEM using ECETOC TRA model. This software is generally used within REACH for exposure estimation according to guidance document R.16. Within this model, considered basic compartments/pathways with relevance to the water cycle are the sewage treatment plant (STP), surface water receiving STP effluent, STP sludge exposure on fields and the field to groundwater pathway as well as volatilisation to air and concomitant deposition from air to soil. Chemicals concentration in raw water are estimated for both, raw water originating from surface water and raw water originating from groundwater with the higher value taken as “drinking water” concentration (actually raw water). For all 64 chemicals (covering a wide range of the physico-chemical property space) an identical release pattern was assumed and degradation was generally set to zero to exclude all parameters influencing raw water concentration other than substance specific physico-chemical properties. Thus, the sole removal processes in the STP (i.e. reducing the discharge into surface water) were emission to air (driven by Henry’s law constant, HLC) and adsorption to sludge (driven by  $K_{OC}$ ).

In result, for these compounds  $K_{OC}$  must clearly be regarded as the key parameter for mobility and the sole one correlating with concentrations for surface and groundwater.  $K_{OW}$  may at best be regarded as indicative, but does not describe all of the processes considered relevant. Water solubility and HLC, in contrast, are clearly not key parameters, but HLC may have some mitigating effect for surface water concentrations at high values. As expected, groundwater concentrations are below surface water concentrations at very low  $\log K_{OC}$  values and steadily increase with increasing  $K_{OC}$  up to a maximum value at about  $\log K_{OC}$  of 3.0. The intersection with surface water concentration (approximately equal concentration) is at a  $\log K_{OC}$  of about 2.4. At  $\log K_{OC}$  values above 3.0, groundwater concentrations decline with ever increasing slope until a nearly constant decline is reached at about  $\log K_{OC}$  of 4.5. Surface water concentration is approximately constant up to  $\log K_{OC}$  of 3.0 and then declines. Concluding from these results, for screening on substances judged to be sufficiently mobile to potentially occur in raw water, a cut-off based on  $\log K_{OC}$  was chosen: *Persistent* compounds are regarded as *mobile* in surface and groundwater, if their  $\log K_{OC}$  is  $< 4.5$ .

Monitoring data from eight model compounds were used to verify model calculations and the suitability of the chosen cut-off level. The few data available point to a pronounced overestimation of groundwater concentrations relative to concentrations in surface water, probably due to the oversimplification of setting the concentration in soil porewater as equal to the concentration in groundwater within TRA / EUSES. Overall however, the few monitoring data available for compounds with  $K_{OC}$  values close to the cut-off level of 4.5 essentially support this value chosen for screening on mobility.

With regard to media, our assessment is focused on mobility in the water cycle. Mobility in the atmosphere, which is decisive for long-range transport of *persistent* chemicals into remote areas, was not further regarded here. Net loss into the atmosphere for chemicals with high Henry’s law constant however was, but found to

be not decisive in most cases (see above). Further, bank storage water is not considered here as source of raw water on its own. Rather it is taken as a special form of surface water, which may be regarded a reasonable worst case.

The mobility evaluation scheme as proposed in this project (see section 2.2.3 and flow chart Figure 11) is therefore solely relying on the  $\log K_{OC}$  cut-off value of 4.5, below which substances are assumed to be *mobile* in water (M). Substances with a water solubility of  $\leq 150 \mu\text{g/L}$  are assessed as NOT M. Only chemicals above this minimum water solubility are assumed to potentially occur in raw water to an appreciable extent, independent of their other properties. Most importantly however, mobility assessment also takes into account if a substance has a potential to ionise within the environmentally most relevant range of pH (6.0 to 8.0). For compounds without experimentally determined  $K_{OC}$  values, calculation of  $K_{OC}$  is only admitted if no relevant potential for ionisation was determined beforehand. Ionisable substances without experimentally determined  $K_{OC}$  currently cannot be assessed as reliable methods for calculation are lacking.

The flowchart below summarizes the decision process. However, some details, minor shortcuts and additional options are eliminated in the flowchart for reasons of clarity. The flowchart covers the mobility assessment. For details on the applicability domain for the proposed PMT assessment in general, see section 2.5.1.

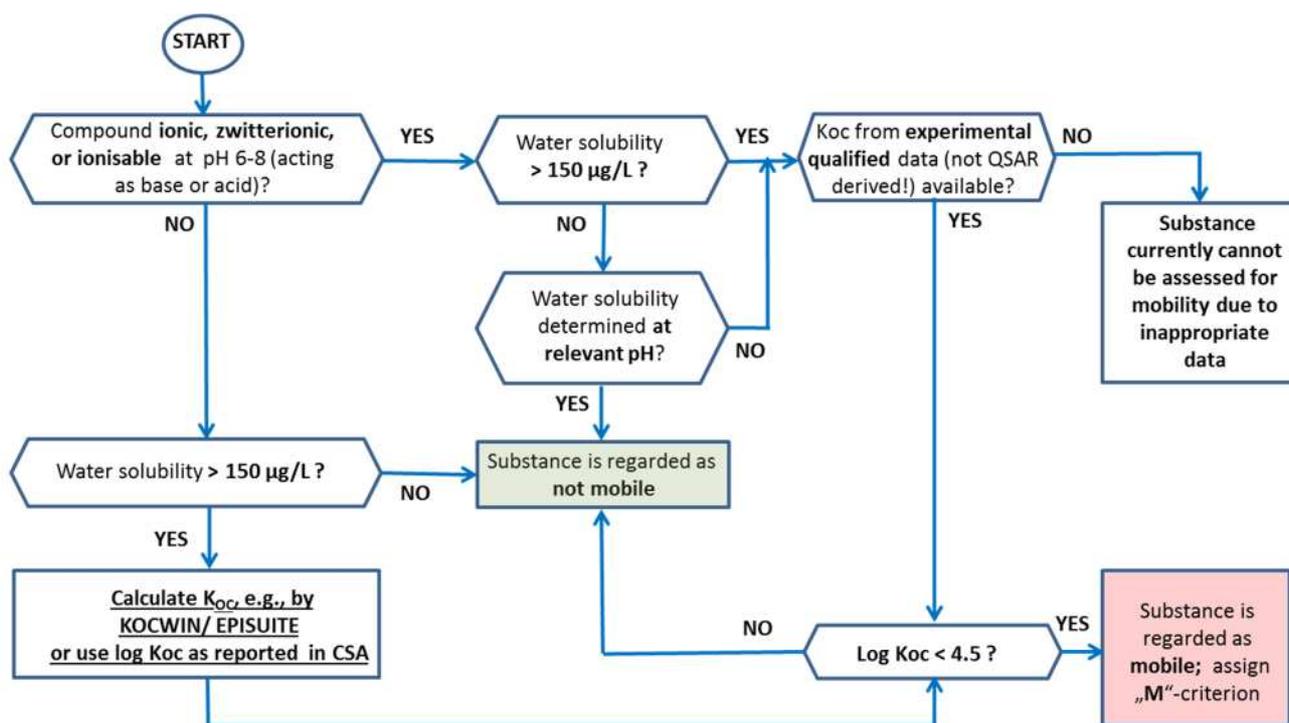


Figure 11: Flowchart outlining mobility assessment. For the sake of clarity, the flowchart is slightly simplified compared to the actual decision tree outlined in the text section.

Finally, it must be noted that all considerations leading to the cut-off value of  $\log K_{OC}$  4.5 for mobility were based on European standard soil (composition, pH) as specified in REACH guidance document on information requirements and chemical safety assessment, part R.16 (ECHA, European Chemicals Agency, 2012e) or were based on intermediate soil properties (e.g. percolation rate of water through soil). The same holds true for adsorption processes on sludge and sediment. While this will satisfy most environmental

scenarios, especially soil composition and pH may vary dramatically and extreme conditions may not be sufficiently covered in spite of the conservativeness of the cut-off value.

Looking at this cut-off value of  $K_{OC} < 4.5$ , the identical numerical value of 4.5 may come into mind, if one remembers the screening cut-off for bioaccumulative substances within PBT assessment ( $\log K_{OW} > 4.5$ ). The question will be raised, whether there is a possible overlap between physico-chemical properties pointing to a bioaccumulation potential and those indicating mobility.

Table 22 outlines criteria used for assessment of bioaccumulative properties and mobility. Screening criterion for bioaccumulation is the  $\log K_{ow}$ : according to REACH guidance, compounds with a  $\log K_{ow}$  larger than 4.5 are regarded as bioaccumulative.

Table 22: Comparison of PBT and PMT criteria for bioaccumulation and mobility

PBT	Bioaccumulation	PMT	Mobility
Criteria according to REACH Annex XIII	Bio-concentration factor (BCF) > 2000	Criteria defined for PMT assessment	$\log K_{OC} < 4.5$
Screening criteria according to REACH guidance	$\log K_{ow} > 4.5$		

As outlined above, the most important parameter inversely determining mobility, namely adsorption quantified mostly in form of the organic carbon normalized adsorption coefficient,  $K_{OC}$ , is not independent from  $\log K_{OW}$  for neutral, non-ionisable compounds. Depending on the compound class, several different linear regression equations have been developed to estimate  $K_{OC}$  from  $K_{OW}$ , e.g.

- 1)  $K_{OC} = 0.41 * K_{OW}$ , valid for pure hydrocarbons without heteroatoms (Schüürmann, et al., 2007)
- 2)  $\log K_{OC} = 0.81 * \log K_{OW} + 0.10$ , valid for predominantly hydrophobic chemicals (EC, 2003; Sabljčić, et al., 1995)

Taking equation 1) a  $\log K_{OC}$  of 4.5 (below of which compounds would be regarded to be *mobile*) would correspond to a  $\log K_{OW}$  of 4.89. Because the cut-off for bioaccumulation is  $\log K_{OW} > 4.5$ , there is an overlap of 0.39 log units with regard to  $K_{OW}$ . This means, that pure hydrocarbons of  $\log K_{OW}$  between 4.5 and 4.89 will be regarded as bioaccumulative and at the same time as *mobile*.

Similarly, taking equation 2) a  $\log K_{OC}$  of 4.5 (below of which compounds would be regarded to be *mobile*) would correspond to a  $\log K_{OW}$  of 5.4, i.e. an overlap of 0.9 log units with the B criterion of  $\log K_{OW} > 4.5$ . This phenomenon is schematically represented in Figure 12, using equation 2) given above for predominantly hydrophobic chemicals (Sabljčić, et al., 1995).

### Mobility versus Bioaccumulation

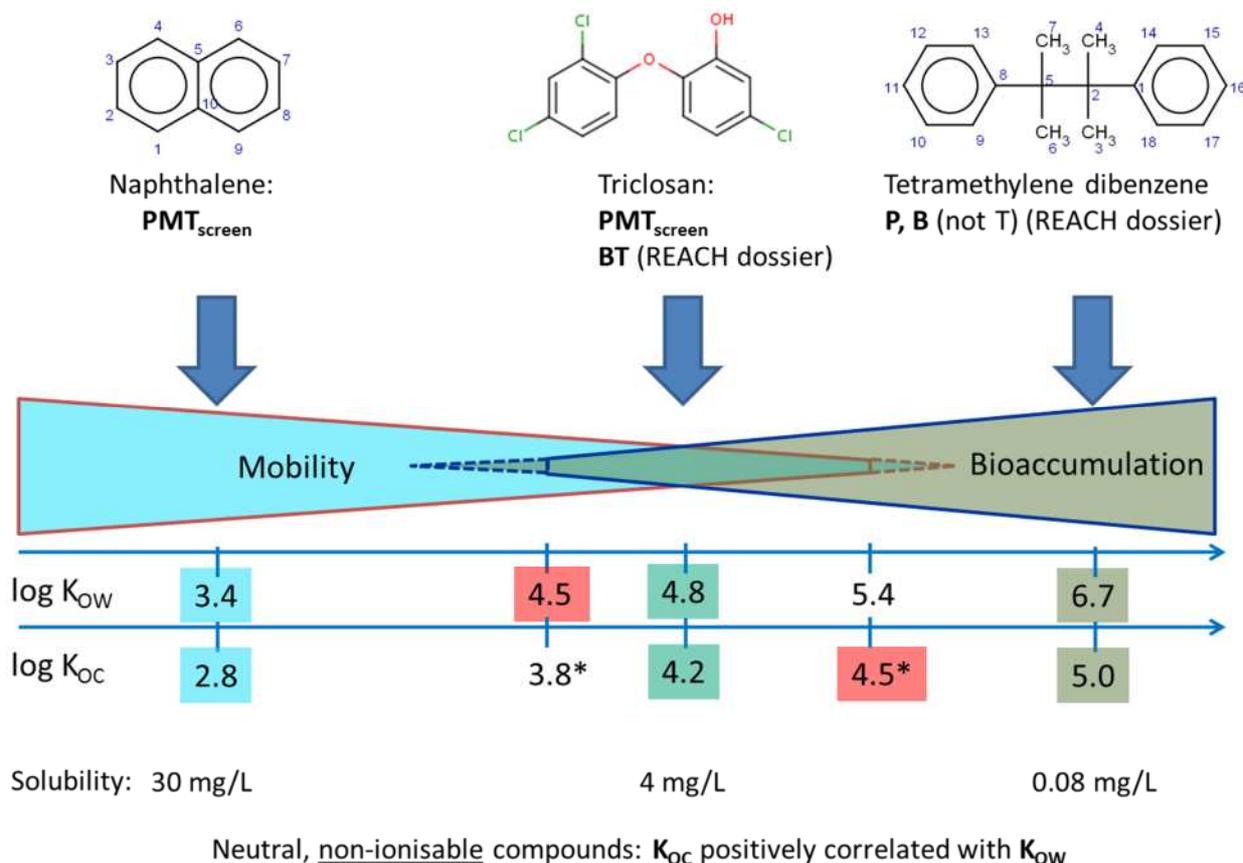


Figure 12: Schematic representation of the overlap between mobility and bioaccumulation for neutral, non-ionisable compounds.

\*) calculated from log K<sub>OW</sub> according to equation:  $\log K_{OC} = 0.81 \cdot \log K_{OW} + 0.10$ , valid for predominantly hydrophobic chemicals (EC, 2003; Sabljic et al., 1995)

Naphthalene was determined to fulfil criteria for P as well as criteria for T at the screening level (no appropriate DNEL available, T<sub>screen</sub> based on Carc.Cat. 2). With a log K<sub>OC</sub> of 2.8, M is clearly fulfilled and the log K<sub>OW</sub> is far below the screening criterion of 4.5 for B. Thus, this compound is clearly not PBT but *critical in raw water at the screening level* (PMT<sub>screen</sub>).

Triclosan is an example for the narrow range of intersection of B and M properites:

It fulfils criteria for P and M based on a log K<sub>OC</sub> of 4.2. Based on screening-level criteria, also T is fulfilled (no appropriate DNEL available, Cramer Class III, indications for endocrine disrupting properties according to Health Canada (2012)). Monitoring results on concentrations in raw water (see section 4.2.6) corroborates the rating as *critical in raw water at the screening level* (PMT<sub>screen</sub>).

At the same time, Triclosan was detected in biota including human (Health Canada, 2012) and assessed to fulfil B according to REACH based on a BCF of 2532 determined in fish. The main transformation product, methyl-Triclosan, is even more *persistent* in the environment (no photo-degradation) and seems also to bioaccumulate at a greater extent (Boehmer, et al., 2004). Based on ecotoxicity tests, it also fulfils T in the sense of PBT (most sensitive trophic level: algae).

Tetramethylene dibenzene (CAS 1889-67-4) is located at the other end of the property scale: According to the REACH dossier (PBT assessment), P and B are fulfilled. However, the  $\log K_{OC}$  is pronouncedly above the cut-off of 4.5, qualifying this compound as being *not mobile* in raw water. In addition, the water solubility of 80  $\mu\text{g/L}$  is clearly below the cut-off of 150  $\mu\text{g/L}$ . Already at lower  $\log K_{OW}$  values, the cut-off for water solubility will often limit a theoretically possible range of intersection between B and M caused by the interdependency of  $K_{OC}$  and  $K_{OW}$  for neutral organic compounds.

It must be emphasized that an intersection between B and M is only possible for neutral, organic compounds, and even for this class is not the rule but rather the exception, as it is confined to a rather narrow property range, delimited by both, the cut-off for  $\log K_{OC}$  ( $<4.5$ ) as well as the cut-off for water solubility (decreasing with increasing  $\log K_{OW}$ ) of  $>150 \mu\text{g/L}$ . However, such an intersection is possible and in fact was shown to occur. Further,  $\log K_{OW} > 4.5$  is a screening criterion for bioconcentration / bioaccumulation, only. The decisive criterion for B is a bioconcentration factor  $>2000$ , and not all compounds with  $\log K_{OW} > 4.5$  may actually fulfil this decisive criterion.

Ionisable or charged compounds mostly will not bioaccumulate to an extent as to fulfil B criteria, but will either be mobile (e.g. true for most – but not all – negatively charged compounds) or immobile (e.g. observed for compounds with several amine groups of alkaline functionality). And as a consequence of the latter, there must be compounds which are neither bioaccumulative nor mobile. Indeed, according to the evaluation of the 64 model compounds used for derivation of the mobility cut-off value of  $\log K_{OC}$  4.5 (see section 2.2.3) 12% fulfilled neither B nor M. This means that – in spite of having a  $\log K_{OW} \leq 4.5$  – their  $\log K_{OC}$  must have been  $\geq 4.5$ , i.e. largely independent from  $K_{OW}$ . The range of  $\log K_{OW}$ -values for these compounds (-0.3 – 3.4) compared to the corresponding range for  $\log K_{OC}$  (4.7 – 6.82) supports this assumption. A closer look on the individual compounds confirms that all are ionisable or ionic and with one exception they are positively charged amino compounds known to bind strongly to negatively charged soil residues.

The question arises, if such a compound can beyond that also fulfil B and M criteria at the same time. As outlined above this is possible, indeed, especially for non-ionisable compounds. This is due to the fact that for these compounds  $K_{OC}$  is not independent from  $K_{OW}$  because  $K_{OC}$  is increasing with  $K_{OW}$ , the extent of increase being compound class specific. However, compounds with  $\log K_{OW}$ -values  $> 4.5$  generally are quite hydrophobic and do not have a high water solubility. Thus, the more hydrophobic ones of these compounds would be assessed as NOT M within the PMT assessment due to their low water solubility below 150  $\mu\text{g/L}$ . In conclusion, the theoretically derived overlap between  $\log K_{OW}$  and  $\log K_{OC}$  between their respective limits of  $> 4.5$  and  $< 4.5$  is in practice reduced by the decrease in water solubility with increasing  $\log K_{OW}$ .

## 2.3 Toxicity assessment

### 2.3.1 Data availability under REACH

A REACH dossier contains information from classification and labelling which may indicate toxic properties or provides respective conclusions. Naturally, the extent of information available on toxic action depends on the tonnage specific information requirements. The higher the annual tonnage, the more in-depth information on toxicity will be available as a basis for classification and labelling. Such classifications will be useful to assign the attribute “toxic” to a substance. An occasionally available harmonised classification can be found in the [C&L Inventory database](#).

Within the PBT assessment under REACH (according to Annex XIII, REACH), the “T” attribute is assigned according to both, ecotoxic and / or toxic properties of a substance. Therefore, a T assigned with regard to PBT assessment may not be relevant in the framework of this project, where only human toxicity is of concern.

However, human toxicity criteria used to assign T within PBT assessment may be useful also within T assessment for raw water protection. The following human toxicity criteria apply for T (according to Annex XIII, REACH):

- Carcinogen Cat. 1A or 1B
- Germ cell mutagen Cat. 1A or 1B
- Toxic for reproduction Cat. 1A or 1B or 2
- Specific target organ toxicity after repeated exposure (STOT RE category 1 or 2)

However, further information under REACH from long term toxicity may also be relevant to be considered for the T criterion, if available:

According to article 14 (REACH) a chemical safety report (CSR) is required for all substances registered for more than 10 Tons/ year per registrant. Generally, the chemical safety assessment part (including the DNEL derivation) has to be performed for all those substances. However, exposure assessment and risk characterisation is necessary only for those compounds *classified as hazardous substances* according to Directive 67/548/EEC (dangerous properties directive) or Regulation (EC) 1272/2008 (CLP regulation).

A DNEL for oral, long term exposure (general population) will not be derived in many cases (ECHA, European Chemicals Agency, 2012b):

- it may not be derived, if no direct exposure of consumers as consequence of the intended uses is expected and if the pathway “humans via the environment” is not assessed (if no exposure assessment is performed for the non-classified substances, this easily results in waiving/ omission of this pathway; also see section 2.6.2),
- (overlapping to the first bullet, above: ) it may not be derived, if for the route, duration and frequency of exposure for this part of the population there is no need assumed for such a derivation (note that the criteria to decide on this are not fully defined and may deviate from the interpretation in this project),
- it may not be derived, if local long term effects after inhalation are regarded the much more relevant health endpoint compared to oral exposure,

- it may not be derived, if it is not possible to identify a DNEL (however, has to be clearly stated and fully justified),
- it may not be derived, because a substance is registered as on-site isolated intermediate,
- it may not be derived, because a substance is registered as transported isolated intermediate.

These limitations are well confirmed by experience from many consulted registration documents analysed within this projects' activities or beyond (Eurostat, 2012). Although, the guidance (ECHA, European Chemicals Agency, 2012b) states:

".. long-term DNELs may need to be set for the general population if the substance is present in consumer-available products or is released to the environment and present as an environmental contaminant" (R.8.7.3), current interpretation of this guidance often is far more restrictive.

Therefore, in case of appropriate DNEL values are lacking, it is inevitable to substitute these by estimation using structure-activity relationships as outlined above (calculation of Cramer classes using e.g. TOXTREE). This gives at least a "worst case" estimate of the toxic potency of a substance registered under REACH.

However, it should be referred to the given citation from ECHA guidance (R.8) in order to enforce the supplementation of respective DNEL assessments.

### 2.3.2 Parameters determining toxicity

The word *toxic* is also used as a hazard statement in classifications according to the CLP regulation addressing an acute human health hazard. For example, hazard statement H301 indicates: "*toxic* if swallowed" after acute oral exposure. However, in the framework of this project, when selecting a PMT substance, we use a more extensive definition for *toxic*, covering also potential effects after chronic exposure.

It may generally be problematic to link a definition of *toxic* only to classified substances according to CLP. Not all of the substances to be assessed for their potential effects in raw water will be classified. Similarly, a strict linkage to a *DNEL* (derived no effect level; general population, oral, long term) as it should be published for registered substances under REACH, may not be fully sufficient, because such a DNEL often is not derived or documented. Therefore we have to generate a definition for *toxic*, which also allows identifying substances as *toxic*, which are not yet classified and with no assigned DNEL.

Provision and conservation of clean raw water asks for a broad definition of *toxic*, which does not only address the tip of the iceberg. However, it has to be proportionate and relate to a potential health effect assuming regular exposure conditions. Therefore, we cover the following properties within the definition of *toxic* within the framework of this project:

- all substances with total annual production volume of 10 Tons or above with *no threshold* for health effects (even small consumption quantities of that substance are assumed to potentially impair human health or contribute to such impairment),
- all substances with total annual production volume of 10 Tons or above with thresholds for health effects, but a *threshold which is low* (therefore already limited consumption of that substance is assumed to potentially impair human health or contribute to such impairment),

- all substances with total annual production volume of 10 Tons or above with *structural alerts*, giving reason to assume that there are *no thresholds* for health effects (even though those substances are not (yet) classified),
- all substances with total annual production volume of 10 Tons or above with *structural alerts*, giving reason to assume that there are *low thresholds* for health effects (even though those substances are not (yet) classified).

In order to define what we call *limited consumption*, we compare the usual daily intake of a substance (mg substance/ kg bodyweight x day) with the respective tolerable daily intake of that substance (given either as a DNEL or estimated from structural alert). We assume the consumption of about 2 Litres of water per day for an adult and a lifetime exposure (ECHA, European Chemicals Agency, 2012b). There still should be a large margin of safety compared to an assumed threshold as an upper bound exposure. Some properties should result in the assignment of “T”, which do not need a potency consideration. For example, a genotoxic carcinogen should be regarded as toxic, even if of low potency, and even after consumptions of small amounts.

### ***CMR substances***

According to the definition above, classified carcinogenic and mutagenic substances (*CM substances*) are regarded as *toxic* because they are assumed to have no concentration threshold to potentially impair human health. If formally assessed under REACH or from earlier risk assessments, the respective substances have been assigned Category 1A or 1B for carcinogenicity or Category 1A or 1 B for (germ cell) mutagenicity. Hazard statements would be H350, and/or H340. The pathway specific hazard statement H350i (*may cause cancer by inhalation*) would not indicate carcinogenicity after oral exposure to drinking water, if assigned in isolation.

We have to be aware that some carcinogens may, in fact, have a threshold, especially, if the mode of action (*MoA*) is not linked to a direct interaction with the genetic material. However, because of the uncertainties of mechanistic approaches and the serious health consequences, we do not differentiate MoA within the scope of this project and we generally regard carcinogens and mutagens as *toxic*. Note that some substances may be carcinogenic in high doses but have anti-carcinogenic properties in low doses. Even though the occurrence of these substances in raw water would thus be beneficial to health, we regard it inappropriate to permit their regular discharge from industrial processes or use into the water cycle. This potentially beneficial effect could be acknowledged for by maintaining the natural, geogenic background level in water or by targeted supply with such beneficial substances, instead. In case of geogenic occurrence, monitoring results would not be indicative for industrial discharge.

Some substances are classified as suspected carcinogens or mutagens (hazard statements: H351, H341; suspected of causing cancer, suspected of causing genetic defects) in combination with a classification to Category 2 of carcinogens or mutagens, respectively. For mutagens with Category 2, there should be no difference to those classified as Category 1A or 1B. Therefore Category 2 mutagens should be regarded as being *toxic* within the framework of this project.

Usually, also carcinogens assigned with carcinogenicity category 2 should be regarded as toxic. If, however, in a higher tier assessment the registrant can demonstrate that the carcinogenicity of this substance may, if confirmed, definitely be linked to a sufficiently high and quantifiable threshold, then this substance should not be regarded as *toxic* within the framework of this project.

Reproductive toxicants (referring to the “R” within the group of CMR substances) are also regarded as *toxic*, if linked with category 1A or 1B for reproduction. The respective hazard statements are H360F, H360D, H360FD (*may damage fertility, may damage the unborn child*). It is acknowledged that often there will be a threshold for reproductive effects upon exposure to a single reproductive toxicant. However, in case of an endocrine MoA there is a high uncertainty on the existence and the dose for such a threshold. In case of a multi substance exposure also sub threshold doses of the single substances may contribute to adverse effects. In addition, the effect in question is generally regarded as a very serious toxicological endpoint. Thus, because of the uncertainties of mechanistic approaches and the serious health consequences, we do not differentiate MoA for reproductive toxicants within the scope of this project. Note that labelling for reproductive effects is sometimes linked to high concentrations. Even though the occurrence of these substances in raw water would thus not impair health, we regard it inappropriate to permit their regular discharge from industrial processes or use into the water cycle. This non-toxic concentration could be acknowledged for by maintaining the natural, geogenic background level in water, instead. In case of geogenic occurrence, monitoring results would not be indicative for industrial discharge.

Suspected reproductive toxicants linked with category 2 for reproduction may usually also be regarded as *toxic*. This is in line with PBT assessment under REACH: According to Annex XIII, also compounds classified as reproductive toxicants category 2 fulfil the criterion *toxic* (T). While in some cases it may be possible in a higher tier assessment to demonstrate that the reproductive effects of a substance in question may definitely be linked to a sufficiently high and quantifiable threshold, this possibility is not accounted for within the framework of this project. Rather the substance is considered to fulfil criteria for T at this level of assessment.

Substances assigned with a hazard statement H362 (may cause harm to breast-fed children) are regarded as reproductive toxicants and therefore as *toxic* within the framework of project. The lipophilic character of these substances indicates an accumulation and long half-life in humans and should therefore be avoided.

Note that CMR substances (category 1A, 1B) will be regarded as substances of very high concern under REACH anyway. Therefore regulatory action may usually be assumed regardless of the exposure via raw water<sup>33</sup>.

### ***Substances with a low DNEL***

Other substance classification characteristics apart from CMR provide no or no sufficient indication that a substance should be regarded as *toxic*. Potency may be very different and we hesitate to rank most hazards according to their health implications, as this objective ranking may substantially deviate from subjective concerns. Therefore it is preferred to define *toxic* according to effect potency.

The DNEL, if provided for oral long term exposure and related to general population, is such a suitable potency indicator.

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<sup>33</sup> Substances of very high concern are those substances defined in article 57 (REACH). However, regulatory action will only be taken if also confirmed by entering the candidate list (<http://www.reach-info.de/kandidatenliste.htm>; [http://echa.europa.eu/documents/10162/13607/procedure\\_identification\\_of\\_svhc\\_v\\_01\\_en.pdf](http://echa.europa.eu/documents/10162/13607/procedure_identification_of_svhc_v_01_en.pdf)).

The German Umweltbundesamt proposed a concentration of 0.1 µg/litre in drinking water to be a health based orientating concentration (“Gesundheitlicher Orientierungswert”; GOW) below which there is no or low health concern, even for genotoxic and carcinogenic substances (Dieter, 2009; 2011). This means that no relevant health effects are expected if all substances in drinking water were restricted to maximum concentrations of 0.1 µg/litre. Assuming a daily water consumption of 2 litres and additionally assuming a body weight of 60 kg for an adult according to REACH (ECHA, European Chemicals Agency, 2012b), a drinking water concentration of 0.1 µg/Litre corresponds to (about) 0.003 µg/kg bodyweight x day as a safe intake for most substances ( $0.003 \times 60 = 0.18 \approx 2 \times 0.1$ ). Only substances with a threshold of 3 ng/kg body weight x day or less, would lead to potential health problems, if this GOW is met. The *risk characterisation ratio* (RCR)<sup>34</sup> as calculated under REACH would then exceed 1, if exposure concentration (PEC) is 0.1 µg/Liter or above. However, this approach only addresses the most toxic substances (“tip of the iceberg”).

The DNEL for 95 percent of substances with high biological reactivity is at or above 1.5 µg/kg bodyweight x d (Barlow, 2005)<sup>35</sup>. The DNEL for 95 percent of substances with moderate or low biological reactivity is at or above 9 µg/kg bodyweight x d. Therefore an appropriate DNEL as a cut-off for *toxic* substances should be proportionate to these benchmarks. We propose to set the cut-off at the higher end of this range.

Thus,

**substances with a DNEL of  $\leq 9 \mu\text{g/kg x d}$  (oral, long term, general population) will be regarded as *toxic* within the framework of this project.**

With this cut-off, substances which lead to adverse effects at or below concentrations of 270 µg/Liter in raw water<sup>36</sup> are regarded to be *toxic*. It is obvious that this is a precautionous cut-off as there is a factor of 3 orders of magnitude compared with the GOW of 0.1 µg/Liter.

To keep the T-assessment in line with REACH PBT assessment in regard to human toxicity, compounds classified for specific target organ toxicity upon repeated exposure (STOT RE) category 1 or 2 are also regarded as *toxic* within the framework of this project. Toxicity cut-offs for classification for STOT RE categories 1 and 2 approximately translate in DNEL-like values which are slightly below and above, respectively the cut-off value of 9 µg/kg x d set for the DNEL (see box above).

### ***Substances with structural alerts: endocrine disruptors***

Endocrine disrupters (EDs) are substances of high concern with regard to human (and environmental) health. There is no adequate classification under REACH or CLP yet, to precisely address endocrine disrupting potential or potency. Some EDs may be classified as reproductive toxicants (see above), but not necessarily are. EDs are assumed to have no threshold or the substance specific threshold may not be quantified

<sup>34</sup> Risk characterisation ratio (RCR) = PEC/DNEL (exposure/threshold); should be below 1 to indicate safe exposure

<sup>35</sup> This conclusion is derived from the concept of “threshold of toxicological concern” and the calculated human exposure threshold derived in this concept. This threshold is defined similarly to the DNEL. For a more detailed discussion see section “substances with structural alerts, reactive structure” below.

<sup>36</sup> 9 µg/kg x d multiplies with 60= 540 µg/person x d; divided by 2 Liters daily consumption, i.e.  $540/2 = 270$ ; → 270 µg/Liter

according to existing extrapolation procedures. Therefore, we regard all endocrine disruptors as *toxic* within the framework of this project. This includes classified EDs (if there will, in future, be a reference to a clear-cut classification) and suspected EDs (if there will, in future, be a generally accepted and widely recognized reference structural alert assessment tool for this ED alert). More precise definitions and demarcations are currently prepared at European level (EC, 2013) and have to be consulted for a definite assignment.

### ***Substances with structural alerts: reactive structure***

If no DNEL (oral, long term, general population) is provided in a registration document, a direct assignment on the criterion *toxic* may not be possible. However, not (yet) classified substances should also be assessable with regard to their toxic potency. This assessment needs advanced expertise as a prerequisite for the approach proposed below:

In 2005, for a very large number of substances the assumed thresholds for adverse effects after chronic oral exposure (general population) had been listed and were evaluated (Barlow, 2005). These assumed thresholds were similarly defined as the DNELs<sup>37</sup>. It was found that the 95-percentile of the thresholds were above an intake dose of 0.09 mg/ person/ day in that study, if just those substances were included into the assessment which had a chemical structure that indicates a high biological reactivity (with regard to human health). The structural activity assessment was performed according to a proposal by Cramer et al. (1978). If less reactive substances were assessed, the 95-percentile was accordingly associated with lower toxicity and thus higher thresholds, the subsequent class with an associated intake dose of 0.54 mg/ person/ day<sup>38</sup>. This assessment gained great relevance as it was used to establish conservative estimates for a threshold of toxicological concern (TTC) for substances, which were not adequately tested in long term tests (Kalkhof, et al., 2012; Munro, et al., 2008; Patlewicz, et al., 2007; Tluczklewicz, et al., 2009). In this methodology, some groups of chemicals with specific properties were exempted, i.e.,

- metal containing compounds,
- polyhalogenated dibenzodioxins, -dibenzofurans, or -biphenyls,
- organophosphates,
- aflatoxin-like compounds,
- azoxy- or N-nitroso-compounds,

most of which may have a higher toxicity and should be assessed separately.

As proposed above, a DNEL at or below 9 µg/kg bodyweight x day should be regarded as criterion for a *toxic* substance. However, in many cases, there will be no DNEL (oral, long term, general population) available. Therefore, we have to provide a procedure to estimate potency for health effects for substances, which are not classified as *toxic* due to other criteria discussed in this section.

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<sup>37</sup> i.e., chronic NOAEL / 100, similarly defined as DNEL or “acceptable daily intake” (ADI) or “tolerable daily intake” (TDI), according to World Health Organisation (WHO), with  $100 = 10 \times 10$  with a factor of 10 for interspecies extrapolation and a factor of 10 for intraspecies extrapolation.

<sup>38</sup> See above: this benchmark of 0.540 mg/kg x d was used to define *toxic* for substances with a given DNEL, resulting in a concentration of up to 270 µg/L (or below) regarded as *toxic*.

We propose to link this procedure to the TTC concept as already discussed above. The methodology of a semi-quantitative risk assessment is based on the system of the Cramer classification (Cramer, et al., 1978; Chemical Relation Database (CRD) principle) and the resulting TTC for organics.

In a free online application called Toxtree<sup>39</sup> the Cramer rules as well as the Cramer rules with extension (Curios-IT, 2009) can be applied automatically to substances with known chemical structure, thus leading to the assignment of one of the Cramer classes. In order to apply this program, at least two-dimensional information in form of a SMILES code is necessary.

All substances classified as CRAMER class III (highly reactive in biological systems) according to this procedure should be regarded as *toxic* within the framework of this project. Substances classified as CRAMER class II or I are not regarded as toxic. However, structural alert classification is always a less qualified tool compared to DNELs provided in the REACH registration document or CMR-classifications, as discussed above.

Polyhalogenated dibenzodioxins, -dibenzofurans, or -biphenyls, organophosphates, and azoxy- or N-nitroso-compounds, for which the Cramer-class classification is not applicable or not applicable without modifications are regarded as *toxic* within the framework of this project.

Metal-containing compounds and aflatoxin-like toxins are currently excluded from this methodology.

If adequate substance specific data are available the assessor may move to a second tier, if he does not agree with the classification as *toxic* according to this procedure. He may then derive a DNEL (oral, long term, general population) and demonstrate that the threshold is above 9 µg/kg bodyweight x day. Note, that many Cramer-class III substances may, in fact, have a DNEL higher than 9 µg/kg bodyweight x d. But a more specific substance specific assessment is necessary to confirm this possibility. Otherwise all Cramer-Class III substances have to be regarded as *toxic*.

### ***Substances with structural alerts: genotoxic substances or carcinogens***

Above, we regarded classified CM substances as *toxic*. However, also not (yet) classified substances should be assessable with regard to their potential mutagenic or carcinogenic hazard. We provide this method for cases, where the registrant wants to assess the criterion *toxic* in advance to a registration or for transformation products, which may not be classified.

This assessment needs advanced expertise and information may not be easily drawn from registration documents which are incomplete with respect to these properties. In a weight of evidence approach the assessment is based on all available experimental data supplemented by structural alerts on genotoxicity/carcinogenicity. In case of lacking experimental data, the assessment is restricted on structure activity relationship (SAR) data. In general, the following models may be used, which were also included in the Toxtree<sup>39</sup> application:

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<sup>39</sup> For this specific toxicological assessment Toxtree version 2.5.0 is proposed and the “Cramer tree with extensions”, which is basically a copy of the original decision tree plus minor extensions. Available at: [http://ihcp.jrc.ec.europa.eu/our\\_labs/computational\\_toxicology/qsar\\_tools/toxtree](http://ihcp.jrc.ec.europa.eu/our_labs/computational_toxicology/qsar_tools/toxtree)

- Benigni/Bossa rulebase (for mutagenicity and carcinogenicity; Benigni, et al., 2008) and
- structure alerts for the *in vivo* micronucleus assay in rodents (Benigni, et al., 2009).

These models work on the principle of structural alerts (SA) which are correlated with genotoxic carcinogenicity or genotoxic activity in bacteria. The Italian Health institute („Istituto Superiore de Sanita“, ISS; by Romualdo Benigni and Cecilia Bossa) developed both models in collaboration with the Joint Research Centre of the European Commission. These models are contained in the QSAR Application Toolbox (project of the European Chemicals Agency (ECHA), stakeholders from member countries, chemical industry and NGOs (particularly the OECD)).

The Benigni/Bossa rulebase (BB rulebase) contains 33 structural alerts in total (Serafimova, et al., 2010), which relate to the knowledge of genotoxic carcinogenicity and/or which also apply for reverse mutation tests in bacteria. Non-genotoxic carcinogens are described within five of the structural alerts (SA). The model is only an elimination method (i.e. no discriminating analysis) as the presence of a SA indicates a certain potential of the substance in question, but the absence does not indicate that the property investigated is absent in the molecule. In consequence this means that only a positive result is to be interpreted considering the specificity and sensitivity values of the model. The given SAs are approximately to 65% accurate concerning rodent carcinogenicity data, and are having an accuracy of even 75% with Salmonella mutagenicity data according to Benigni et al. (2008). In addition to the SAs, the BB rulebase contains discriminating models for  $\alpha,\beta$ -unsaturated aldehydes and aromatic amines (three QSAR models<sup>40</sup>).

The existing structural alerts on genotoxic properties (BB rulebase) were optimised and expanded to a total of 35 structural alerts indicating a positive test result for the *in vivo* micronucleus assay (MNT). This is a rough screening for genotoxic potential of substances in this *in vivo* assay with rodents overall.

The following read out parameters are chosen to estimate genotoxic and/or carcinogenic potential:

- At least one positive structural alert for *in vivo* MN Test (yes or no) OR
- Structural alert for genotoxic carcinogenicity (BB rulebase; yes or no) OR
- Structural alert for non-genotoxic carcinogenicity (BB rulebase; yes or no)

For classified substances we assume that there was at least the required minimum data set available for assessment of a possible genotoxic potential of the respective substance. Thus, if there is no classification concerning genotoxic or carcinogenic effects for a compound with a full registration under REACH (i.e. assessed for classification), this is regarded to overrule structural alerts on genotoxic or carcinogenic properties.

### 2.3.3 Systematic toxicity assessment in this project

As regards the implementation of the assessment for T (*toxic* in the framework of this project) in the PMT assessment tool (see section 3) as outlined in Figure 13, some further aspects need explanation:

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<sup>40</sup> QSAR 6: mutagenic activity of aromatic amines in the *Salmonella typhimurium* TA100 strain;

QSAR 8: carcinogenic activity of the aromatic amines in rodents (summary activity from rats/mice);

QSAR 13: mutagenic activity of  $\alpha,\beta$ -unsaturated aldehydes in the *Salmonella typhimurium* TA100 strain.

General considerations for the systematic decision tree concept:

- In principle, different toxic actions may lead to different decisions (D1, D2, ...) leading to possibly different conclusions for the respective aspects of toxicity. The most severe one will determine the final conclusion on T.
- Classified substances most probably were checked for genotoxicity / carcinogenicity: Screening-assessment for genotoxicity / carcinogenicity would not be reasonable.
- For CMR Cat. 1A, B; Muta. / Repr. Cat.2; H362; STOT RE Cat. 1, 2: DNEL derivation not applicable: Either no threshold may be quantified or sub-threshold (precursor) effects are possible, or a low DNEL is implicit (STOT RE).
- While endocrine action is a property which may be associated with a substance independent from other toxic properties, no additional knowledge can be gained from Cramer classes where previous decisions resulting in T were derived.

Currently, there are no agreed criteria for classification of endocrine disrupting substances. EU level criteria for identification and categorisation of those compounds are under development and discussion<sup>41</sup>. However, European Joint Research Committee (JRC) established the Endocrine Active Substances Information System database<sup>42</sup> with suspected compounds, and further relevant databases or eventually QSAR based classifications might be used to demonstrate suspected endocrine action. Because a finalized list of endocrine disrupting chemicals (EDC) is not yet available, the procedure provides the option to insert a respective validated list of endocrine disruptors later in future. As long as agreed classification criteria are lacking, we propose to assign  $T_{\text{screen}}$  to compounds suspect of endocrine action to refer to this preliminary character of classification.

Similarly, other deterministic qualified inventory lists, elaborated by authorities, may optionally be inserted. Such an inventory could be derived from competent authorities' lists of compounds regarded as toxic, e.g. drinking water directive 98/83/EC. Being part of the inventory, a compound would be regarded as *toxic* in the framework of this project, obviating the need of a full assessment for T.

For compounds classified as Carc. Cat. 2 it may be possible to derive a threshold for carcinogenic action (expert level,  $\text{Threshold}_{\text{Carc.}}$ ). Such a threshold is given equal weight to a DNEL (if available in parallel). If no threshold for carcinogenic action can be derived, the substance is suspect of being a non-threshold carcinogen and concluded to be T in the framework of this project. In case of a lack of expert knowledge to decide upon a threshold or in case of insufficient data, the option *unknown* leads to the conclusion  $T_{\text{screen}}$  regarding carcinogenic properties.

To account for uncertainties associated with structure-activity relationships (SAR), positive structure based screening from the BB rulebase (genotoxicity/carcinogenicity) or Cramer III classification leads to  $T_{\text{screen}}$ , only.

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<sup>41</sup> See <http://www.efsa.europa.eu/de/efsajournal/doc/3132.pdf> and [http://ec.europa.eu/environment/chemicals/endocrine/index\\_en.htm](http://ec.europa.eu/environment/chemicals/endocrine/index_en.htm)

<sup>42</sup> [http://ihcp.jrc.ec.europa.eu/our\\_activities/food-cons-prod/endocrine\\_disruptors/eas\\_database](http://ihcp.jrc.ec.europa.eu/our_activities/food-cons-prod/endocrine_disruptors/eas_database)

In effect, the following final conclusions are possible depending on the compound specific data set:

- T
- $T_{\text{screen}}$
- No decision on T possible
- not T.

#### 2.3.4 Summary and discussion

The process to define a *toxic* substance with respect to PMT assessment is summarized below in Figure 13. The procedure proposed above identifies substances regarded as *toxic* with a definition adapted to the purposes of this project. It is acknowledged that this definition deviates from the existing terminology, where the term *toxic* is understood differently. In an extensive and precautionary approach, regulatory action with regard to contaminants in raw water can be just linked to PM substances (*relevant in raw water*). However, we want to provide the alternative approach which places regulatory activities to those substances with some significant associated health effects. This approach may be used instead or in addition to regulatory consequences just based on PM properties.

It was regarded appropriate to suggest some mixed criteria to define toxicity,

- some based on a substance's hazardous properties (toxic potential), and
- some based on a substance's effect strength (toxic potency).

For the most serious endpoints, where a large agreement exists on the concern, we argued to use hazard properties in this definition (i.e. CMR substances and endocrine disruptors). Often, for such properties no threshold may be quantified or sub-threshold (precursor) effects are possible. This understanding is identical to the one currently relating to *substances of very high concern according to article 57 a,b, c (REACH), or article 57 f (with regard to endocrine disruptors)*.

For most other endpoints there is a broad debate, which effects are regarded more or less serious and the potency for substances with identical classifications may vary considerably, anywhere from very potent to very weak (i.e., large or small doses associated with health effects). Therefore we propose to use the DNEL as potency indication for long term, oral exposure as the most relevant criterion to include or exclude substances from being regarded as *toxic*.

In combination with the PM criteria, it is argued that substances fulfilling in addition T (i.e. PMT) may give rise to an equivalent level of concern and may thus also be regarded as SVHC. Therefore we had to find a compromise also with regard to potency considerations included into to T criterion. Those should cover more than just the "tip of the iceberg", but at the same time realistically indicate potential health effects in concentrations expected to occur in raw water. We therefore proposed a cut-off of 9 µg/ kg body weight and day (as DNEL, with equal or lower DNELs being judged as indicating *toxic* substances). We believe that this is a proportionate cut-off and we provided the respective rationale. However, other cut-offs may be implemented instead, as it is not a matter of science to conclude what is finally regarded as a "substance of equivalent concern".

It was emphasized that it often may be necessary to derive a DNEL or to use quantitative structure activity relationship information (QSAR) to estimate health effect potency or to establish a structural alert for genotoxicity and/or carcinogenicity. Note, that the respective proposals need scientific qualifications by the

assessor (flagged with \* or \*\* in Figure 13), which are beyond routine analysis of a REACH registration document. There may be further problems, if a classification or DNEL-derivation is not possible because of substantial lack of data.

For transformation products there may be no sufficient data and not even adequate information on the identity of those substances. We have to acknowledge that this is a gap, which may currently not be filled with the methodology proposed.

In discussions, which substances should be avoided to occur in raw water, it was argued that substances with a very bad taste or smell when discharged to raw water (e.g., with agrid or foul smelling) should also prompt regulatory action. However, consequences may be different from those for clearly *toxic* substances.

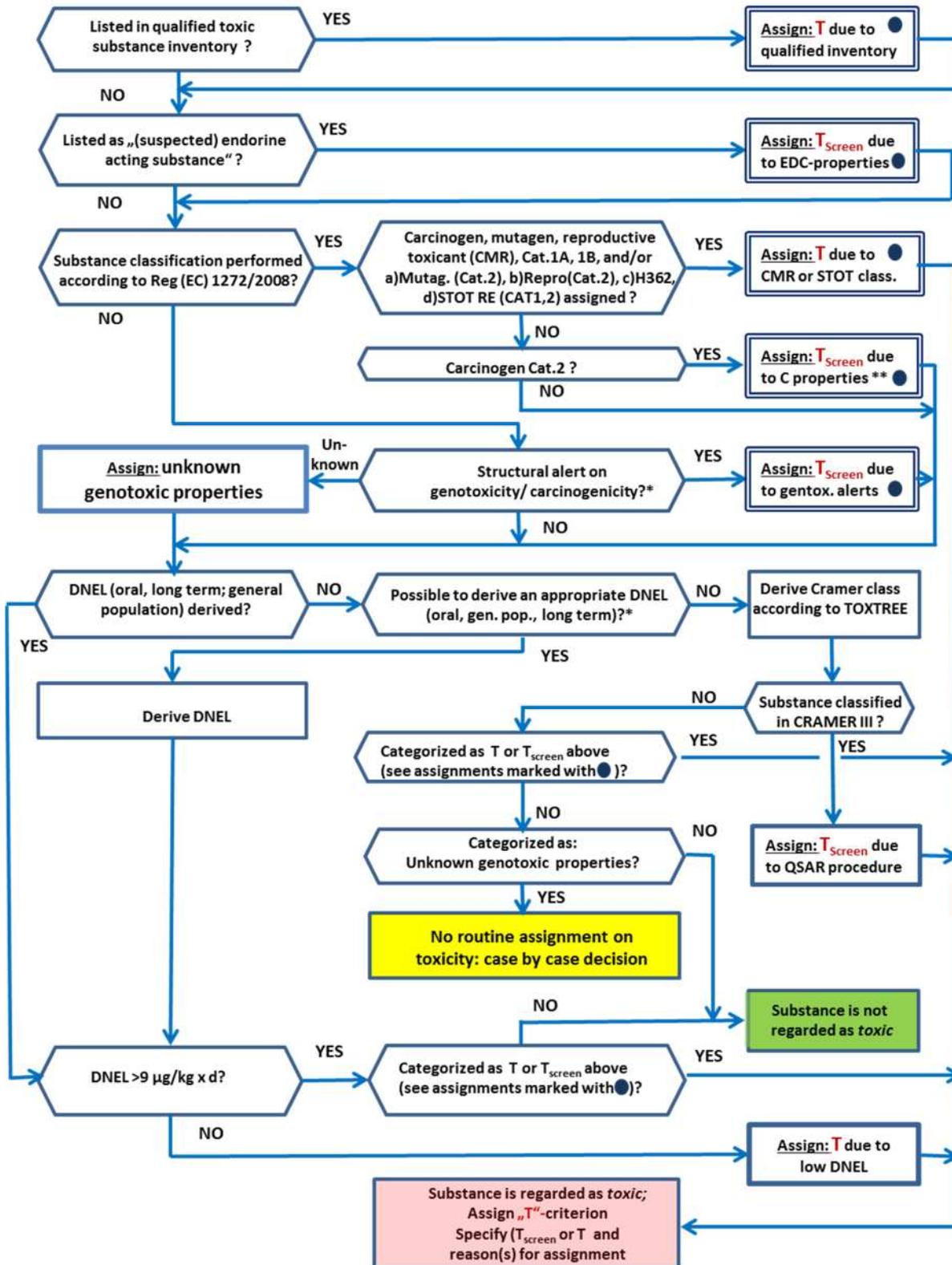


Figure 13: Flowchart for the assessment of the criterion *toxic* with respect to PMT assessment. T / T<sub>screen</sub> assigned in parallel are integrated to derive the final conclusion. \*) refers to expert level assessment (optional); \*\*) here, at expert level a Threshold<sub>carc.</sub> may be derived (see sect. 2.3.3)

## 2.4 Tiered approach for determining the exposure term for substances *pervious or relevant in raw water*

An introduction to exposure modelling under REACH as well as associated important basic information and definitions were given already as a background to the modelling approach applied to determine the  $K_{OC}$  based threshold value for mobility (see section 2.2.3, Exposure estimation with ECETOC TRA). In the following subsections, a tiered approach is described to assess the potential for environmental exposure.

The tiered approach to exposure assessment, which supplements the PMT assessment, consists of three different steps at different stages of the overall assessment:

- Tier E1: Exclusion of emissions to the environment
- Tier E2: Exclusion of uses in combination with tonnage, indicating low environmental exposure
- Tier E3: Calculation of PEC and related RCR (ratio of PEC and DNEL) in raw water

Tier E3 usually is identical to the exposure assessment, and may be requested as a routine element of the REACH registration process.

Tiers 1 and 2 will be described and discussed in this section.

### 2.4.1 Tier E1: Exclusion of emissions to the environment

1. At a very early stage, substances can be excluded from the assessment of their PMT properties, if they are not expected to enter the environment to any significant extent due to their use pattern. This primarily relates to intermediates that are handled under strictly controlled conditions and are therefore registered only as an intermediate<sup>43</sup>.

According to ECHA statistics, 22% of all registrations up to 31 May 2013 related to intermediate registrations (78% full registrations). In terms of the substances covered by these registrations, 3,174 registrations (42%) related to intermediate registrations and 4,306 (58%) to full registrations. It should be noted, however, that submissions for a substance can consist of both full and intermediate registrations. As a consequence, the sum of the substances (3,174 + 4,306 =) 7,480 from the statistics according to registration type is higher than the total number of substances when evaluated according to total tonnage band (Table 23). The total tonnage is calculated from the actual tonnages in all full registrations for a substance and excludes intermediates.

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<sup>43</sup> “Substance is only manufactured and used under strictly controlled conditions in that it is rigorously contained by technical means during its whole lifecycle. Control and procedural technologies shall be used to minimise emission and any resulting exposure”, (Article 17 (3), REACH), for further details see Article 18(4), REACH)

Table 23: Number of substances registered according to total tonnage band and submission type<sup>44</sup>

Tonnage Band	Number of substances	% of total
100,000,000-1,000,000,000 tpa	5	0.1%
10,000,000-100,000,000 tpa	45	0.7%
1,000,000-10,000,000 tpa	161	2.4%
100,000-1,000,000 tpa	327	5.0%
10,000-100,000 tpa	617	9.4%
1,000-10,000 tpa	1,062	16.1%
100-1,000 tpa	1,235	18.7%
10-100 tpa	370	5.6%
1-10 tpa	309	4.7%
Intermediate use <b>only</b>	2,467	37.4%
Total	6,598	
Submission type		
Registered as full registration	4,306	58%
Registered as intermediate	3,174	42%
Total	7,480	

Two major findings emerge from these data:

- About 37% of all substances were registered as intermediates only (i.e. strictly controlled conditions have been confirmed). These substances would exit the entire assessment as addressed in this project at this early stage. This, however, would not preclude other potential consequences under REACH, which have to be examined independently from a PMT assessment.
- A substantial number of (3,174 – 2,467 =) 707 substances were registered both as an intermediate and with a full registration.

It must be noted that these figures change continuously as more substances are registered. The evaluation above is based on data retrieved in June 2013. A brief re-analysis in November 2014 indicates, however, that the fraction of substances registered with intermediate use only is stable at about 37%.

Overall, Tier E1 will exclude only those substances that have an intermediate registration only at any stage. All substances with a full registration or NONS (Notification of New Substances under Directive 67/548/EEC) are retained in the assessment. The decision is simply described by one question:

<sup>44</sup> <http://echa.europa.eu/web/guest/information-on-chemicals/registration-statistics>, accessed: 21 June 2013

○ Substance used only as an intermediate under strictly controlled conditions (i.e. intermediate registration only)?

- ➔ YES: No further action required within PMT assessment, follow usual REACH procedure
- ➔ NO: Proceed to PMT assessment

#### 2.4.2 Tier E2: Exclusion of uses in combination with tonnage, indicating low environmental exposure

At this stage, the substance to be evaluated is already identified as “PM substance”, i.e. fulfilling the P *and* M criteria and is regarded to be *pervious* to raw water. Tier E2 basically seeks to identify those substances with a use pattern that would suggest only low releases to the environment and that therefore are not given priority for a more detailed assessment.

Two options are described below for an assessment of environmental exposure as alternatives: Option 1 excluding manufacture of the substance for reasons outlined below and Option 2 under consideration of manufacture besides all uses of the substance. Further alternative options may be imagined including one where even low environmental exposure is included when defining *relevant in raw water* or *critical in raw water*. As indicated in section 1, this cut-off may not be defined merely on scientific grounds. The presentation of options 1 and 2 demonstrates the flexibility of the methodology.

The extent of environmental releases critically depends on a) the tonnage and b) the release factor for each particular use. Obviously, there is a continuum and a high enough tonnage may lead to considerable environmental release even if the release factor is extremely low (but not zero).

Indications for environmental exposure are therefore derived from environmental release categories (ERCs) in combination with tonnage. The evaluation is based on Table R.16-23 (REACH Guidance Chapter R.16: Environmental Exposure estimation, Version 2.1 –October 2012), see Table 24, below. The focus is on the release to water (before STP).

##### Option 1: Exclusion of manufacture

“Manufacture of a substance” always involves a high tonnage and a comparatively high release factor of 6% to wastewater (ERC1) as a default assumption. The inclusion of manufacture in this tier would therefore select *all* substances manufactured within the EU as leading to environmental exposure. As a consequence, a differentiation would be impossible. In option 1, ERC 1 is therefore excluded from the tier E2 procedure described in the next paragraphs. There are also some other issues to consider in support of this approach:

- The release factors given in the ECHA Guidance (ECHA, European Chemicals Agency, 2012e) for manufacture (ERC1) are default worst-case values. They assume that 6% of the tonnage manufactured are emitted to wastewater and 5% to air, i.e. 11% of the total amount manufactured are assumed to be emitted. These release factors were taken from the EU TGD (EC, 2003) and allegedly include data for manufacture of basic chemicals and chemicals used in synthesis as well as for the petrochemical industry and the metal extraction and refining industry taken from this source. However, a maximum value of 2% is given in EC (2003) for emissions to wastewater in all manufacturing scenarios and the value of 6% relates to the leather processing industry as well as colorants in some other industries (e.g. paper and textiles). The value of 6% itself may therefore be questioned.

Table 24: Default parameters to derive the environmental release rate (Source: ECHA, REACH Guidance, Chapter R.16)

Note	No	ERC	Default worst case release factors resulting from the conditions of use described in the ERCs. Grey cells indicate release factors which are used for the regional release estimation only (and not for the local one).		
			to air	to water (before STP)	to soil
1,7	1	Manufacture of chemicals	5%	6%	0.01%
2,7	2	Formulation of mixtures	2.5%	2%	0.01%
2,7	2	Formulation in materials	30%	0.2%	0.1%
3, 7	4	Industrial use of processing aids	100%	100%	5%
4,7	5	Industrial inclusion into or onto a matrix	50%	50%	1%.
5,7	6A	Industrial use of intermediates	5%	2%	0.1%
5,7	6B	Industrial use of reactive processing aids	0.10%	5%	0.025%
5,7	6C	Industrial use of monomers for polymerisation	5%	5%	0%
5,7	6D	Industrial use of auxiliaries for polymerisation	35%	0.005%	0.025%
6,7	7	Industrial use of substances in closed systems	5%	5%	5%
3,7	8A	Wide dispersive indoor use of processing aids, open	100%	100%	n.a.
5,7	8B	Wide dispersive indoor use of reactive substances , open	0.10%	2%	n.a.
4,7	8C	Wide dispersive indoor use, inclusion into or onto a matrix	15%	1%	n.a.
3,7,8	8D	Wide dispersive outdoor use of processing aids, open	100%	100%	20%
4,7	8E	Wide dispersive outdoor use of reactive substances, open	0.10%	2%	1%
4,7	8F	Wide dispersive outdoor use, inclusion in matrix	15%	1%	0.5%
6,7	9A	Wide dispersive indoor use in closed systems	5%	5%	n.a.
6,7	9B	Wide dispersive outdoor use in closed systems	5%	5%	5%
8	10A	Wide dispersive outdoor use of long-life articles, low release	0.05%	3.2.%	3.2%
9,10	10B	Wide dispersive outdoor use of long-life articles, high or intended release	100%	100%	100%
8	11A	Wide dispersive indoor use of long-life articles, low release	0.05%	0.05%	n.a.
9,10	11B	Wide dispersive indoor use of long-life articles, high or intended release	100%	100%	n.a.
10	12A	Industrial processing of articles with abrasive techniques (low release)	2.5%	2.5%	2.5%
10	12B	Industrial processing of articles with abrasive techniques (high release)	20%	20%	20%

- Even the release factor of 2% in EC (2003) is related to low tonnages of less than 1,000 t/a, while a release factor of 0.3% is assumed for higher tonnages, because these sites are believed to have more efficient RMMs in operation. This tonnage-dependence has been disregarded in the ECHA Guidance (ECHA, European Chemicals Agency, 2012e), but in fact supports the decision taken here.

High tonnage manufacturing sites will also be likely to be the subject of several national and international pieces of legislation (e.g. wastewater legislation, industrial emissions directive (IED, the successor of the integrated pollution prevention and control (IPPC) directive)), effectively limiting the release of chemicals into the environment

Disregarding manufacture, substances with a use pattern that would suggest significant releases to the environment can be identified on the basis of ERCs and their associated default release factors for wastewater (the latter being considered particularly relevant for raw water). The release factors assigned to specific ERCs in the ECHA Guidance (ECHA, European Chemicals Agency, 2012e) have been analysed and grouped into five different categories representing low to high release factors (Table 25, with the general idea (for exceptions, see below) that

- further evaluations within the PMT assessment may not be required, if the use pattern of a substance is described only with ERCs belonging to categories of low release factors (A-B, see below) and
- the PMT assessment must be continued if the use pattern description for a substance contains any of the ERCs belonging to categories C-E.

As stated above, the tonnage is also an important input to describe the environmental release of a substance. Therefore, an additional tonnage element is included, which ensures that substances used in applications with consistent high release factors are nonetheless excluded from further assessment (within the context of this PMT assessment), if the tonnage is below a certain threshold (see below for the tonnage limits). Conversely, low release factors become more relevant the larger the tonnage is and their exclusion is only justified, if their tonnage does not exceed a certain cut-off value

The initial classification was entirely based on the combination of release factors (according to ERCs) and the tonnage of the substances. UBA experts then made additional adjustments considering typical uses and products that can be assigned to the respective ERCs (proposals are shown in Table 25).

Table 25: Differentiation of ERC-related release factors and conclusions for raw water relevance<sup>45</sup>

Category (description)	ERCs*	Conclusion: <i>relevant</i> in raw water
A (low)	6A, 6D, <b>11A</b>	YES if tonnage is > 10,000 tpa
B (low-medium)	1, 2, 3, 6B, 6C, 7, <b>9A, 9B, 12A</b>	YES if tonnage is > 1,000 tpa <sup>1</sup>
C (medium)	<b>8B, 8E, 10A, 12B</b>	YES if tonnage is > 1,000 tpa <sup>1</sup>
D (medium-high)	<b>8C, 8F</b>	YES if tonnage is > 100 tpa
E (high)	4, 5, 8A, 8D, <b>10B, 11B</b>	YES if tonnage is > 10 tpa

1) It is acknowledged that category B and C could be combined to a single category.

\*) Wide-dispersive uses highlighted; ERC 1 included here for assessment under option 2.

## Option 2: Inclusion of manufacture

The general approach described above is also possible with inclusion of manufacture (ERC 1). The data in Table 25 show that ERC 1 is assigned to category B and exiting the PMT assessment is only possible if the tonnage is < 1,000 tpa. As shown in Figure 14, this relates to about 30% of all substances currently registered. This figure will increase with registration of the lower tonnage bands by 2018.

Note that in the approach discussed here, a substance manufactured at e.g. 50 tpa will nonetheless be retained in the assessment if it is used in applications described by ERCs 4, 5, 8A, 8D, 10B or 11B.

In both options, the tonnage information referred to above relates to the *total* tonnage band as displayed on ECHA CHEM. This figure is aggregated from all full registrations (i.e. excluding intermediates) as described above. Obviously, relating the total tonnage to specific ERCs introduces an error in the evaluation. However, a more meaningful procedure would involve analysing tonnages per use (i.e. per ERC) and the respective figures will generally only be available, if a complete environmental exposure assessment has been performed. Both for authorities and for companies, the screening procedure described here, allows the identification of particularly relevant (or irrelevant) substance-use combinations without entering much detail.

If several full registrations exist for a given substance, the upper end of the highest tonnage band will be used.

The tonnage cut-off values are more or less arbitrary, but are based on the following considerations:

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<sup>45</sup> It is acknowledged that category B and C could be combined to a single category. However, in order to provide meaningful potential cut offs for alternative groupings, we maintain categories B and C in this presentation.

- The cut-off values are based on total tonnages (i.e. from all full registrations) and should therefore be somewhat equal or higher than the respective limits for individual companies (e.g. the requirement to perform a chemical safety assessment: 10 tpa).
- The logic presented here implies that the entire tonnage is used in applications with the highest release factor, which will rarely be the case. Rather, there will usually be a mixture of applications with low-high release factors.

Overall, the procedure outlined above ensures that many typical industrial uses (often described by ERC 4 or 5 with the default assumption of very high (100% and 50%, respectively) releases to wastewater) are generally not excluded from the assessment (except for the general cut-off of 10t for CSA; see Table 25).

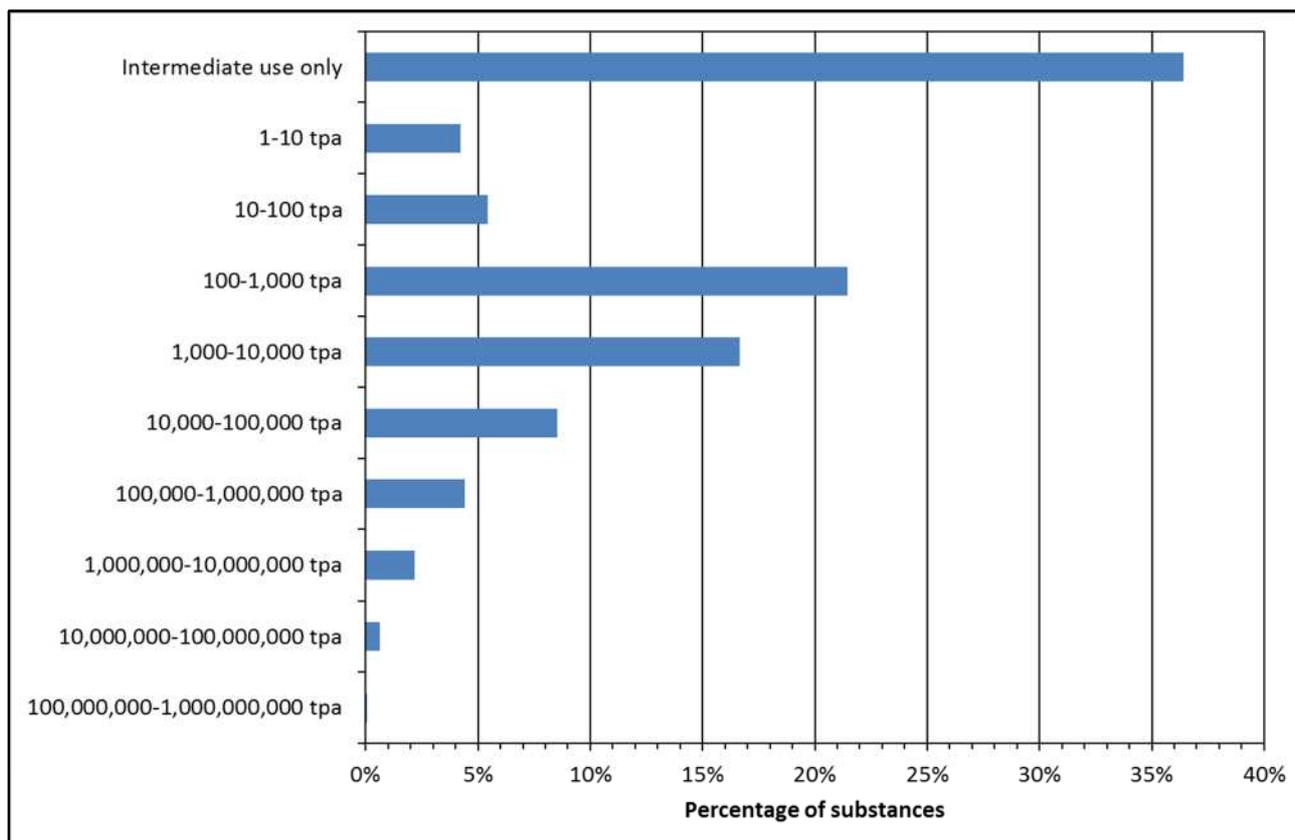


Figure 14: Substances registered per total tonnage band

<http://echa.europa.eu/web/guest/information-on-chemicals/registration-statistics>, accessed: 02 December 2013

### 2.4.3 Tier E3: Risk-based full exposure assessment

Tier E3 is not described below. It includes the “usual” calculation of PEC, in general, by applying TRA or EUSES software. As a final step at the end of the exposure assessment this information is combined with DNEL-data (general population, long term oral exposure) to derive a *risk characterisation ratio* (RCR). Note that the procedure deviates somewhat for carcinogens or other “non threshold” substances (not further discussed below).

Again, this procedure may be split up in several tiers, which are usually followed, if an RCR of  $\leq 1$  is not yet met at a lower tier. Similarly, exposure may be assessed at a higher quality level, if a PEC of 0.1 ( $\mu\text{g/L}$ ) is not yet achieved (which is an important cut-off within the assessment of PMT substances, critical in raw water). Within a PMT assessment, tier E3 is performed for PMT substances. However, this exposure assessment may also be demanded within the routine REACH procedure for “non-PMT” substances.

Note that, for some substances, a full scale exposure assessment may already be available in advance to a PMT assessment, as addressed in this project. In this particular case, the preceding exposure assessment tiers E1 and E2 will be included implicitly within tier E3 and therefore are not needed as separate assessment elements.

## 2.5 Demarcation

### 2.5.1 Applicability domain (types of substances)

Not all types of chemicals may be easily compared to one another and certain types of chemicals may pose specific problems which have to be treated on their own. At this point in time, for this first methodological approach to identify PMT substances, the following substance classes will be excluded for the reasoning given:

- Inorganic compounds including metals and their compounds: These are all not biodegradable, their solubility and toxicity often depends on their redox state, and adsorption to solids is triggered by fundamentally different mechanisms (mostly complexation and ionic interactions) compared to organic compounds. This is in line with REACH guidance documents generally relating to organic chemicals only. The one exception is a special guidance document on metals / metal compounds<sup>46</sup>. REACH Annex XIII (PBT assessment) explicitly states that it is not valid for inorganic compounds.
- Due to their complexity, UVCB and multi-constituent substances currently are excluded from PMT assessment. According to ECHA<sup>47</sup> “A multi-constituent substance is a substance, defined by its quantitative composition, in which more than one main constituent is present in a concentration  $\geq 10\%$  (w/w) and  $< 80\%$  (w/w). A multi-constituent substance is the result of a manufacturing process.” “Substances of Unknown or Variable composition, Complex reaction products or Biological materials, also called **UVCB** substances, cannot easily be identified by their chemical

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<sup>46</sup> Guidance on information requirements and chemical safety assessment Appendix R.7.13-2: Environmental risk assessment for metals and metal compounds

<sup>47</sup> ECHA, 2012. Guidance for identification and naming of substances under REACH and CLP

composition, because: The number of constituents is relatively large and/or the composition is, to a significant part, unknown and/or the variability of composition is relatively large or poorly predictable.“ These substances are identified by user dialogue and excluded from assessment.

- Organometallic compounds: These are usually instable in water or may react vigorously with water and generally are reactive chemicals which are used as catalysts or reaction intermediates in synthetic chemistry. Thus, instead of the compounds themselves rather reaction products thereof might be of concern for raw water contamination.
- Surface active compounds: The derived criterion for mobility applies to single molecules, only. Detergent-like behaviour, i.e. formation of micellar aggregates, is not accounted for. Supramolecular assemblies may behave pronouncedly different compared to single molecules. Thus, surface active compounds currently cannot be evaluated regarding mobility and are therefore excluded from assessment.
- Transition metal complexes with organic ligands: Within the assessment tool (3) these compounds are identified by user dialogue and principally can be evaluated for PMT properties. However, because the SMILES code used as input for most QSAR models cannot take account of such complex molecular formations based on non-covalent interaction, only experimentally derived values for  $K_{OC}$  and biodegradation may be used for the assessment (QSAR is not applicable). Similarly, toxicity assessment must be based on experimental values, as e.g. CRAMER classification based on Toxtree<sup>48</sup> will not be possible (also here, SMILES codes are the prerequisite for application of the respective decision tree structure). Further, biodegradation is confined to the organic part of the substance.
- Ionic organic compounds, zwitterionic organic compounds, ionisable organic compounds (acids, bases): These compounds are problematic in regard to adsorption behaviour, as adsorption in their ionized form is a composite of non-ionic interaction (mostly with organic carbon) which can be calculated very well by QSAR models; and ionic interactions: repulsion by the surplus of negative charges in most soils for anionic compounds and ionic binding for positively charged compounds which currently needs to be experimentally determined. In addition, for ionisable compounds  $\log K_{OW}$  being one of the important parameters determining partitioning in the environment is dependent on the pH (i.e. fraction of ionized versus neutral compound). Binding constants of cationic substances are often orders of magnitude higher than predicted by QSAR models. Out of these reasons these compounds may currently be assessed only, if an experimentally determined  $K_{OC}$  value is available. The only accepted method is the “Batch Equilibrium Method” according to OECD 106 or similar guidelines. Experimental values determined by OECD 121 (HPLC screening method) are not accepted for ionisable or charged compounds and neither are estimated values from QSAR.

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<sup>48</sup> [http://ihcp.jrc.ec.europa.eu/our\\_labs/computational\\_toxicology/qsar\\_tools/toxtree](http://ihcp.jrc.ec.europa.eu/our_labs/computational_toxicology/qsar_tools/toxtree)

## 2.5.2 Transformation products

Currently our approach cannot assess possible transformation products of parent compounds in regard to PMT properties. This is mainly due to a lack of necessary information under REACH and insufficient possibilities to model transformation processes by QSAR. Only in exceptional cases REACH will provide information on possible transformation products (see section 2.6.2). As no separate section in IUCLID software (used to generate registration dossiers) is foreseen for identification of transformation products this information - if available at all - will have to be manually extracted from the individual study summaries of study types potentially giving information in this regard (OECD TG 111 - hydrolysis, 307 – simulation test soil, 308 – simulation test sediment, and 309 – simulation test surface water). In most cases, however information given is not sufficiently precise to allow an assessment. On the other hand, it is highly questionable if prediction of stable intermediates / transformation products by QSAR tools is possible and – equally important – sufficiently reliable to be used. CATALOGIC may be one of the few tools trying to use known metabolic pathways involving metabolites for prediction of biodegradation (Karabunarliev, et al., 2012). While reliability of predictions with regard to stable transformation products would have to be carefully assessed, it is a commercial software tool not commonly available. Freely available is the *University of Minnesota Biocatalysis/Biodegradation Database*<sup>49</sup> (Ellis, et al., 1999; Ellis, et al., 2006).

While data on transformation products are mostly lacking or insufficient, this is an issue of high concern, especially for raw water protection: Because in most cases oxidation events play a major role for degradation while hydrolysis is equivalent to the addition of water (i.e. insertion of a polar hydroxy moiety), transformation products most often are more polar than the parent and may therefore be of higher mobility in water. Further, certain compound classes, like epoxides, by nature will hydrolyse in the aquatic environment, making the parent compound by default irrelevant for raw water. The resulting hydrolysis product (apart from the reactive epoxy group nearly unchanged in case of epoxides) may, however, prevail in the environment and possibly be of concern.

An example for a compound leading to a relevant transformation product in the environment and demonstrating at the same time an exception from the rule of thumb that these are mostly of higher polarity, is Triclosan: Methyl-Triclosan was identified as both, a more stable and more bioaccumulative transformation product in soil and water systems (Health Canada, 2012), with increasing concentrations in muscles of fish from German rivers (Boehmer, et al., 2004). While Triclosan is photodegradable, especially at pH-values  $\geq 8$ , methyl-Triclosan is not (Lindström, et al., 2002).

As regards PMT assessment methodology elaborated within this project, while an assessment of transformation products currently is not possible by default given the limitations outlined above, whenever transformation products may become relevant, within the developed assessment tool (see section 3) the user is reminded to take account of the possible raw water relevance of transformation products (e.g. in case of hydrolysis or primary biodegradation of the original compound) and to assess major transformation products themselves for mobility and toxicity. Thus, taken for granted the necessary data are available, transformation products may very well be assessed for PMT properties, just like any other compound complying with the applicability domain.

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<sup>49</sup> <http://umbbd.ethz.ch/index.html>

## 2.6 Discussion

### 2.6.1 Ranking approach for identification of PMT substances and similar approaches in the literature

As discussed above, substances properties may be assessed according to the procedures described in sections 2.1 - 2.3 to select PMT substances, which may occur in raw water. This is a semi-quantitative approach with respect to exposure and a qualitative approach with respect to persistence, mobility and toxicity, and no further grading beyond categorisation as P, M, T or –with regard to exposure – *pervious* to or *relevant* in raw water is proposed. However, a number of different priority lists may be generated from this selection process:

If interested, the user may generate lists just fulfilling one or two of the three PMT properties. E.g., he may want to find the *persistent* and *mobile* (PM) or just *toxic* substances (T), or a combination of PT substances. However, as explained above, criteria established for mobility are linked to persistence. Therefore, mobility alone (independently from P) may currently not be assessed with this methodology. Because of this, also MT substances (not fulfilling P) currently cannot be specified.

In general, while the cut-off criteria suggested for PMT assessment are justified by considerations given in the respective sections, they may easily be changed according to altered objectives, and resulting consequences are reflected by different lists of target compounds.

Further, the exposure term assessed to decide on *relevant in raw water* or *critical in raw water* may be included or excluded.

As indicated, we propose not to extend the PMT assessment over a qualitative (PMT) to a graded output (e.g. different severity grades for P, M and T), because of the heterogeneity of input data precluding a scientifically valid weighing against each other: It will often hardly be possible to weight e.g. existing information on persistence for compound A based on screening test data against data on persistence for compound B including simulation test data: Some compounds tend to be easier degraded in screening tests (due to higher test item concentrations), other compounds are out of exactly the same reasons poorly degraded in screening tests (toxicity at higher concentrations), but may degrade well in simulation tests (higher tier). Further, if possible only low tier information enters the grouping and calculations. Therefore, (theoretically possible but usually not proportionate) more detailed higher tier calculations could change the exact sequence and hierarchy. Therefore, the qualitative grouping is regarded as the appropriate output. More detailed reasoning is given in the following paragraphs reviewing literature on prioritisation (ranking) of compounds.

A scaled PMT assessment of chemicals will only be reasonably possible by integrating persistence, environmental distribution (including mobility) and toxicity with exposure data, which leads however to a risk assessment like approach (see e.g. Arnot and Mackay, 2008; Daginnus, et al., 2011) different from the one followed here: A highly toxic compound needs to be less *persistent* to yield environmental concentrations exerting effects compared to a less toxic compound, a compound with higher environmental exposure and a given toxicity needs to be less *persistent* to reach environmental concentrations exerting toxicity than a compound with the same given toxicity but lower environmental exposure etc.

Götz et al. (2010) perform a grading based on a) distribution modelling (which is exactly what is not intended by our approach) b) biodegradability and c) input dynamics (exposure characteristics).

Biodegradability grading is possible as it is based solely on QSAR-data. As such, a uniform basis of data is given enabling graduation. While there is a controversial discussion if BIOWIN data can be used for a more elaborate answer than fast degradable / ultimately degradable (i.e. the approximate time frame by BIOWIN 3 seems to be not very accurate) (Aronson, et al., 2006), our approach is based on experimental data wherever possible. However, these are very heterogeneous as outlined above and cannot easily be compared to one another. Grading according to input dynamics (continuous input versus periodic input) is an interesting approach, however generally will need a more elaborate assessment of exposure data than would be feasible within our approach (a fast and easily applicable tool for assessment of PMT properties based on readily accessible data).

Reemtsma et al. (2006) propose a water cycle spreading index (WCSI) for grading of polar compounds according to their potential to spread along a partially closed water cycle from discharge in municipal waste waters to raw and finally drinking water. However, monitoring data from waste water treatment plant (WWTP) effluents together with the relative removal in WWTPs are the basis for calculating the index. Both of these data will mostly not be available for chemicals registered within REACH, therefore such an approach will not be feasible in this context. Further, while our approach of an PMT assessment is prospective, i.e. aimed at recognizing possible substances of high concern before they are spread in the environment and are causing harm, the approach by Reemtsma et al. (2006) is a retrospective, i.e. measurements following exposure are used to filter the most problematic substances. Other retrospective approaches are the one by ter Laak et al. (2012) who propose to apply high resolution and accurate mass spectrometry to capture a wide range of organic chemicals simultaneously for water quality analysis, Murray et al. (2010) who combined occurrence data with toxicity data for prioritisation or Ortiz de García et al. (2013), who used QSAR predictions for persistence, bioaccumulation and toxicity for known pharmaceuticals and personal care products of concern together with production volumes for prioritisation.

Boriani et al. (2013; 2010) try to integrate firstly compartment-specific (soil, water-sediment, air) hazards in respect to the environment, human toxicity and cancerogenicity, secondly compartment specific exposure, thirdly environmental fate properties (water solubility, vapour pressure, adsorption, bioconcentration and persistence) and fourthly to integrate over several compounds relevant for a certain emission scenario into a single index to mirror overall environmental risk. Scoring methodology is hardly to follow as it is solely referred to the supplementary information parts of the journals not publicly available and no reasoning is given in the actual articles. Such a scoring system – taken for granted that it is sufficiently validated - may be useful for an overall risk assessment of a certain local area. However, in the end valuable information is lost by the integration process and consequently, it will not be obvious anymore as to what extent the risk stems from environmental effects, human toxicological effects or increased cancer risk. Further, it is very questionable if it is reasonable to add up risks regarding these very different endpoints over different compartments. Due to missing reasoning regarding the indexing system no conclusions regarding our PMT assessment scheme may be drawn.

The ranking approach by IfW (2010; 2011) is dismissed due to several methodological inconsistencies and/or limitations (see below).

In conclusion, for the purpose of a prospective assessment of PMT properties regarding relevance to raw water based on readily available data from the REACH registration process, we refrain from any further grading as this would not be meaningful given the heterogeneous data base and the other reasons outlined in the above paragraphs.

Several important publications on other approaches for determining raw water relevant substances are discussed within the background sections on persistence (2.1.2) and mobility (2.2.2), and the reader is referred to these sections.

Generally, assessment of raw water contamination is often restricted on surface waters. The reviews by (Lapworth, et al., 2012) and (Stuart, et al., 2012) are therefore of special interest as they summarize in a comprehensive way scientific work concerned with groundwater contamination. They discriminate classes of emerging groundwater contaminants, possible pathways of groundwater contamination, review risk assessments of pesticides (incl. metabolites) and emerging contaminants in regard to groundwater and important analytical work. It is interesting to note, that e.g. Worrall et al. (2000, as cited in Stuart, et al., 2012) also integrated  $K_{OC}$  as part of a so-called “probability index for predicting groundwater contamination risk”:  $\log K_{OC} > 4.0$  was used in this regard together with information on degradation to qualify non-leachers. This cut-off is very close to the one proposed in this project ( $\geq 4.5$ ) to qualify immobility, valid for *persistent* compounds (no degradation assumed).

As outlined in the background sections on persistence (2.1.2) and mobility (2.2.2), in a preceding work IfW elaborated an index system for prioritisation of chemicals according to their potential to enter raw water (IfW, 2011). With regard to physico-chemical and environmental fate related properties, three index groups were established, each giving at maximum 7 points, which are finally summed up for the total index (with a maximum of 21 points). These properties are

- $\log K_{OW}$
- water solubility
- $DegT_{50}$  (which relates to persistence).

This system has been questioned above (for details, see sections 2.1.2 and 2.2.2). Most importantly,  $\log K_{OW}$  is not the relevant property determining mobility, while  $\log K_{OC}$  is. This holds true especially for ionisable or ionic compounds. Water solubility is not decisive for mobility, and it is not independent from  $\log K_{OW}$ . Adding indexes of dependent properties leads to an overweighting. With regard to degradation, weighing of different tests/pathways was criticized.

In their work, IfW evaluated about 340 compounds with their indexing system. We investigated their results with respect to differences in the outcome regarding potential to enter raw water. However, the following obstacles were observed:

3. 80% of the compounds analysed by IfW are plant protection products, biocides or pharmaceuticals, usually not registered within REACH
4. A full REACH registration was found for only 19 substances. Only for these, necessary data for evaluation of PMT properties were available
5. Obviously, ionisable compounds, which would have been most interesting to compare ( $\log K_{OW}$  versus  $\log K_{OC}$  based assessment), were only exceptionally present. If they were, these were acidic (phenol group) or negatively charged compounds. For these, in *most* cases  $K_{OW}$  may be used as an *approximate* indicator of adsorption potential. This would *not* be the case for positively charged compounds.

Thus, those 19 compounds were mostly not critical with regard to evaluation of their mobility, i.e. the difference in using  $\log K_{OW}$  instead of  $\log K_{OC}$  was not decisive in these cases.

Nonetheless, in Table 26 three compounds evaluated by IfW (2011) were assessed with the method of this report, to illustrate the impact of the methodological differences:

Nitrilotriacetic acid was evaluated to be *mobile*, but not *persistent* in water using our methodology. The substance received a corresponding score by IfW of 14 (maximum possible: 21). The score was composed of solubility (6),  $K_{OW}$  (7) and  $DegT_{50}$  (1). According to our approach, the substance is *not pervious*, because it is not *persistent* in raw water. According to IfW, however, nitrilotriacetic acid had 2/3 of the maximal possible score due to the overweighing of  $K_{OW}$  / water solubility and the evaluation based on a graded total score.

Table 26: Comparison of results: PMT assessment versus IfW scoring system (IfW, 2011)

CAS	Name	PMT assessment results				IfW scoring system			
		P	M; log $K_{OC}$	T	Conclusion	Score WS	Score $K_{OW}$	Score P	Total score
139-13-9	nitrilo-tri-acetic acid	No	Yes; 1.4	$T_{screen}$ (Carc. cat. 2)	Not <i>pervious</i> to raw water; <i>not relevant</i> in raw water	7	6	1	14
637-92-3	2-ethoxy-2-methyl-propane	Yes (PBT ass.)	Yes; 1.3	--	<i>Relevant</i> in raw water (but not <i>critical</i> )	6	5	2	13
88-72-2	2-nitro-toluene	Yes (based on inherent biodegradability)	Yes; 2.6	T (Muta. 1B, Carc. 1B, Repr. Cat 2)	PMT (E2 not fulfilled)	4	4	2	10

The next example, 2-ethoxy-2-methyl-propane, is evaluated to be *relevant* in raw water (i.e. P, M, E2 fulfilled), but not *critical* (not T) following our methodology. Here, the different approach to assess persistence becomes obvious: the scoring of 2 for persistence according to IfW is equivalent to  $DegT_{50}$  values between 10 and 40 days, while the compound is assessed to be *persistent* according to REACH PBT assessment. Taking the total score of 13, this compound had even 1 point less than nitrilotriacetic acid, in spite of being *relevant* in raw water, while the former is not.

As a third example: according to our assessment, 2-nitro-toluene, is PMT and it would be a regarded critical in raw water<sup>50</sup>. This PMT compound receives the lowest total score of all three substances if the IfW method is applied, i.e. 10. Like before, persistence obviously does not highly considered (score: 2), and further, the higher log  $K_{OW}$  and lower solubility compared with the two other compounds reduce the score disproportionately. This reduction is actually not justified. This becomes clear from our background results on mobility taken to derive the cut-off of log  $K_{OC} < 4.5$  for mobility. According to these, a log  $K_{OC}$  of 2.6 implicates an only slightly lower surface water concentration compared to log  $K_{OC}$  of 1.3/1.4 as given for the other two compounds. However, according to the TRA model, groundwater concentration is higher instead

<sup>50</sup> if E2 would be fulfilled, which is however not the case (combination of ERCs and tonnage level suggests low environmental exposure).

(actually increasing up to a log  $K_{OC}$  of about 3.0 (see Figure 9)). IfW did not consider the groundwater pathway.

Further, toxicity was no criterion for IfW. In contrast, our assessment methodology allows for prioritisation of compound according to their (human) toxicity by discriminating compounds *relevant* in raw water (P, M, E2) from those being *critical* in raw water (P, M, E2, T).

In conclusion, the review of these three substances demonstrates that the scoring, applied in the precursor-project, provided questionable scoring results a) with respect to PMT classification of single substances, b) with respect to a meaningful priority ranking (relative interpretation of results for different substances).

## 2.6.2 REACH: current deficits in reporting with regard to raw water protection

### Limited requirements for full scale exposure assessment (incl. man via the environment)

Most generally, environmental exposure estimation and risk characterisation under REACH is currently necessary only when a Chemical Safety Report is required, i.e. for substances registered at the level  $\geq 10$  t/a and when the substance is classified.

The exposure of humans via drinking water is assessed under REACH in the context of human exposure via the environment. While the term *raw water* is not explicit under REACH, the calculations exemplified in the following sections show that the term *drinking water* under REACH relates to *raw water* rather than to true *drinking water* (after specific treatment). The Guidance on Information Requirements and Chemical Safety Assessment (Guidance IR & CSA), Chapter R.16 (ECHA, European Chemicals Agency, 2012e) stipulates that such an assessment of indirect exposure of humans via the environment is generally only conducted if:

- the tonnage  $>1,000$  t/a or
- the tonnage  $>100$  t/a and the substance is classified

as “Toxic” with a risk phrase “R48” (this would translate into H372 under the CLP Regulation); or

as a carcinogen or mutagen (of any category); or

as toxic to reproduction (category 1 or 2; this would translate into categories 1A or 1B under the CLP Regulation).

Despite these provisions in the Guidance IR & CSA, Chapter R.16 (ECHA, European Chemicals Agency, 2012e), the most recent “illustrative example CSR” from ECHA<sup>51</sup> (provided in November 2012) calculates both local and regional exposure of humans via the environment for a substance in the 100-1,000 t/a band that is not classified for hazards given above. More generally, ECHA’s CHEmical Safety Assessment and Reporting tool (CHESAR) calculates the concentration in drinking water and the intake via this pathway for the local scale for all substances assessed with the tool and these values are documented in the CSR created with this tool (only the total oral intake is given for the regional scale). An RCR specific for drinking water is not provided.

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<sup>51</sup> See <http://echa.europa.eu/web/guest/support/practical-examples-of-chemical-safety-reports>

From the above it becomes clear that the concentration of a substance in drinking water (raw water) is not calculated under REACH for

- substances registered at tonnages below 10 t/a
- substances registered at  $\geq 10$  t/a that are not classified
- substances registered at 100-1,000 t/a that are not “toxic” or CMR substances (see criteria above), but CHESAR will automatically calculate such figures.

For substances, for which the concentration in drinking water is calculated as part of the assessment of the exposure humans via the environment, the output is limited to the concentration itself and the intake via this pathway at the local scale, without providing e.g. a separate RCR for the drinking water pathway or the relative importance of this pathway compared to intake via food.

An assessment of the concentration in drinking water (calculated as part of the assessment of the exposure humans via the environment) in relation to potential PMT properties is not part of these assessments under REACH.

#### **Availability of information on transformation products**

Only in exceptional cases REACH will provide information on possible transformation products. The possible importance of transformation products for raw water protection is discussed above at several instances (see, e.g., section 2.5.2). There are two reasons for this reporting deficit:

- 1) Requirements to identify transformation products are limited
- 2) The structure of the reporting file (IUCLID) does not support a (voluntary or obligatory) implementation of adequate (and sufficiently detailed) reporting

As no separate section in IUCLID software (used to generate registration dossiers) is foreseen for identification of transformation products, this information - if available at all - will have to be manually extracted from the individual study summaries of study types potentially giving information in this regard (OECD TG 111 - hydrolysis, 307 – simulation test soil, 308 – simulation test sediment, and 309 – simulation test surface water). In most cases, however information given is not sufficiently precise to allow an assessment. In other words, major transformation products are not identified unequivocally as to allow for e.g. at least an assessment based on QSAR.

If the requirement of REACH Annex IX (applicable for substances registered for a tonnage level  $> 100$  t/a), no. 9.2.3 “Identification of degradation products” for compounds not shown to be readily biodegradable, would be given more weight, other implications on requirements for transformation products within REACH incl. guidance documents would also gain more importance. To achieve this, within IUCLID software used for compilation of registration dossiers, a separate structured entry for “Identification of degradation products” would be necessary.

### 3 Assessment Tool

Besides the general analysis and development of guidelines for precautionary measures to protect raw water, the implementation of the developed guidelines in a software tool was an important goal of this project. With the software tool, the guidelines are accessible for expert and non-expert users in a clearly structured fashion and a batch assessment of a large number of substances becomes possible, given the needed information is available. This section describes context, design, and implementation of the developed tool.

#### 3.1 KnowSEC

As the basis for the implementation of the assessment tool, the collaborative decision support and documentation system KnowSEC, used internally at the German Federal Environmental Agency, was chosen. In the context of the expert evaluation report FKZ 3600 1060<sup>52</sup> and the research and development grant UFOPLAN 3711 63 420<sup>53</sup>, KnowSEC was specifically designed, implemented<sup>54</sup>, and deployed for and within the working group IV 2.3 of the German Federal Environmental Agency, which is responsible for the assessment of chemicals registered under REACH. Since 2012 KnowSEC is in daily use to help with regulatory responsibilities of the working group.

KnowSEC allows for the documentation and decision support of substance-related decisions. Members of the working group IV 2.3 are able to view information on substances via a central *info page* mechanism, providing one wiki page for each substance known to the system.

Additionally, KnowSEC provides a large number of *dynamic lists*. Those lists show substances known to the system to fulfill specified list criteria. The lists are not manually maintained, but are dynamically generated and updated by the system itself, based on the information provided on the different info pages. A substance will automatically appear or disappear on the lists, when new information is entered on the info page of the substance.

Information can be added to KnowSEC in different ways. Being based on a wiki, informal content can be added easily at any time on a wiki page. On info pages of substances, semi-formal information can be added via *memos*. Memos allow plain text input by the users, but are also attributed with structured information like author, date, and formal decisions. The structured information can be used as constraints during the definition of a dynamic list. As an example for a memo, a user can describe that, based in the information of various sources, the substances are assumed to be toxic. To allow the easy use in dynamic lists, the user can then also attach the formal decision “Substance is toxic”.

The most formal way to add information about substances in KnowSEC is via question-answer interviews that are also available on the info pages. For a variety of topics so called *modules* were implemented asking

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<sup>52</sup> Conception and development of a prototype for decision support for the identification of environmentally relevant chemicals and necessary regulatory measures in the context of REACH

<sup>53</sup> Clarification of technical and juridical possibilities and development of solutions for the usage of data generated under REACH for environmentally relevant management options on all planes of German agencies and laws

<sup>54</sup> For the implementation of KnowSEC, the open-source system KnowWE was extended. KnowWE is a full-featured semantic wiki for the development of diagnostic knowledge bases and OWL/RDF(S) ontologies. For a recent and more detailed overview of KnowWE we refer to (Baumeister et al, 2012).

questions to be answered by users working on the substances. Based on the given answers and problem-solving knowledge specified for each module, KnowSEC derives appropriate decisions. These decisions are then displayed in a summary on the info page and are again usable for constraints in dynamic lists.

The screenshot shows the KnowSEC interface for the substance 'Kryptonite'. The top header includes the user name 'G'day, Albrecht Striffler (authenticated)', 'Log out', and 'My Prefs'. The main content area is divided into several sections:

- Navigation:** A sidebar menu with options like Home, Teams, Internet Resources, Glossary, Administration, Recently Changed, Substance Lists, and Support.
- Decisions (4):** A summary of derived decisions:
  - Relevance: Activities of Agencies (Substance is handled by another agency in Germany)
  - Ecotoxicity: Final decision: Not T (for PBT); Aquatic toxicity (Aquatic Tox - Not T)
  - PBT: Final decision: Not PBT
- Memos (3):** A list of user-generated notes:
  - Literature says...**: Joachim Baumeister, Ökotoxikologie-Team, 26.11.2013 12:52h. Aquatic Tox - Not T (**Established**). Literature XXX proved...
  - Toxic**: Joachim Baumeister, Ökotoxikologie-Team, 21.10.2013 07:25h. T-Criterion fulfilled (Drinking Water) (**Established**). Superman: The Man of Steel Sourcebook (1992), while non-canon, concurs, referring to Kryptonite as "the common ore of the super-actinide Kryptonium, an unusually stable transuranic element, whose atomic number is believed to be 126". Kryptonium is given a radioactive half-life of 250,000 years. (from Wikipedia)
  - Initial Memo**: Joachim Baumeister, Abbau-Team, 21.10.2013 07:24h. This is a example page!!! Kryptonite is a fictional substance known from the Superman world. As a radioactive element originating from Superman's home planet of Krypton.
- Identifier:** A table of substance identifiers:
 

Identifier	Value
EC Number	123-456-3
CAS Number	12345-67-4
IUPAC Name	Not found
SMILES	Not found
Substance Name	Kryptonite
	Cryptonite

Figure 15: Example info page of the imaginary substance Kryptonite. Shown are the identifiers of the substance on the right, summary of derived decisions on the upper centre, memos in the lower centre of the page. Modules are on the lower left side.

The guidelines for the precautionary protection of raw water were implemented as an additional *module* in KnowSEC, called "Raw Water Protection". It is a full-featured module in addition to other modules on domains like relevance (based on political, regulatory, or research related considerations), exposure (indications for release of chemicals to the environment), and the raw water independent assessment of persistence, bioaccumulation, and toxicity. It can be used by the members of the working group IV 2.3 for their daily work. In the long term, usage of the tool in a stand-alone edition outside the Federal Environmental Agency independent of KnowSEC is possible and planned.

### 3.2 The module „Raw Water Protection“

KnowSEC allows the creation of new modules for decision support directly within the system. Questionnaires and the contained questions and answers as well as the respective derivation knowledge can be added and edited by domain specialists in the administration part of the system. Changes to the software are not necessary; on the contrary, the changes can be made during normal daily operation. This allows simple adjustments to the derivation knowledge of the module, for example in case there are changes to the agreed upon cut-off values in the future.

### 3.2.1 Terminology of the module "Raw Water Protection"

As described in this report, the assessment of substances in the context of raw water comprises the three main aspects *persistence*, *mobility*, and *toxicity*. Additionally, the assessment of exposure allows shortcuts in the assessment of substances, and some substances have to be excluded from assessment, because of special properties not covered in this project. Therefore, similar to the practical guide, the module "Raw Water Protection" in KnowSEC comprises the following aspects:

- Exposure Evaluation (Tier 1): Can exposure to the environment be excluded due to usage only as "intermediates under strictly controlled conditions"?
- Substance Characterisation: Is the module competent to assess the given substance?
- Persistence: Is the substance persistent in water?
- Mobility: Is the substance mobile in water?
- Exposure Evaluation (Tier 2): Can the substance be excluded because of insignificant exposure to the environment based on registered ERCs and tonnages?
- Toxicity: Is the substance toxic in water?

For each of those aspects, the module uses its one or multiple wiki pages to define the contained questions, answers, and decisions, as well as the knowledge describing how decisions are derived given certain answers. While each aspect defines its own decisions like "P Criterion fulfilled" or "No relevant exposure potential for raw water" that are derived completely from within the given aspect (in this case Persistence and Exposure Evaluation), there are also overall decisions summarizing the combined output of all aspects for the module, e.g. "Critical in raw water".

In the following sections, the questions, answers, and decisions of each aspect will be presented. They are the result of the guidelines given in the previous chapters of this work implemented in the software. While some of the terminology is directly apparent from working through the guidelines (e.g. "What is the log  $K_{OC}$  of this substance?"), other questions are used to automatically show or hide follow-up questions and thus improve the user experience (e.g. "Enhanced Ready-Test available?").

Questions with deeper indentations are follow-up questions of the ones above. After each question, the type of the question is shown. The annotation [yn] stands for Yes-No-Questions; [oc] stands for One-Choice-Questions, where only one of the given answers can be selected at any time. With [mc] as annotation, multiple answers can be selected at the same time. For questions marked with [num], a numerical answer is expected. Numerical questions may also have attached a unit (e.g.  $\{\mu\text{g/L}\}$ ) and an expected value range (e.g. (0-14)).

#### Exposure Evaluation (Tier 1)

Questions:

- Substance used only as an intermediate under strictly controlled conditions? [yn]
  - May environmental exposure safely be excluded for other reasons? [yn]

Decisions:

- No relevant exposure potential for raw water
- Relevant exposure potential for raw water

#### Substance Characterisation

Questions:

- Is the substance inorganic (including metals and their compounds) or organometallic? [yn]
- Is the substance a transition metal complex with organic ligands? [yn]
- Is the substance a salt with at least one organic constituent? [yn]
- Is the substance multi-constituent or UVCB? [yn]
- Is the substance surface active (surfactant), i.e. has detergent-like properties? [yn]
- Is the substance ionic, zwitterionic or ionisable at environmentally relevant pH? [oc]
  - What is the calculated  $pK_a$ ? [num]
  - What is the calculated  $pK_b$ ? [num]
- What is the water solubility of this substance? [num] { $\mu\text{g/L}$ }
  - At what pH was the water solubility determined? [num] (0 14) {pH}

#### Decisions:

- Substance can currently not be evaluated for raw water relevance (wrong type of substance)
- Raw water contamination can reasonably be excluded
- Raw water contamination cannot reasonably be excluded
- Substance is ionisable
- Substance is non-ionisable
- Each constituent has to be assessed separately.
- Only experimentally derived values for  $K_{OC}$  and biodegradation may be used.
- Ionisation information missing

#### Persistence

##### Questions:

- Test on Ready Biodegradability available (OECD 301 A-F, OECD 310)? [oc]
  - Test on READY Biodegradability performed according to relevant guideline without relevant deviations?" [yn]
    - Readily Biodegradable within 28 days? [yn]
    - ThCO<sub>2</sub> (% degradation in 28 days) [num] (0 100) { % }
    - ThOD (% degradation in 28 days) [num] (0 100) { % }
    - "DOC (% degradation in 28 days)" [num] (0 100) { % }
- Enhanced Ready-Test available? [oc]
  - ThCO<sub>2</sub> (% degradation during possibly elongated time frame (up to 60 d)) [num] { % }
  - ThOD (% degradation during possibly elongated time frame (up to 60 d)) [num] { % }
  - DOC (% degradation during possibly elongated time frame (up to 60 d)) [num] { % }
- Tests OECD 302 B on Inherent Biodegradability available?" [oc]
  - % Degradation (DOC removal) within 7 days" [num] { % } (0 100)
  - Log-Phase (OECD 302 B) [num] (Kleinhans and Dayss) (0 1000)
  - % removal before degradation occurs [num] (0 100) { % }
  - Pre-adapted inoculum used? (OECD 302 B) [yn]
- "Tests OECD 302 C on Inherent Biodegradability available? [oc]
  - % Mineralisation (O<sub>2</sub> uptake) within 14 d (0 100) { % } [num]
  - Log-Phase (OECD 302 C) (Kleinhans and Dayss) [num]
  - Pre-adapted inoculum used? (OECD 302 C)" [yn]
- Test on Hydrolysis (OECD 111) available? [oc]
  - Half-life hydrolysis (OECD 111) determined at pH 7 (Kleinhans and Dayss) [num]
  - At which temperature was the half-life determined? { °C } [num]

- "Simulation test on aerobic mineralisation in surface water (OECD 309) or similar test (e.g. River die away test, OECD 314 D) available? [oc]
  - Ultimate biodegradation half-life DT50 (mineralisation to CO<sub>2</sub>) (Kleinhans and Days) [num]
  - Primary biodegradation half-life (DT50) (Kleinhans and Days) [num]
- QSAR Screening BOWIN
  - PBT assessment under REACH performed and published (ECHA-Chem)? [yn]
  - What was the result of the PBT assessment? [oc]
    - P or vP, Not P, Inconclusive
  - Result of QSAR Screening on P based on binary combinations of BOWIN modules (2/3 or 6/3) [mc]
    - P1, P2, Neither P1 nor P2

Decisions:

- P Criterion fulfilled (Raw water)
- Not P (Raw water)
- Unable to decide about P (Raw water)
- READY Test: Readily biodegradable
- READY Test: Inherently biodegradable
- Enhanced READY Test: Pass levels reached
- Not ultimately degradable in enhanced READY-Test
- OECD 302 B: Inherently biodegradable
- OECD 302 C: Inherently biodegradable
- OECD 302 B: Not inherently biodegradable fulfilling specific criteria
- OECD 302 C: Not inherently biodegradable fulfilling specific criteria
- OECD 111: Hydrolysable
- OECD 309: Ultimately biodegradable
- OECD 309: Primary biodegradable
- OECD 309: Not biodegradable
- QSAR: Biodegradable
- QSAR: Not biodegradable
- PBT assessment: P or vP
- PBT assessment: Not P

**Mobility**

Question:

- What is the log K<sub>OC</sub> of this substance? [num]
- How was the log K<sub>OC</sub> determined? [oc]
  - Experimentally (like OECD 106)
  - Experimentally (like OECD 121)
  - Calculated

Decisions:

- M Criterion fulfilled (Raw water)
- Not M (Raw water)
- Unable to decide about M (Raw water)

- Evaluation of M criterion only possible for persistent substances
- Substance can currently not be evaluated for raw water relevance (no log K<sub>OC</sub> available)
- Substance can currently not be evaluated for raw water relevance (calculated log K<sub>OC</sub> not suitable)
- Substance can currently not be evaluated for raw water relevance (log K<sub>OC</sub> from OECD 121 not suitable)

### Exposure Evaluation (Tier 2)

#### Questions:

- What is the highest tonnage band the substance is registered for? [oc]
  - Tonnage band confidential
- Select the specified ERCs (environmental release categories) for this substance [mc]
  - 1, 2, 3, 4, 5, 6B, 6C, 6D, 7, 8A, 8B, 8C, 8D, 8E, 8F, 9A, 9B, 10A, 10B, 11A, 11B, 12A, 12B
  - None specified
  - ERCs are confidential

#### Decisions:

- Relevant due combined assessment of ERCs and total tonnage
- Not relevant due combined assessment of ERCs and total tonnage
- Assumed to be relevant due to lacking data on tonnage
- Assumed to be relevant due to lacking information on environmental release

### Toxicity: Is the substance toxic in water?

#### Questions:

- Substance part of a qualified toxic substance inventory (raw water)? [yn]
- Is the substance suspected endocrine acting? [yn]
- Is the substance classified according to REGULATION (EC) No 1272/2008 (CLP)? [yn]
  - Indication for genotoxicity/carcinogenicity (WOE incl. SAR) (Expert)? [yn]
  - Select the appropriate carcinogen category of this substance [oc]
    - 1A, 1B, 2, None
  - Select the appropriate reproductive toxicant category of this substance [oc]
    - 1A, 1B, 2, None
  - Select the appropriate mutagen category of this substance" [oc]
    - 1A, 1B, 2, None
  - Select the appropriate STOT RE category of this substance" [oc]
    - 1, 2, None
  - Is the substance assigned as H362? [yn]
  - May Threshold (Carc.) be derived? [yn]
- Is DNEL (oral, long term; general population) derived? [yn]
  - May DNEL (oral, gen. pop., long term) be derived? [yn]
    - What is the Cramer classification according to TOXTREE? [oc]
      - Cramer I, Cramer II, Cramer III
  - DNEL [num] {µg/kg x d}
  - Threshold (Carc.) [num] {µg/kg x d}

#### Decisions:

- T Screening (Raw water)
- T Criterion fulfilled (Raw water)
- Not T (Raw water)
- Unable to decide about T (Raw water)

### Overall decisions

- Pervious to raw water
- Not pervious to raw water
- Relevant in raw water
- Not relevant in raw water
- Critical in raw water
- Critical in raw water (Screening)
- Not critical in raw water
- Unable to decide about PMT
- Final decision: Not PMT
- Final decision: PMT, criterion considered to be definitely fulfilled
- Final decision: PMT (Screening), criterion considered to be definitely fulfilled
- Final decision: PM, criterion considered to be definitely fulfilled

To improve the readability, the questions, answers, and decisions displayed above are the short versions of the ones displayed in the actual interview in KnowSEC. KnowSEC allows the definition of more detailed textual prompts that are shown in the interview. Also explanation text then shown as tool tips can be added.

In case the substance in question is not covered by this work or environmental exposure can be excluded in the first place, the aspects about substance characterisation and exposure can be used to abort the assessment of a substance. Compliance to the given order of aspects or questionnaires is recommended to make use of these shortcuts. An assessment independent of the given order will however still yield decisions that are correct on the basis of the information currently known to the system. If for example the questionnaire *Persistence* is assessed prior to the questionnaire *Substance Characterisation*, then it is possible that decisions will be retracted, because the substance is later known to be of a kind not covered by the module.

### 3.2.2 Derivation knowledge of the module

To derive decisions based on given answers by the user, KnowSEC allows the usage of different knowledge representations. Flowcharts and text rules, the two representations used the most in the implementation of the module "Raw Water Protection", will be shown in more detail.

Since the amount of knowledge used in the module is quite extensive, only excerpts are shown in this document. Because the terminology and knowledge of modules is done completely within KnowSEC itself using easy to read wiki markup languages, it is still very accessible, even for non-software developers.

### DiaFlux flowcharts

From the practical guidelines generated in this project, it is directly apparent, that visual flowcharts are an important and intuitive tool to communicate even complicated sequential instructions, as given in the domain at hand. With the workflow language DiaFlux, KnowSEC allows drawing flowcharts that are still visual and easy to comprehend for humans, but can also be interpreted and executed by the system. For further technical details about DiaFlux, see (Hatko et. al, 2011).

As an example, Figure 16 shows the DiaFlux flowchart describing the knowledge underlying the aspect "Exposure Evaluation Tier2". As soon as the user reaches this part of the module, the flowchart is executed by the system, starting at the green node with the label "start". The yellow nodes are questions directly answered by the user. Depending on the given answers, the respective outgoing edges are expanded. Grey nodes are variables for which the outgoing edge may be decided by other knowledge representations like text rules or tables instead of the direct input of a user. As soon as the violet nodes are reached, the decisions assigned to these nodes are established and shown to the user. If the user later saves the progress in the interview of module, the decisions are also propagated to the rest of the system. After decisions are established, flowcharts usually reach red exit nodes. Similar to the green start nodes, exit nodes are connectors to be used in flowcharts of higher tier. Those higher tier flowcharts can call sub-flowcharts. There, sub-flowchart are represented as nodes with the different exits nodes as the labels for possible outgoing edges to be connected to other sub-flowcharts or other ordinary nodes.

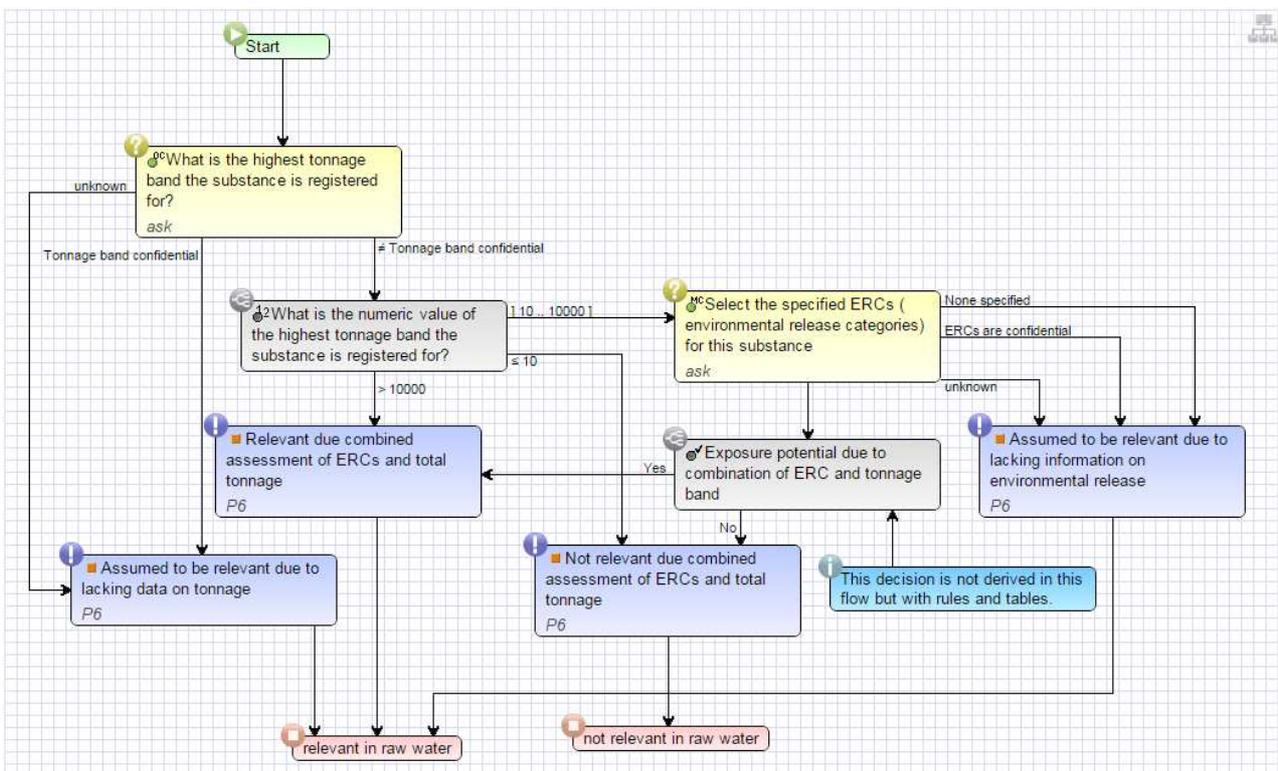


Figure 16: The DiaFlux flowchart used for the aspect "Exposure Evaluation Tier2".

**Text rules**

Many knowledge-based system use simple text rules as primary knowledge representation. They allow for the specification of relations between facts that are often difficult to represent in other, more specialized representations, or would produce a disproportional amount of overhead and verbosity.

```

IF "P-Criterion fulfilled (Raw water)" = established
  AND "M-Criterion fulfilled (Raw water)" = established
  AND "T-Criterion fulfilled (Raw water)" = established
EXCEPT "Substance can currently not be evaluated for raw water relevance (wrong type of substance)" = established
THEN "Final decision: PMT, criterion considered to be definitely fulfilled" = P6

IF "P-Criterion fulfilled (Raw water)" = established
  AND "M-Criterion fulfilled (Raw water)" = established
  AND "T Screening (Raw water)" = established
  AND NOT("T-Criterion fulfilled (Raw water)" = established)
EXCEPT "Substance can currently not be evaluated for raw water relevance (wrong type of substance)" = established
THEN "Final decision: PMT (Screening), criterion considered to be definitely fulfilled" = P6

```

Figure 17: Text rules defining abstract criteria to derive the overall decisions for PMT substances.

As an example, Figure 17 show two rules deriving the overall decisions about whether a substance is a PMT substance or not. Only if all the necessary intermediate decisions (P, M and T) from the different aspects are established, the overall decision PMT is derived. The decision “Substance can currently not be evaluated...” after the keyword “EXCEPT” prevents the derivation, in case a wrong substance type was determined in the aspect “Substance Characterisation”.

### 3.3 Assessment of substances

After the implementation of the module in KnowSEC, it appears on all substance info pages in the left menu under the headline “Decision Making” (see Figure 15 above and Figure 18). Selecting the module in the given list will replace the right side of the substance info page with the questions and the available answers of the module. The user can then start selecting or entering the appropriate answers. Some questions or answers might require additional clarification or information to be correctly handled by the user. KnowSEC allows adding tool tips in this case (see Figure 20). Questions and answers providing a tool tip are marked with a trailing start (\*).

The screenshot displays a web-based decision-making interface. On the left is a sidebar menu titled 'Decision Making' with a 'Filter' input. The menu lists various categories: Relevance, Exposure, Persistence (with a badge '1'), Bioaccumulation, Ecotoxicity (with a badge '1'), PBT (with a badge '1'), Endocrine Disrupting Properties, Human Toxicity, Human Biomonitoring Program, C&L, Mobility Properties, Raw Water Protection (expanded), Exposure Evaluation Tier 1 concerning Raw Water (with a badge '1'), Substance Characterization concerning Raw Water (with a badge '2'), Persistence concerning Raw Water (with a badge '2'), Mobility concerning Raw Water, Exposure Evaluation Tier 2 concerning Raw Water, Toxicity concerning Raw Water (with a badge '1'), Climatic Change Potential, Commenting, CCH (with a badge '1'), and TBE (with a badge '2').

The main content area has a top toolbar with 'Save', 'Memo', and 'Back' buttons. Below this, a question asks for the experimentally determined water solubility of a substance, with a text input field and a dropdown menu showing 'µg/L' and 'unknown'. A section titled 'Persistence concerning Raw Water' contains several sub-questions:

- 'Test on Ready Biodegradability available (OECD 301 A-F, OECD 310)?' with options 'available', 'not available', and 'unknown'.
- 'Test on READY Biodegradability performed according to relevant guideline without relevant deviations? \*' with options 'Yes', 'No', and 'unknown'.
- 'Readily Biodegradable within 28 days? \*' with options 'Yes', 'No', and 'unknown'.
- 'ThCO2 (% degradation in 28 days) \*' with a text input '10' and options '%', 'unknown'.
- 'ThOD or BOD (% degradation in 28 days) \*' with a text input '0 - 100' and options '%', 'unknown'.
- 'DOC (% degradation in 28 days) \*' with a text input '0 - 100' and options '%', 'unknown'.
- 'Enhanced Ready-Test available? \*' with options 'available', 'not available', and 'unknown'.
- 'Tests OECD 302 B on Inherent Biodegradability available?' with options 'available', 'not available', and 'unknown'.
- 'Tests OECD 302 C on Inherent Biodegradability available?' with options 'available', 'not available', and 'unknown'.
- 'Test on Hydrolysis (OECD 111) available?' with options 'available', 'not available', and 'unknown'.
- 'Half-life hydrolysis (OECD 111) determined at pH 7 \*' with a text input '56' and options 'days', 'unknown'.
- 'At which temperature was the half-life determined?' with a text input '25' and options '°C', 'unknown'.
- 'Simulation test on aerobic mineralization in surface water (OECD 309) or similar test (e.g. River die away test, OECD 314 D) available?' with options 'available', 'not available', and 'unknown'.

A section titled 'QSAR-Screening BIOWIN' contains:

- 'PBT-assessment under REACH performed and published (ECHA-Chem)?' with options 'Yes' and 'No'.
- 'What was the result of the PBT-assessment?' with options 'P or vP \*', 'Not P', and 'Inconclusive \*'.

Figure 18: The question-answer-interview of the aspect "Persistence" in the module "Raw Water Protection". On the left, specific other aspects of the module and also other modules available in KnowSEC can be selected. On the right, questions can be answered. Follow-up questions are automatically expanded after selecting respective answers, but they can also be expanded manually.

Using the button "Back" in the top tool bar will bring back the original content of the info page at any time.

While answering questions, decisions will already be derived in the background, but they are not yet communicated to the rest of the system or other users. Instead they will be available as previews via the grey badges in the left menu behind the labels of the different modules and aspects. The badges show the number of currently derived decisions for the given module or aspect, clicking them will display the decisions as shown in Figure 19. After the user has finished his current session, clicking the button "Save" in the toolbar at the top will make the changes permanent and also propagate them to the rest of the system, e.g. to update dynamic lists.

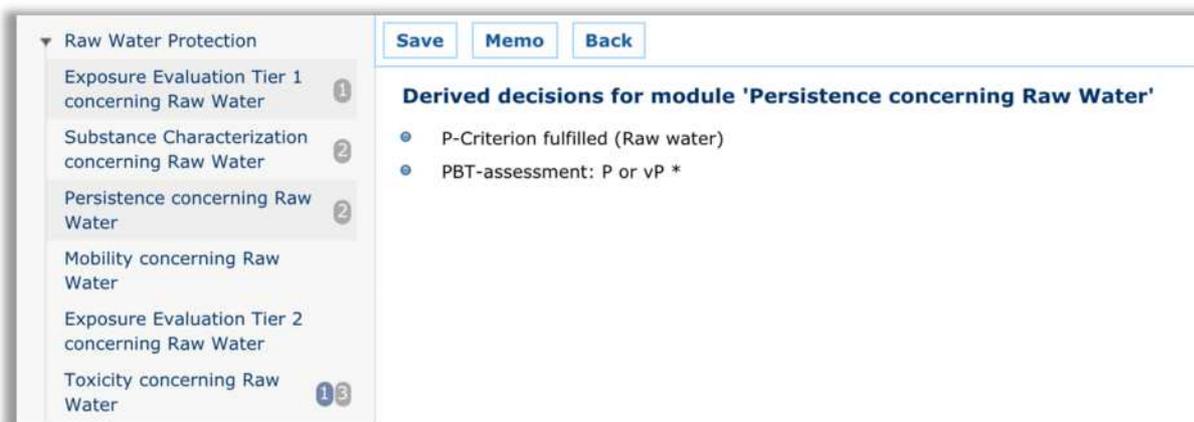


Figure 19: The decisions derived for the aspect "Persistence" in the module "Raw Water Protection" in an example substance.

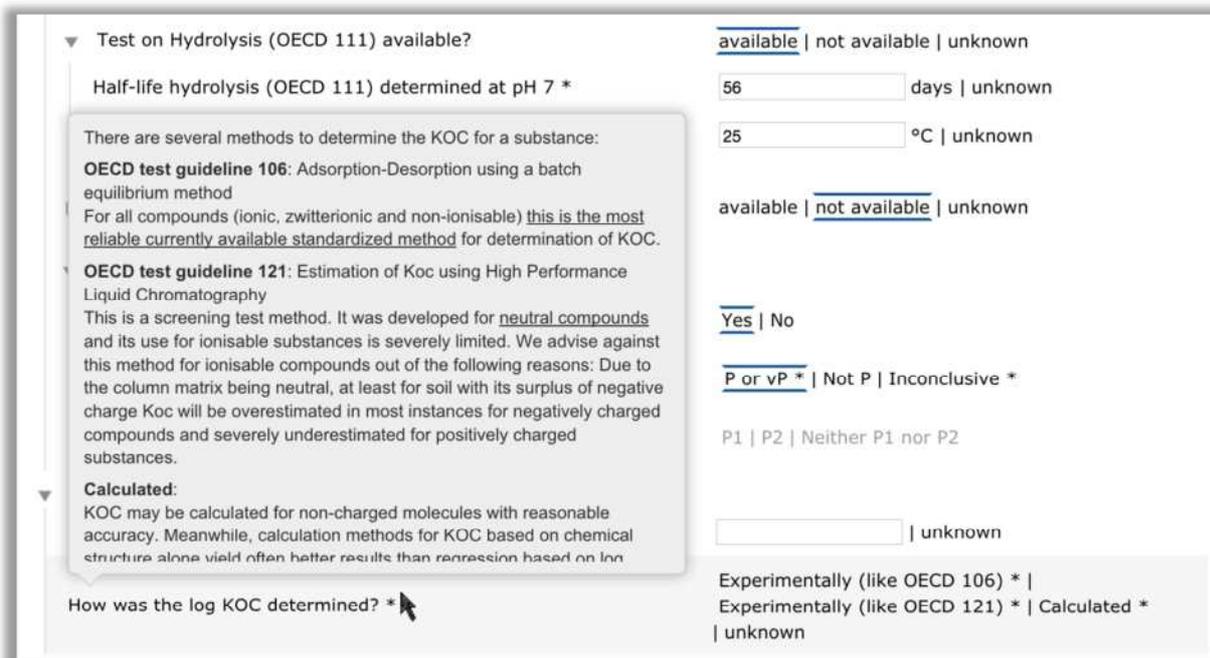


Figure 20: Example of a (scrollable) tool tip, that can be added to more complex questions in KnowSEC.

### 3.4 Tool validation

As described in the following chapter, a number of substances were chosen for testing the appropriateness of the PM(T) assessment methodology that was developed in this project. Additionally, in order to validate the correctness of the developed software tool, the substances were first assessed manually without the usage (establishing a gold-standard) and later processed with the tool. This way, the results of the manual and the tool assisted assessment could be compared and potential differences found and fixed. Also, the result of the assessment of the substances regarding their PM(T) classification is not only available in this report, but also digitally on the different substance info pages and also the dynamic lists in KnowSEC. The assessment in KnowSEC comprises the 84 mono-constituent compounds described in section 4.2 and also the 9 compounds selected from monitoring data in section 4.3.

The final results of both the manual and the tool assisted assessments are equivalent.

## 4 Example Substances for Validation of PMT Assessment Methodology and for Illustration

An analysis of an extended number of example substances was performed in order to

- test the appropriateness of criteria for PM(T) classification,
- determine the PMT properties of chemicals substances found in ground- or surface water, and to
- improve the decisions structure within this methodology and the assessment tool if required.

In fact, some important improvements of the methodology were indicated in the process of example assessments. These are already included in the methodology of PMT assessment as described in this report and are not presented and discussed separately.

### 4.1 Derivation of initial substance pool from REACH registered substances for assessment of PMT properties

#### 4.1.1 Property search and results

##### Step 1: Data retrieval via eChemPortal from ECHA CHEM

eChemPortal<sup>55</sup> allows to search for substances with user defined properties (“Chemical property data search”) and allows for setting of the database used for selection. The sole database used was ECHA CHEM. The following constraints were set:

1.  $K_{oc}$ :
  - Experimental, calculated, QSAR or read-across
  - Reliability 1 or 2
  - Log  $K_{oc}$ : -4.5 – 4.5

---

<sup>55</sup> [http://www.echemportal.org/echemportal/index?pageID=0&request\\_locale=en](http://www.echemportal.org/echemportal/index?pageID=0&request_locale=en)

- Search result: 1008 hits
2. Biodegradation in water: screening tests:
- Experimental, calculated, QSAR or read-across
  - Reliability 1 or 2
  - Not inherently biodegradable / under test conditions no biodegradation observed
  - Search result: 2317 hits
3. Combination of results with additional constraints  $\log K_{OC} \leq 4.5$  AND *not biodegradable* resulted in 608 hits

### Step 2: Delete substances without CAS

- Removes multi-constituent substances (reaction masses of...) and some UVCBs (checked individually)
- Result: 523 hits remaining

### Step 3: Check for full dossier

- Removes substances registered with an intermediate registration only
- Result: 484 hits remaining, representing
- 92 unique chemical substances

### Step 4: Screen in OECD QSAR toolbox for additional information

Information used in the following steps, e.g. SMILES-codes

### Step 5: Check for multi-constituent substances and UVCBs

Partially performed by UBA, or manually derived from dossiers by FoBiG.

<b>Result: 65 mono-constituent potential PM substances remaining</b>
--

#### 4.1.2 Drinking water directive (DWD, Directive 67/548/EEC)

Annex I part B contains a list of 26 chemicals / sum parameters (e.g. PAH) to be monitored in drinking water with upper levels specified. Compounds being part of this list are included because of their toxicity. This list was processed the following way:

- removal of inorganics
- removal of sum parameters (exception: tri- and tetrachloroethylene)
- removal of generic entry for plant protection products

**Result: 9 potential T substances remaining**

#### 4.1.3 Compound selection based on screening-type information

A second set of further compounds were selected based on mostly screening-type information. The following criteria were applied:

- Mono constituent substances
- High tonnage band
- Strong suspicion on P
- No hydrolysis
- No suspicion on B

54 compounds resulted, two of which (trichloroethylene and tetrachloroethylene) were already included within the compounds derived from DWD. Thus, in effect 52 new compounds could be derived from this selection.

These were filtered for prioritisation by the following criteria based on classification and labelling plus some additional information:

- CMR Cat. 1 or 2 (acc. to Directive 67/548/EEC) compounds removed (n= 2): These will be in the regulatory focus anyway.
- Muta. Cat. 3 or Repr. Cat. 3 (acc. to Directive 67/548/EEC) compounds removed (n= 6): These will most probably be also in the regulatory focus.
- R48 (acc. to Directive 67/548/EEC) to select for repeated dose toxicity: 4 compounds resulted, all of which were selected for PMT assessment.
- Carc. Cat. 3 (acc. to Directive 67/548/EEC): 4 compounds resulted, 2 of which were selected based on random for PMT assessment.
- Compounds listed for CoRAP

**Result: 10 mono-constituent potential PM compounds selected for PMT assessment**

## 4.2 Application of PMT criteria on initial substance pool - results

The initial substance pool comprised by results from sections 4.1.1 and 4.1.3 amounted to 84 monoconstituent substances. SMILES codes were derived from OECD QSAR toolbox or from ECHA-Chem.

**Total initial substance pool for further assessment of PMT properties:  
84 mono-constituent compounds**

#### 4.2.1 Exposure evaluation tier 1 (E1)

Except for the 10 compounds selected based on screening-type information (section 4.1.3), all compounds had been verified to fulfil E1 from the very beginning.

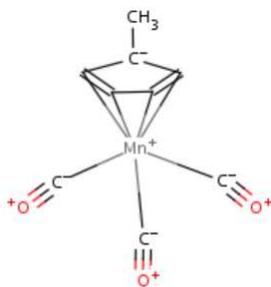
With regard to the former, 2 compounds (6-chloro-N,N'-diisopropyl-1,3,5-triazine-2,4-diamine, CAS 139-40-2; Atrazine, CAS 1912-24-9) were registered under REACH as intermediate, only. Because of this, the potential for raw water contamination is regarded to be negligible (E1 not fulfilled). These compounds are therefore concluded to be *not relevant* in raw water and are not further assessed for PMT properties. Being *not relevant* in raw water is however only valid with respect to the registration under REACH. Atrazine was widely used as a plant protection product (herbicide, EU-authorisation withdrawn 2003, prohibited in Germany since 1992) and is still of concern with regard to groundwater contamination. Using the data available from the intermediates dossier, it would indeed be evaluated as *persistent* (P, due to not readily biodegradable plus predicted to be *persistent* by QSAR – P1, P2) and *mobile* (non-ionisable within relevant pH-range; calculated log  $K_{OC}$  2.35) according to the criteria elaborated in this work. The other compound (with the trivial name Propazine) is a triazine herbicide. No further information was available to us.

In conclusion, the initial substance pool is reduced by 2 compounds to a remaining of 82 compounds.

#### 4.2.2 Substance characterisation - results and conclusions

Multi-constituent substances and UVCB were already excluded as described above (section 4.1.1, step 5). For the pool of 82 mono-constituent substances, the remaining aspects of applicability of the PMT assessment methodology were evaluated. Important results, observations and occasionally resulting amendments of the substance characterisation module are outlined in the following paragraphs:

- Inorganics cannot be assessed, thus one inorganic compound was dismissed (calcium cyanamide, CAS 156-62-7). Inorganic compounds from Directive 67/548/EEC had been dismissed earlier as described under section 4.1.2.
- Tricarbonyl(methylcyclopentadienyl)manganese (CAS 12108-13-3)



was determined to be a transition metal complex with organic ligands. The SMILES code used as input for most QSAR models cannot take account of such complex molecular formations based on non-covalent interaction. Instead, all constituents of the above molecule would be given separately resulting in a chaotic assembly of the constituents, giving a poor picture of the true situation. Transition metal complexes were not yet accounted for in the applicability domain. Thus, the domain was further specified, in that transition metal complexes are in principle within the applicability domain with the restriction that only experimentally derived values for  $K_{OC}$  and

biodegradation may be used for the assessment (QSAR is not applicable). Further, biodegradation is confined to the organic part of the substance.

- Diphosphoric acid, compd. with piperazine (CAS: 66034-17-1) is an example for a salt soluble in water. The applicability domain not yet accounted for salts. The substance characterisation was amended by explicitly accounting for salts with at least one organic constituent: Due to environmental distribution and partitioning as well as buffer effects, anions and cations of soluble salts will distribute separately and thus, each constituent has to be assessed separately. Further, as with the given example (the anion is inorganic, i.e. not in the scope of the assessment), only organic ions are relevant for assessment (in the example given the cation piperazine as an amine with alkaline functionality).
- Water solubility: Two non-ionisable substances were dismissed due to very low water solubility below the cut-off of 150 µg/L: 1,1'-(1,1,2,2-tetramethylethylene)dibenzene (CAS 1889-67-4) and octamethyltrisiloxane (107-51-7).
- Assessment of ionisation potential: To this end, for all compounds registration dossiers (ECHA CHEM) were checked for experimental  $pK_a$  values. Further,  $pK_a$  values for acidic and alkaline functionality were calculated using the “[ACE and JChem acidity and basicity calculator](#)” in “JChem.” mode. As a result,  $pK_a$ -thresholds for determination of ionisability were found to be too strict (too wide), such that too many compounds were determined to be ionisable within environmentally relevant pH-range 5-9, implicating the need for an experimentally determined  $K_{oc}$  by the batch equilibrium method. Due to these data being infrequently available (mostly HPLC screening assessment according to OECD 121 applied), such compounds would be dismissed as being not assessable due to inappropriate mobility data. As a compromise between taking account of environmentally relevant physico-chemical properties and keeping the applicability domain for assessment as broad as possible, the commonly most relevant pH-range was set as pH 6-8 (i.e. ionisation potential for  $pK_a < 8.5$  for acidic and  $> 5.5$  for alkaline functionality). With these cut-offs, 7 compounds were not assessable due to relevant ionisation potential and inappropriate adsorption data. For further 5 compounds with relevant ionisation potential HPLC screening data were accepted (expert judgement, see details below). Appropriate experimental data allowed for assessment of another 5 to 20 compounds with relevant ionisation potential (depending on counting of 16 relatively similar compounds in the set explicitly or including only 1 as representative). Where available, experimentally determined  $pK_a$  /  $pK_b$  values were compared to calculated ones using “[ACE and JChem acidity and basicity calculator](#)”. In conclusion, the output of the QSAR-tool proved to be in good agreement with the experimental data. Further, even for large and complex compounds calculation proceeded in a reasonable time with acceptable results. Thus, the ACE calculator seems to be very appropriate to assess ionisation potential within the PMT assessment.

#### 4.2.3 Persistence assessment - results and conclusions

For all compounds registration dossiers (ECHA CHEM) were checked for data on stability (hydrolysis) and biodegradation. While property search using eChemPortal selected for compounds with results from screening tests pointing to persistence, from the 65 monoconstituent substances retrieved as described in section 4.1.1 only 32 (49%) turned out to be *persistent* applying the criteria as elaborated earlier and summarised in section 2.1.4. The reason for this is threefold:

Firstly, 2 substances with very low water solubility below the cut-off of 150 µg/L were not assessed further for degradability.

Secondly, for 22 compounds the only relevant data for biodegradation were from test results on Ready Biodegradability, with the result of being neither readily nor inherently (as judged from Ready-test data) biodegradable. Under these circumstances, QSAR-assessment evaluating results of BIOWIN 2/3 and 3/6 is decisive for assessment of P or not P in water (with the exception of conclusive data from PBT assessment being available, see below). As a result of QSAR application, 13 compounds of 22 were assessed to be not *persistent* (59%) in water, while 9 *persistent* compounds remained (41%).

Thirdly, especially for high production volume compounds often a higher number of screening tests is available (resulting in redundant entries). Thus, selecting for “not inherently biodegradable” / “under test conditions no biodegradation observed” and RL 1 or 2 may result in compounds which in parallel have reliable tests demonstrating ready biodegradability (e.g. 1,4-dichlorobenzene, CAS 106-46-7), but due to inoculum toxicity and high initial test item concentrations in other tests results may be available fulfilling applied selection criteria (which is the case for 1,4-dichlorobenzene). Further, in case of pass levels for ready biodegradability were just barely missed, this may be interpreted as inherent biodegradability, and again the compound would be evaluated as being not *persistent* in water (not P in water). Moreover, besides biodegradability, hydrolysis may be relevant: For 10 compounds hydrolysis in water (degT50 at pH7, 12°C ≤ 40d) was the decisive degradation result for assessment of the parent compounds as not P in water. Then however, transformation products must be regarded as *persistent* in most instances and therefore should be identified and assessed for fulfilment of M and T properties. Data provided under REACH are, however, yet insufficiently precise for such a follow-up assessment of transformation products.

From the 10 compounds included based on screening-type information (see section 4.1.3), 4 had been evaluated to be rapidly hydrolysed at pH 7 by OECD 111, in spite of screening-type information indicating hydrolytic stability (see section 4.1.3):

- N-(1,3-benzothiazol-2-ylsulfanyl)-2-methylpropan-2-amine
- 2-cyclohexylsulfanylisindole-1,3-dione
- Disulfiram (Disulfide, bis(diethylthiocarbamoyl))
- tetramethylthiuram disulfide

For further 2 compounds (Cumene hydroperoxide, CAS 80-15-9; diphenyl methanone, CAS 119-61-9) insufficient experimental data on biodegradability were available for a conclusion on P. Therefore, QSAR using BIOWIN modules was decisive, predicting biodegradability. As a result, these 6 compounds were concluded to not fulfil PMT properties. However, for the 4 rapidly hydrolysable compounds major transformation products might be of relevance and should be assessed themselves for PMT properties. Further, 4-tert-butylbenzene-1,2-diol (CAS 98-29-3) proved to be inherently biodegradable, thus also not fulfilling criteria for P and consequently being no PMT compound. Naphthalene (91-20-3), the only remaining compound of the set of 10 compounds selected based on screening-type information, was concluded to fulfil P criteria due to being not inherently biodegradable (OECD 302c; 2% within 28 days).

Generally, criteria were very well applicable and no need for substantial changes became obvious. However, for e.g. 1,2-dichloroethane (CAS 107-06-2), only non-guideline screening tests were available and results heterogeneous and difficult to interpret. In such cases it seemed reasonable to resort to the PBT assessment under REACH as far as being available from ECHA-Chem. The persistence assessment part is expected to

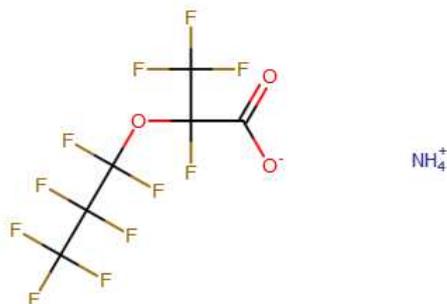
conclude on persistence by a weight of evidence approach considering all relevant available data. However, persistence assessment under REACH differs from persistence assessment with regard to raw water as elaborated within this work in that also degradation in other media is accounted for as far as relevant in regard to environmental distribution and as far as data are available (e.g. sediment, soil, atmosphere). Therefore, conclusion on P from PBT assessment is used only in a very constricted way under special conditions.

#### 4.2.4 Mobility assessment - results and conclusions

For all compounds registration dossiers (ECHA CHEM) were checked for data on adsorption-desorption. While property search using eChemPortal selected for compounds with  $K_{OC}$  values below  $\log K_{OC}$  4.5, due to the occasional availability of more than one test per compound or several  $K_{OC}$  values from one test (e.g. for different soils from one batch equilibrium test) entries in eChemPortal are redundant. Because of that, still three of the recruited mono-constituent compounds were judged to be immobile with  $\log K_{OC}$  values above 4.5 (these were, however, not P in water). In case of several  $\log K_{OC}$  values from one test or several tests of equal applicability and reliability, the geometric mean  $K_{OC}$  was calculated as the decisive value (equivalent to the arithmetic mean of the log-values). One of these compounds was tetraethyl N,N'-(methylenedicyclohexane-4,1-diyl)bis-DL-aspartate (CAS: 136210-30-5), identified as ionisable compound (calculated  $pK_a$  for alkaline functionality of 6.3 – 7.3). Because of its positive charge at relevant environmental pH-values, normally HPLC screening test data would not be accepted and the compound dismissed as currently not accessible due to inappropriate adsorption data. However, for positively charged compounds the HPLC method rather underestimates adsorption (strong ionic binding to predominantly negative net charge of soil). Because the mean  $\log K_{OC}$  from the HPLC screening study was already 4.7 and actual adsorption in soil due to ionic interaction is assumed to be even stronger, the compound was judged as being immobile. An example for a compound from the pool where increasing positive charge clearly lead to decreased binding on the HPLC column (OECD 121) is 2-[(1-methylpropyl)amino]ethanol (CAS: 35265-04-4). The  $pK_a$  for alkaline functionality is 10.1 (experimentally determined value, excellent agreement with calculated value from ACE-tool), and  $\log K_{OC}$  values increased with increasing pH equalling to decreasing fraction being positively charged: 1.6 at pH 5, 3.0 at pH 7 and 4.2 at pH 9. Due to the net-negative charge of most soils, rather the contrary is expected. This corroborates our assessment scheme which per default only accepts batch equilibrium data for ionisable compounds, not adsorption values derived by the HPLC screening method.

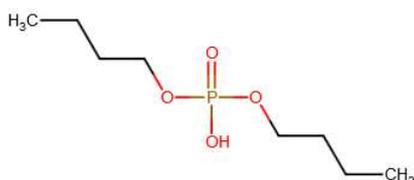
For some ionisable compounds exclusively negatively charged at environmentally relevant pH-values  $\log K_{OC}$  values derived from the HPLC screening method were accepted in spite of the developed methodology, normally requiring data from the batch equilibrium test (OECD 106) for ionisable compounds. These compounds were:

- Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate (CAS: 62037-80-3),  $\log K_{OC}$  1.1:



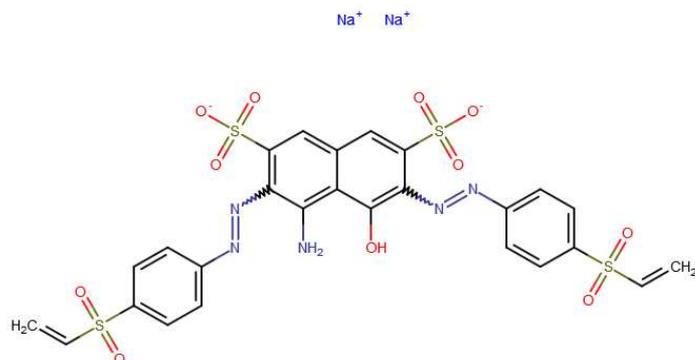
The substance is highly soluble, precipitation or complexation within soil is unlikely and due to the net negative charge of most soils adsorption will be rather lower than estimated by HPLC due to repulsion in soil → *mobile*

- dibutyl hydrogen phosphate (CAS: 107-66-4),  $\log K_{OC}$  0.5:



The substance bears one negative charge, is highly soluble, precipitation or complexation within soil is unlikely and due to the net negative charge of most soils adsorption will be rather lower than estimated by HPLC due to repulsion in soil → *mobile*

- disodium 4-amino-3,6-bis((2-[4-(ethenesulfonyl)phenyl]diazen-1-yl))-5-hydroxynaphthalene-2,7-disulfonate (CAS: 100556-82-9),  $\log K_{OC} < 1.25$ :

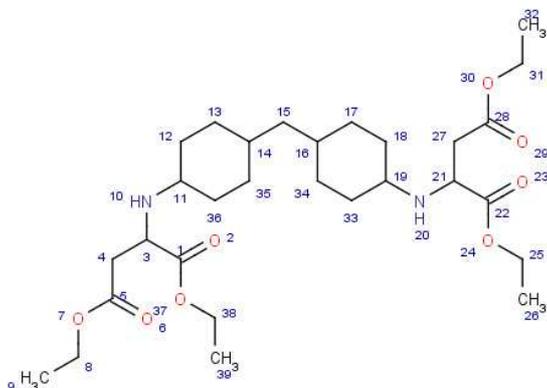


Only the sulfonyl groups will be negatively charged at environmentally relevant pH (2 times negatively charged). The molecule is highly soluble, precipitation or complexation within soil is unlikely and due to the net negative charge of most soils adsorption will be rather lower than estimated by HPLC due to repulsion in soil → *mobile*

For one ionisable compound with alkaline functionality predicted to be positively charged at environmentally relevant pH-values ( $pK_a$  for alkaline functionality calculated: 6.3-7.3)  $\log K_{OC}$ -values derived from the HPLC

screening method were accepted in spite of the developed methodology, normally requiring data from the batch equilibrium test (OECD 106) for ionisable compounds. This compound was:

tetraethyl N,N'-(methylenedicyclohexane-4,1-diyl)bis-DL-aspartate (CAS: 136210-30-5)



The mean  $\log K_{OC}$  determined by the HPLC screening method was 4.7, i.e. being above the threshold for mobile substances of  $\log K_{OC} < 4.5$ . It may be assumed with high certainty that adsorption to soil will at any case not be lower. Rather, due to the positive charge binding to net negatively charged soil particles is expected to be considerably stronger. This justifies acceptance of the HPLC screening data → *immobile*

Over all, from 38 *persistent* monoconstituent substances, 33 were determined to be *mobile* (i.e. 33 PM compounds), including 21 ionisable compounds.

#### 4.2.5 Toxicity assessment - results and conclusions

Predominantly, toxicity was only assessed for compounds determined to be P and M before (i.e. 33 PM compounds). Assessment followed the methodology summarised in section 2.3.4.

DNEL-values (general population, oral, long term) were available for 25 of these compounds. All DNELs were above the cut-off for T of  $9 \mu\text{g}/\text{kg bw}$  per day. In addition, classification and labelling data were available for these compounds and led to assessment of 2 compounds as T and 3 compounds as  $T_{\text{screen}}$  (i.e. *toxic* at the screening level).

For 8 compounds determined to be PM, no DNEL-values (general population, oral, long term) were available, 7 of these fulfilling E2 criteria. Thus, at least for the latter 7 PM compounds environmental exposure cannot be excluded a priori and DNELs should have been derived. From the 8 compounds without DNEL-values from ECHA-Chem, from classification and labelling data 5 could be determined to be T and 1 to be  $T_{\text{screen}}$ . From the remaining 2 compounds, both fall into Cramer class III ( $T_{\text{screen}}$ ).

#### 4.2.6 Identified PMT compounds

As a result of application of PMT criteria described in the preceding sections 4.2.1 to 4.2.5, 7 PMT compounds and 5  $PMT_{\text{screen}}$  (P, M, screening-level T) compounds were identified (see Table 27).

1-methyl-4-(methylsulfonyl)-2-nitrobenzene was found to be not readily and not inherently biodegradable, and thus *persistent* (P) according to the assessment scheme. Because it is not ionisable, the  $\log K_{OC}$  of 2.3 determined by HPLC screening according to OECD 121 is applicable for categorisation as M. While no DNEL (general population, oral, long term) is available from the REACH registration dossier, it fulfils T

because it is classified for reproductive toxicity category 2 (suspected of damaging fertility). According to exposure assessment tier 2 (E2), no relevant environmental exposure is to be expected (E2 not fulfilled). In conclusion, the compound is assessed to meet the characteristics of a PMT compound. Because E2 is not fulfilled, it is regarded to be *pervious* but not *critical* in raw water.

The E2-result can neither be corroborated nor questioned by monitoring data, as monitoring data on environmental exposure could not be identified. Neither CAS-number nor structure is provided within ChemIDplus<sup>56</sup>.

For ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate, only the anion of the salt is relevant for PMT assessment (CAS for acid: 13252-13-6). The compound is not readily biodegradable (0% within 28 days). Because no further experimental data are available, QSAR evaluation as P1 (BIOWIN 2/3) and P2 (BIOWIN 3/6) is decisive for classification as P. Being an organic acid (experimental  $pK_a$  3.8) it will be negatively charged in the environment. Nonetheless, by expert judgment (see section 4.2.4) the  $\log K_{OC}$  of 1.1 determined by HPLC screening according to OECD 121 is accepted leading to a categorisation as M. Due to classification for specific target organ toxicity after repeated exposure category 2 (may cause damage through prolonged or repeated exposure: blood and liver) it also fulfils T criteria. The derived DNEL (general population, oral, long term) of 50  $\mu\text{g}/\text{kg bw} \times \text{d}$  is above the cut-off (9  $\mu\text{g}/\text{kg bw} \times \text{d}$ ). Exposure assessment tier 2 (E2) was positive due to worst case assumptions on ERCs (no ERCs specified). In conclusion, the compound is assessed to meet the characteristics of a PMT compound. Because E2 is fulfilled, it is regarded to be critical in raw water.

As regards environmental monitoring data, all there is available is a weak indication for environmental exposure, at least in the USA: According to a “CONSENT ORDER ISSUED UNDER THE WATER POLLUTION CONTROL ACT WEST VIRGINIA CODE, CHAPTER 22, ARTICLE 11”<sup>57</sup>, permission is given for the company DuPont for mean/peak emissions of dimer acid/salt (CAS 13252-13-6 and CAS 62037-80-3) warranting concentrations equal to or below 17.5  $\mu\text{g}/\text{L}$  in the receiving stream (Ohio river). The compounds are used as a “new-generation processing aid for the production of high-performance fluoropolymers”.

4-aminophenol was not readily biodegradable (OECD 301c: 6%), only with acclimated sludge could biodegradation be observed (92% within 28 days, non-guideline). The compound is therefore evaluated to be inherently biodegradable not fulfilling specific criteria, equivalent to P. It is not ionisable in the most relevant pH-range 6 to 8 (exp.  $pK_a$  values for acidic and alkaline functionality, respectively: 10.5 and 5.48). Thus, the  $\log K_{OC}$  of 0.59 determined by HPLC screening according to OECD 121 is accepted, leading to a categorisation as M. It also fulfils T because it is classified for germ cell mutagenicity, hazard category 2 (suspected of causing genetic defects). Despite the fact that environmental exposure cannot be excluded (E2 fulfilled), no DNEL (general population, oral, long term) was derived (exposure based waiving). In conclusion, the compound is assessed to meet the characteristics of a PMT compound. Because E2 is fulfilled, it is regarded to be critical in raw water.

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<sup>56</sup> <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?CHEM>

<sup>57</sup> <http://www.dep.wv.gov/pio/Documents/DuPont.pdf>, accessed 2014-03-25

4-aminophenol is a metabolite of paracetamol (Gartiser, et al., 2011), a widely used analgetic. Further, it is a known degradation product of certain pesticides, but also widely used directly in industrial applications (Santos, et al., 2013). An OECD SIDS document (OECD, 2010) is available, stating “As p-aminophenol is not readily bio-degraded, the possibility of environmental release may exist, and it is thought that the water compartment is the main target....no information on the amount of release and transfer of p-aminophenol is reported.” The same document gives some environmental monitoring results from 2004 for Japan: From 9 surface water sites, at one site concentrations between 0.02 and 0.05 µg/L were determined. A more recent monitoring of 7 rivers located in northern Portugal detected 4-aminophenol in 5 rivers, 4 times in quantifiable concentrations: 0.4, 0.52, 1.25, and 1.63 µg/L (Santos, et al., 2013). This corroborates results of the E2 module together with the PM assessment.

Table 27: Identified PMT compounds: Most relevant data on persistence (P), mobility (M) and toxicity (T) as well as environmental exposure (E)

CAS	Name	Con- clusion	Relevant result for P	Degrad.-test / QSAR	Ionisa- bility*	log K <sub>oc</sub> for M	Mob. test	Toxicity	Relevant data T	E2 fulfilled ? **	t/a***	Env. monit.
1671-49-4	1-methyl-4-(methylsulfonyl)-2-nitrobenzene	PMT	Not inherently biodegradable	Not readily biodegradable; OECD 302B	N	2.30	HPLC-method (OECD 121)	T (C&L)	Repr. 2 H361f	N	(1-10) x10 <sup>3</sup>	No data
62037-80-3	Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate	PMT	P1P2	Not readily biodegradable; BIOWIN	Y (pK <sub>a</sub> 3.8, neg. charged)	1.10	HPLC-method (OECD 121)	T (C&L)	STOT RE 2 H373	Y (wc)	10 - 100	weak indication
123-30-8	4-aminophenol	PMT	inherently biodegradable <u>not</u> fulfilling specific criteria	non-guideline, degradation with acclimated sludge only	N (pK <sub>a</sub> 10.5, pK <sub>b</sub> 5.48)	0.59	HPLC-method (OECD 121)	T (C&L)	Muta. 2 H341	Y	(1-10) x10 <sup>3</sup>	quantified in surface waters (low µg/L-range)
12108-13-3	tricarbonyl(methylcyclopentadienyl)manganese	PMT	Not inherently biodegradable (1)	Enhanced ready test (OECD 301D)	N	3.40	HPLC-method (OECD 121)	T (C&L)	STOT RE 1 H372	N	100 - 1,000	No data
143-33-9	cyanide	PMT	inherently biodegradable <u>not</u> fulfilling specific criteria	non-guideline, adapted sewage	N (pK <sub>a</sub> 9.5)	2.87 (2.6 - 3.1)	Batch Equil. (OECD 106)	T (C&L) (2)	STOT RE 1 H372 (thyroid gland)	Y (high tonnage)	(1-10) x10 <sup>4</sup>	relevant emissions

CAS	Name	Con- clusion	Relevant result for P	Degrad.-test / QSAR	Ionisa- bility*	log K <sub>oc</sub> for M	Mob. test	Toxicity	Relevant data T	E2 fulfilled ? **	t/a***	Env. monit.
107- 06-2	1,2- Dichloroethane	PMT	PBT assess- ment: P	non-guide- line screening tests, hetero- genous results	N	1.60	KOCWIN, MCI	T (C&L)	Carc. 1B H350	Y (high tonn- age)	(1- 10) x10 <sup>6</sup>	relevant emis- sions
79- 01-6	Trichloro- ethene	PMT	DegT50 > 40d	Not readily biodegra- dable; non-guide- line simu- lation test	N	2.15	Exp. (ECHA / RAR)	T (C&L)	Muta. 2 H341 Carc. 1B H350	Y (high tonn- age)	(1- 10) x10 <sup>4</sup>	relevant emis- sions
127- 18-4	Tetrachloro- ethene	PMTsc reen	PBT assess- ment: P	non-guide- line screening / simula- tion tests: only anaerobic degra- dation	N	2.15	Exp. (ECHA / RAR)	Tscre en (C&L)	Carc. 2 H351	Y (high tonn- age)	(1- 10) x10 <sup>5</sup>	relevant emis- sions
107- 66-4	dibutyl hydrogen phosphate	PMTsc reen	inherent- ly bio- degra- dable <u>not</u> fulfil- ling spe- cific criteria	Not readily biodegra- dable; OECD 302B: 97% within 14 d; 9% within 7 d	Y (pK <sub>a</sub> 1.9, neg. charg ed)	0.50	HPLC- method (OECD 121)	Tscre en (C&L)	Carc. 2 H351	Y	(1- 10) x10 <sup>2</sup>	Weak indica- tion: few data in ng/L range

CAS	Name	Con- clusion	Relevant result for P	Degrad.-test / QSAR	Ionisa- bility*	log K <sub>oc</sub> for M	Mob. test	Toxicity	Relevant data T	E2 fulfilled ? **	t/a***	Env. monit.
867- 13-0	triethyl phosphonoaceta te	PMTsc reen (Cram er)	Not in- herently biodegra- dable	Not readily biodegra- dable; OECD 302B	N (pK <sub>a</sub> 9.5 for C1)	< 1.25	HPLC- method (OECD 121)	Tscre en (Cram er)	Cramer class III	N	(1- 10) x10 <sup>2</sup>	No data
3380 -34- 5	triclosan	PMTsc reen (Cram er)	inherent- ly bio- degra- dable <u>not</u> fulfil- ling spe- cific criteria	Not readily biodegra- dable; OECD 302B: High adsorption (19% 3h)	Y (pK <sub>a</sub> 7.9 to 8.14)	4.18	Batch Equil. (Karnjanap iboonwong et al. (2010): sandy loam/silt loam: 4.3 / 4.05	Tscre en (Cram er)	Cramer class III	Y	(1- 10) x10 <sup>3</sup>	relevant concen- trations reported - stable metabo- lite: methyl- triclo- san
91- 20-3	naphthalene	PMTsc reen	Not in- herently biodegra- dable	OECD 302C: 2% within 28 d	N	2.8	Batch Equil. (sandy soil from agricultur al area): K <sub>oc</sub> 664 L/kg	Tscre en (C&L)	Carc. 2 H351	Y	(1- 10) x10 <sup>5</sup>	relevant emis- sions

(\*) In case of missing experimental values, estimated values (<https://ace.chem.illinois.edu/ace/public/pKa.jsp>, JChem-mode) - pK<sub>b</sub> is defined here as pK<sub>a</sub> for alkaline functionality; (\*\*) wc = worst case: no information on ERCs given, exposure assumed to be relevant; (\*\*\*) tonnage band as given by ECHA; (1) rapid primary degradation by photolysis in sunlight exposed waters; (2) in addition: WHO 12 µg/kg\*d; Directive 67/548/EEC: 1.7 µg/kg x d (50 µg/L; 2L/day, with 60 kg bw)

The transition metal complex tricarbonyl(methylcyclopentadienyl)manganese (MMT) was not readily and not inherently biodegradable in an enhanced ready test (OECD 301D; 4% within 56 days). Further, it turned out to be hydrolytically stable (OECD 111). It is thus evaluated to be P. However, rapid primary degradation by photolysis in sunlight exposed waters (degT50 approximately 1 min) is reported. Because it is not ionisable, HPLC screening data on adsorption (OECD 121) may be used for mobility assessment. From a log  $K_{OC}$  of 3.4 it is judged to be *mobile*. While the DNEL (general population, oral, long term) of 13  $\mu\text{g}/\text{kg bw x d}$  was close to but above the cut-off (9  $\mu\text{g}/\text{kg bw x d}$ ), it is assessed to be T due to classification and labelling for specific target organ toxicity after repeated exposure, category 1 (STOT RE 1: lungs, inhalation). According to E2 module, environmental exposure is not probable. In conclusion, the compound is assessed to meet the characteristics of a PMT compound. Because E2 is not fulfilled, it is regarded to be *pervious* but not *critical* in raw water.

No environmental monitoring data could be identified. According to WHO (2004) and Garrison et al. (1995), the compound was/is (?) used as a fuel additive to substitute lead. It is further stated that “MMT has been found to be *persistent* in natural aquatic and soil environments in the absence of sunlight, with a tendency to sorb to soil and sediment particles. Calculated half-lives of MMT in aquatic and soil environments range from approximately 0.2 to 1.5 years at 25 °C”. These data essentially corroborate PM assessment results and are not in contradiction to E2.

Cyanide (e.g. sodium cyanide) is inherently biodegradable not fulfilling specific criteria (non-guideline test using adapted sewage), i.e. fulfilling P criteria. It is not ionisable in the most relevant pH-range 6 to 8 (calculated  $pK_a$  for acidic functionality: 9.5). In any case, for this compound log  $K_{OC}$  was determined by the batch equilibrium method applicable also for ionisable compounds. Due to a mean log  $K_{OC}$  of 2.87 (arithmetic mean of log-values, i.e. geometric mean of  $K_{OC}$  values), the compound is categorized as *mobile* (M). Due to classification for specific target organ toxicity after repeated exposure, category 1 (STOT RE 1: thyroid gland), cyanide is assessed to be T. In spite of environmental exposure being probable (fulfilling E2), no DNEL (general population, oral, long term) had been derived (exposure based waiving). WHO (WHO, 2003) derived a tolerable daily intake (TDI) of 12  $\mu\text{g}/\text{kg bw x d}$ , which is close to the cut-off set for the DNEL (9  $\mu\text{g}/\text{kg bw x d}$ ) for T assessment. Further, according to drinking water directive (Directive 67/548/EEC), the upper concentration limit is 50  $\mu\text{g}/\text{L}$  drinking water. With 2 L of water consumed daily by a person of 60 kg body weight, this corresponds to a limit value of 1.7  $\mu\text{g}/\text{kg bw x d}$ . In conclusion, the compound is assessed to meet the characteristics of a PMT compound. Because E2 is fulfilled, it is regarded to be *critical* in raw water.

The total annual release to water (2011) was 148 tonnes by 194 European facilities (The European Pollutant Release and Transfer Register, E-PRTR: <http://prtr.ec.europa.eu/PollutantReleases.aspx>). Further, it was selected as candidate for priority substance within the context of the Water Framework Directive (IOW/INERIS, 2009). This corroborates both, the E2-assessment result as well as the PMT conclusion.

For 1,2-dichloroethane only non-guideline screening test data on biodegradation are available, with heterogeneous results. Because of this, the assessment scheme for P allows (under certain conditions, see sections 2.1.3 and 2.1.4 ) to resort to the persistence assessment within a qualified PBT assessment. This is available for 1,2-dichloroethane and as a result, the compound is regarded as fulfilling P criteria. Because

there is no potential for ionisation, the calculated log  $K_{OC}$  of 1.6 (KOCWIN, MCI method) is applicable for mobility assessment, resulting in categorisation as M. It also fulfils T because it is classified for carcinogenicity class 1B. Despite the fact that environmental exposure cannot be excluded (E2 fulfilled), no DNEL (general population, oral, long term) was derived. In conclusion, the compound is assessed to meet the characteristics of a PMT compound. Because E2 is fulfilled, it is regarded to be critical in raw water.

The total annual release to water (2011) was 8.47 tonnes by 52 European facilities (The European Pollutant Release and Transfer Register, E-PRTR: <http://prtr.ec.europa.eu/PollutantReleases.aspx>). Further, it was selected as candidate for priority substance within the context of the Water Framework Directive (IOW/INERIS, 2009). This corroborates both, the E2-assessment result as well as the PMT conclusion.

Trichloroethene fulfils P criteria because of being not readily biodegradable and showing a  $DegT50 > 40$  days in a higher tier simulation test on aerobic biodegradation. The compound has no potential for ionisation. Because of an experimentally determined log  $K_{OC}$  of 2.15 it is categorized as M. Due to classification as carcinogen category 1B and mutagen category 2 it fulfils also criteria for T. Despite the fact that environmental exposure cannot be excluded (E2 fulfilled), no DNEL (general population, oral, long term) was derived. In conclusion, the compound is assessed to meet the characteristics of a PMT compound. Because E2 is fulfilled, it is regarded to be critical in raw water.

The total annual release to water (2011) was 2.8 tonnes by 34 European facilities (The European Pollutant Release and Transfer Register, E-PRTR: <http://prtr.ec.europa.eu/PollutantReleases.aspx>). Further, it was selected as candidate for priority substance within the context of the Water Framework Directive (IOW/INERIS, 2009). This corroborates both, the E2-assessment result as well as the PMT conclusion.

For Tetrachloroethene only non-guideline screening tests and simulation tests on biodegradation are available, and only anaerobic degradation was observed. It was assessed as P within PBT assessment under REACH and thus, criteria for P are assumed to be fulfilled. The compound has no potential for ionisation. Because of an experimentally determined log  $K_{OC}$  of 2.15 it is categorized as M. It is regarded as *toxic* at the screening level ( $T_{screen}$ ) due to classification as carcinogen category 2 (suspected of causing cancer). The DNEL (general population, oral, long term) was derived as 1.3 mg/kg bw x day and thus being far above the cut-off of 9  $\mu$ g/kg bw x day for categorisation as T because of a low DNEL. Conditions specified in E2 module are fulfilled, thus giving high probability of environmental exposure. In conclusion, the compound is assessed to meet the characteristics of a  $PMT_{screen}$  compound. Because E2 is fulfilled, it is regarded to be critical in raw water (screening level for T).

The total annual release to water (2011) was 5.55 tonnes by 44 European facilities (The European Pollutant Release and Transfer Register, E-PRTR: <http://prtr.ec.europa.eu/PollutantReleases.aspx>). Further, it was selected as candidate for priority substance within the context of the Water Framework Directive (IOW/INERIS, 2009). This corroborates both, the E2-assessment result as well as the PMT conclusion.

Dibutyl hydrogen phosphate (di-n-butyl phosphate, DnBP) is not readily biodegradable, hydrolytically stable (OECD 111) but inherently biodegradable (OECD 302B: 97% within 14 d; 9% within 7 d). It does however not fulfil specific criteria set for inherent test results: according to these, 70% biodegradation have to be reached within 7 days. Thus, the substance fulfils criteria for P. Because of a  $pK_a$  for acidic functionality of 1.9 (calculated, phosphate group), it will be negatively charged in the environment. Nonetheless, by expert judgment (see section 4.2.4) the  $\log K_{oc}$  of 0.5 determined by HPLC screening according to OECD 121 is accepted, leading to a categorisation as M. It is regarded as *toxic* at the screening level ( $T_{screen}$ ) due to classification as carcinogen category 2 (suspected of causing cancer). The DNEL (general population, oral, long term) was derived as 0.22 mg/kg bw x day and thus being far above the cut-off of 9  $\mu\text{g}/\text{kg}$  bw x day for categorisation as T because of a low DNEL. Conditions specified in E2 module are fulfilled, thus giving high probability of environmental exposure. In conclusion, the compound is assessed to meet the characteristics of a  $PMT_{screen}$  compound. Because E2 is fulfilled, it is regarded to be critical in raw water (screening level for T).

According to (BUA, 1993) and SIDS (OECD, 1994) no monitoring data for the environment have been reported. The concentration for water was estimated in the latter to be  $2.5 \times 10^{-7}$  mg/L, and the daily intake through drinking water as  $5.1 \times 10^{-7}$  mg/kg x d. Indeed, also up to more recent years very few monitoring data were available for DnBP (Reemtsma, et al., 2008). Rodil et al. (2012) measured dibutyl hydrogen phosphate in north-western Spain at 6 locations along the Mero river and at one location at the Anllóns river, with 4 times sampling distributed over a year (2007/8). In surface water, DnBP was detected in 50% of all samples, and concentrations were between below LOQ (approximately 0.001  $\mu\text{g}/\text{L}$ ) up to approximately 0.2  $\mu\text{g}/\text{L}$ , with a mean concentration of approximately 5 ng/L (graphical representation). Furthermore, it was quantified in all STP influent samples, corroborating E2 results. Further monitoring data from recent years are for one STP in Berlin, Germany, where the influent concentration was determined as 1.6  $\mu\text{g}/\text{L}$  and the effluent concentration as 0.027  $\mu\text{g}/\text{L}$ , i.e. 1.7% of influent (Quintana, et al., 2006). With a standard dilution factor of 10 for receiving waters, the effluent concentration fits quite well to the mean surface water concentration reported by (Rodil, et al., 2012). Obviously, biodegradation in STP was quite effective. This is in line with reported degradation data for DnBP (see above, OECD 302B) and Wellens (1990), who points out that for the OECD 302B test, duration of the log phase is decisive for degradation efficiency in STP; that duration of the log phase is independent from the duration of the lag phase; while duration of the lag phase may depend on random events and is often not reproducible. Actually, according to test results cited above, DnBP degradation started around day 7 (9%; i.e. lag phase 7 days) and was finalized at day 14 (97% degraded), such that degradation was fast. However, “specific criteria” applied within PBT assessment under REACH (guidance document R.11) attribute a high weight to the lag phase (minimum of 70% degradation within 7 days including the lag-phase), while the lag-phase is of no importance for STP in case of continuous input (adapted bacterial populations). The most recent publication (García-López, et al., 2010) including monitoring data on DnBP (however, focus on analytical methodology, no data given on monitoring location) includes data for three measurements of influent and effluent concentrations of the same STP (discharges from 100,000-inhabitants city) with mean influent concentration (103 ng/L) equalling mean effluent concentration (101 ng/L). This result is therefore in contradiction to the Berlin STP data and interpretation of the inherent test data according to the log phase. The determined concentration of the river receiving effluent of this same STP (5 km downstream) was 65 (+/- 6) ng/L (one sample), singular samples of three other rivers without known discharges of urban wastewater contained 8.0 (+/- 0.6), 8.6 (+/- 0.4) and 30 (+/- 1) ng/L DnBP.

In conclusion, while reported STP influent concentrations for DnBP were mostly low (around 1 µg/L and lower), prediction by E2-assessment in principle was correct but may be somewhat too precautionous. On the other hand, in view of the scarcity of available monitoring data the existence of other sites with much higher emissions is still possible. Further, because of being inherently biodegradable without fulfilling specific criteria, the compound was regarded as P. This borderline state between biodegradability and persistence may be mirrored by the controversial data on actual degradation in STP. In this case, a slightly conservative prediction for P by the PMT assessment scheme is intended. Mobility prediction was in any case correct.

Triethyl phosphonoacetate is neither readily nor inherently biodegradable and therefore fulfils P criteria. It is not ionisable in the most relevant pH-range 6 to 8 (calculated  $pK_a$  for acidic functionality: 9.5). Thus, the  $\log K_{OC}$  of  $< 1.25$  determined by HPLC screening according to OECD 121 is accepted, leading to a categorisation as M. According to classification and labelling, the compound would not be regarded as T. A DNEL has not been derived. Under these circumstances, classification by Cramer is used as a screening assessment for toxicity. With Cramer class III (high class) the compound is regarded to be *toxic* at the screening level ( $T_{screen}$ ). Because Cramer classification mostly leads to conservative results, derivation of a DNEL may or may not corroborate this preliminary assessment. Relevant environmental exposure is not probable as conditions of the E2 module were not met. In conclusion, the compound is assessed to meet the characteristics of a  $PMT_{screen}$  compound. Because E2 is not fulfilled, it is regarded to be *pervious* but not *critical* in raw water.

Confirming the E2-result, no indications for environmental exposure could be identified.

Triclosan has a broad use as antimicrobial agent including consumer products (SCCS, 2010). Biodegradability was assessed in an enhanced ready test (OECD 301B), however pass levels were not reached within 60 days. Further, it proved to be inherently biodegradable but not fulfilling specific criteria due to high adsorption at the 3h-value in an OECD 302B test. It thus fulfils criteria for persistence (P). Triclosan is ionisable in the most relevant pH range 6 to 8 (exp.  $pK_a$  for acidic functionality between 7.9 and 8.14). Adsorption data from ECHA-CHEM were equivocal: Low values from HPLC screening at pH 6 ( $\log K_{OC}$  2.62 – 2.92), and a high value ( $\log K_{OC}$  4.68) with a non-standard adsorption study using sewage sludge solids (i.e. an extremely high organic carbon concentration). In general, HPLC screening data should not be used for ionisable chemicals, while the study summary provided by ECHA-CHEM restricts the results with sludge solids to the sewage treatment plant environment. Thus, further valid data identified by literature search are used for mobility assessment. According to Karnjanapiboonwong et al. (2010),  $\log K_{OC}$  for adsorption to sandy loam and silt loam was 4.3 and 4.05, respectively, giving a mean value of 4.18 used for assessment. This corresponds to high adsorption, but is still below the cut-off for mobility ( $\log K_{OC}$  4.5). Thus, Triclosan is assessed to be *mobile* in raw waters (M). According to classification and labelling, the compound would not be regarded as T. In spite of the fact that conditions of the E2 module were fulfilled, implicating a high probability of environmental exposure, a DNEL has not been derived under REACH. Under these circumstances, classification by Cramer is used as a screening assessment for toxicity. With Cramer class III (high class) the compound is regarded to be *toxic* at the screening level ( $T_{screen}$ ). Because Cramer classification mostly leads to conservative results, derivation of a DNEL may or may not corroborate this preliminary assessment. In conclusion, the compound is assessed to meet the characteristics of a  $PMT_{screen}$  compound. Because E2 is fulfilled, it is regarded to be *critical* in raw water (screening level for T).

Several monitoring data on environmental exposure are published: According to the Norman Network<sup>58</sup>, from 41 individual measurements, n = 14 were above LOD. For these, the arithmetic mean is 0.081 µg/L, the median 0.04 µg/L, the minimum 0.01 µg/L, and the maximum 0.55 µg/L. Measurements were performed within 2005 to 2008. Further, according to (SCCS, 2010), surface water concentrations of Triclosan were between 0.0014 - 40 µg/L, and waste-water effluent concentrations between 0.023 - 5.37 µg/L. Methyl-Triclosan was identified as both, a more stable and more bioaccumulative transformation product in soil and water systems (Health Canada, 2012), with increasing concentrations in muscles of fish from German rivers (Boehmer, et al., 2004). While Triclosan is photodegradable, especially at pH-values  $\geq 8$ , methyl-Triclosan is not (Lindström, et al., 2002). However, according to a more recent publication (Rüdel, et al., 2013) methyl-Triclosan levels in fish of German rivers seem to be declining since 2004, probably as a consequence of the voluntary renunciation of the use of Triclosan in detergents declared by a manufacturer association in 2001.

In conclusion, PMT assessment produced reasonable results considering that Triclosan is a borderline case with regard to mobility (high adsorption) as well as persistence.

Naphthalene is not inherently biodegradable and therefore fulfils P criteria. It is not ionisable. The relevant log  $K_{OC}$  of 2.8 was determined in a batch equilibrium test similar to OECD 106 with one soil (sandy soil from agricultural area) leading to a categorisation as M (the calculated value for  $K_{OC}$  is of similar size and would lead to the same conclusion). In spite of the fact that conditions of the E2 module were fulfilled implicating a high probability of environmental exposure, a DNEL has not been derived under REACH and no PBT assessment is published. According to classification and labelling, the compound is regarded as  $T_{screen}$  (classified as Carc. Cat. 2), and also according to Cramer classification (class III) evaluation as *toxic* at the screening level ( $T_{screen}$ ) would result. In conclusion, the compound is assessed to meet the characteristics of a  $PMT_{screen}$  compound. Because E2 is fulfilled (high tonnage band), it is regarded to be critical in raw water (screening level for T).

According to the European Pollutant Release and Transfer Register (E-PRTR):

<http://prtr.ec.europa.eu/PollutantReleases.aspx>) the total annual release to water in 2011 amounted to 82.5 tonnes by 69 European facilities. Further, it was selected as candidate for priority substance within the context of the Water Framework Directive (IOW/INERIS, 2009). This corroborates both, the E2-assessment result as well as the PMT conclusion.

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<sup>58</sup> [http://www.norman-network.net/empodat/search\\_index.php](http://www.norman-network.net/empodat/search_index.php)

### 4.3 Particular compounds reported to be relevant in raw water from monitoring programs - PMT assessment

Provided that the PMT assessment methodology delivered reasonable results, compounds detected and quantified in relevant concentrations in environmental waters within monitoring programmes and evaluated ex post for PMT properties using our assessment scheme ideally should be classified at least as *relevant* in raw water, that is fulfilling P, M and E2.

To this end, an analysis of a several recently published work on environmental micro-pollutants was performed. Only those compounds were regarded to be of potential interest in the framework of this project, which were fully registered under REACH at this point in time (mid 2014). Therefore, the many drugs and plant protection products being frequently detected (and often in relevant concentrations) in the environment were not considered here, because neither group is pertinent to REACH legislation. A borderline case in this respect is Diuron, which is used as a broad band herbicide in agriculture but at the same time e.g. in the construction sector to prevent the growth of algae on the exterior plaster of buildings. Therefore, this compound is fully registered under REACH.

As a result of this analysis of monitoring data, 20 compounds were considered to be of interest for this validation exercise due to their reported relevance in regard to environmental exposure as well as a prevailing full REACH registration. These compounds are summarized in Table 28. While we believe that we have captured the most important compounds, an in-depth assessment of all available literature was beyond the scope of this analysis and further, depending on the validity and detail of data available, in differing degree also subjective considerations poured into decisions to include or not include compounds into Table 28.

Table 28: 20 compounds from recent literature detected in environmental waters or STP effluents with high frequency and / or in relevant concentrations, and being at the same time registered under REACH (full registration)

CAS	Name	Reference	Environmental concentration or related information	S
108-42-9	3-chloroaniline	IOW/INERIS, 2009	PEC2 0.1 µg/L	
88-72-2	2-nitrotoluene	IOW/INERIS, 2009	PEC2 0.25 µg/L	
88-73-3	1-chloro-2-nitrobenzene	IOW/INERIS, 2009	PEC2 0.5 µg/L	
92-52-4	biphenyl	IOW/INERIS, 2009	PEC2 10 µg/L	
27503-81-7	2-phenylbenzimidazole-5-sulphonic acid, PBSA	Rodil et al., 2012	median STP effluent concentration: 0.24 µg/L; detected in 30% of surface waters (LOQ 73 ng/L)	
4065-45-6	Benzophenone-4, BP-4 (UV screen)	Rodil et al., 2012	median STP effluent concentration: 1.2 µg/L; detected in 75% of surface waters (LOQ 603 ng/L)	X

CAS	Name	Reference	Environmental concentration or related information	S
126-73-8	tri-n-butyl phosphate, TnBP (flame retardant)	Rodil et al., 2012	median STP effluent concentration: 0.32 µg/L; median surface water concentration: 37 ng/l	
13674-84-5	tri(chloropropyl) phosphate, TCP (flame retardant)	Rodil et al., 2012 (1); Reemtsma et al., 2006 (2) Loos et al., 2013 (3)	(1) median STP effluent concentration: 0.57 µg/L; median surface water concentration: 47 ng/l; (2) median STP effluent: ca. 0.8 µg/L; relative removal in STP: -0%; water cycle spreading index: >10 < 100 (3) STP effluent: frequency 100% (LOQ 1 ng/L); mean 1.2 µg/L; median 0.6 µg/L; Per90 2.1 µg/L	X
100-02-7	4-nitrophenol	Loos et al., 2009, River water Loos et al., 2010, groundwater	RW: mean: 99 ng/L, median: 16 ng/L, max. 3.47 µg/L GW: mean: 4 ng/L, median: 0 ng/L, max. 152 n/L	
58-08-2	Caffeine	Loos et al., 2009, River water Loos et al., 2010, groundwater	RW: mean: 963 ng/L, median: 72 ng/L, max. 39.8 µg/L GW: mean: 13 ng/L, median: 4 ng/L, max. 189 n/L	
95-14-7	Benzotriazole, 1H- (corrosion inhibitor)	Loos et al., 2009, River water Loos et al., 2010, groundwater Loos et al., 2013 (2)	RW: mean: 493 ng/L, median: 226 ng/L, max. 8 µg/L GW: mean: 24 ng/L, median: 1 ng/L, max. 1.0 µg/L (2) STP effluents: frequency 97% (LOQ 40 ng/L); mean 6.3 µg/L; median 2.7 µg/L; per90 10.19 µg/L	X
330-54-1	Diuron (herbicide, biocide)	Loos et al., 2009, River water; Loos et al., 2010, groundwater IOW/INERIS, 2009 (2) Loos et al., 2013 (3)	RW: mean: 41 ng/L, median: 10 ng/L, max. 864 ng/L; GW: mean: 3 ng/L, median: 0 ng/L, max. 279 ng/L (2): PEC2: 0.186 µg/L (3) STP effluents: frequency 77% (LOQ 1 ng/L); mean 61.7 ng/L; median 11.6 ng/L; per90 83.7 ng/L	X
80-05-7	Bisphenol A	Loos et al., 2009, River water; Loos et al., 2010, groundwater IOW/INERIS, 2009 (2)	RW: mean: 25 ng/L, median: 0 ng/L, max. 323 ng/L; GW: mean: 79 ng/L, median: 0 ng/L, max. 2299 ng/L PEC2: 0.143 µg/L	X

CAS	Name	Reference	Environmental concentration or related information	S
60-00-4	EDTA (complexing agent)	Schäfer et al., 2011 (1); Reemtsma et al., 2006 (2)	(1) RW: max.: 35 µg/L; detection frequency: 93%; LOQ: 0.1-0.3 µg/L; (2) median STP effluent: ca. 100 µg/L; relative removal in STP: -0%; water cycle spreading index: >1000 < 10000	
139-13-9	nitriлотriacetіc acid (complexing agent)	Schäfer et al., 2011	RW: max.: 10 µg/L; detection frequency: 77%; LOQ: 0.1-0.5 µg/L	X
118-96-7	2,4,6-trinitrotoluene	Schäfer et al., 2011	RW: max.: 3.5 µg/L; detection frequency: 52%; LOQ: 0.09-20 ng/L	X
29385-43-1	4-/5-tolyltriazole (corrosion inhibitor: deicing fluids, dishwashing agents)	Reemtsma et al., 2006 (1) Loos et al., 2013 (2)	(1): median STP effluent: > 1 <10 µg/L; relative removal in STP: ca. 10%; water cycle spreading index: >10 <100 (2): STP effluent: frequency 100% (LOQ 40 ng/L); mean 2.9 µg/L; median 2.1 µg/L; per90 4.7 µg/L	X
55589-62-3	Acesulfame K (Sweetener); 6-methyl-1,2,3-oxathiazin-4(3H)-one 2,2-dioxide, potassium salt	Loos et al. (2013): EU Wide Monitoring survey on waste water treatment plant effluents	STP effluent: mean: 76 µg/L; median 14.3 µg/L; per90: 61 µg/L; frequency: 93%	X
3147-75-9	2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol (UV 329) (UV screen)	Wallberg et al., 2014	75% detection frequency in biota, both in urban and in background locations - no concentrations in water, but point source water assumed	
32388-55-9	Acetyl cedrene (AC, fragrance)	Wallberg et al., 2014	High detection frequency in effluent water	

Abbreviations: RW: river water; GW: groundwater; LOQ: limit of quantification; per90: 90<sup>th</sup> percentile; STP: sewage treatment plant; S = selected - only those compounds labelled in this column were regarded of sufficient priority to be selected for assessment of PMT properties.

From Table 28, 9 compounds were selected regarding their relevance for further assessment for PMT properties, all of these are REACH registered compounds. The selection of compounds for assessment (column S in Table 28) generally was based on the frequency of detection in monitoring programmes, the level of quantified concentrations as well as the number of independent different monitoring programmes which reported quantifiable concentrations.

At the beginning, for each compound an explanation is given as to why this compound was selected for assessment. Then, based on REACH registration documents (if not explicitly stated otherwise), according to PMT assessment schemes exposure, substance characteristics, persistence, mobility and toxicity are examined.

#### 4.3.1 Benzophenone-4 (BP-4) / 2-Hydroxy-4-methoxybenzophenone-5-sulfonic acid, CAS: 4065-45-6

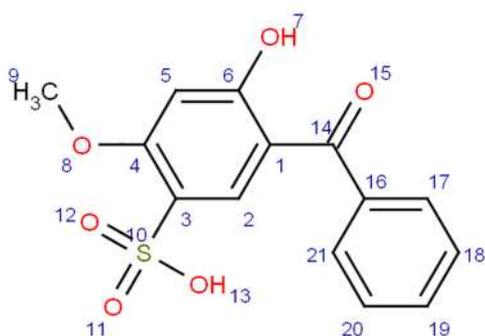
The compound is used as an UV screen and was selected due to high concentrations reported for STP effluents (median concentration 1.2 µg/L) and a high frequency of detection in surface waters in relevant concentrations (75%, LOQ: 0.6 µg/L; see Table 28) (Rodil, et al., 2012).

##### Exposure

As the substance is fully REACH registered, E1 (exposure tier 1) is fulfilled. Due to a tonnage band of 100 to 1000 tons per year and ERC 8a (“Wide dispersive indoor use of processing aids in open systems”) the substance also fulfils E2. Therefore, the plausibility assessment for exposure based on REACH registration data is in agreement with observed environmental exposure from monitoring programs.

##### Substance characterisation

The substance has the following structure:



The substance is in the applicability domain, highly soluble and characterized to be ionisable in the environmentally relevant pH range due to the following predicted values (JChem):

$pK_a$  (lowest): -2.4 (sulfonate group)

The compound will therefore be negatively charged in the environment.

##### Persistence assessment

No experimental tests are available, only QSAR estimations using US EPA’s PBT profiler or US EPA’s EPI Suite (BIOWIN). Likewise, no experimental data on hydrolysis are available. This is not compliant with REACH requirements: At least a test on ready biodegradability has to be performed and, in case of negative results, a test for hydrolysis as a function of pH in addition to the first.

As a conclusion, per default the substance is not assessable due to the minimum experimental data required according to REACH are missing. According to the persistence evaluation scheme, QSAR is only applicable if at least a (negative) test on ready biodegradability is available (which is not the case).

Performing a BIOWIN based QSAR estimation, anyway, the compound would be regarded as not readily biodegradable (BIOWIN 6 << 0.5), however not to be *persistent* (BIOWIN 3: 2.66, i.e. > 2.25). Indeed,

according to Rodil et al. (2012), the compound had a mean removal in STPs slightly higher than 50%. Obviously, however, degradation efficiency in STPs is not high enough relative to the given extent of environmental exposure. While the tonnage level is intermediate (100 -1000 t/a), ERC 8a is associated with high environmental release. BP-4 is a UV-filter reported to be used in sunscreens. It was even detected in several tap water samples in Spain up to a maximum concentration of 62 ng/L (Rodil, et al., 2012).

### Mobility assessment

In a strict sense, mobility criteria do only apply to *persistent* compounds. Nonetheless, data are analysed here for mobility based on criteria developed under the assumption of persistence. According to monitoring results the compound proved to be not easily degradable both, in STPs and in environmental waters. The substance is therefore assumed to be sufficiently *persistent* to allow for application of mobility criteria.

However, again no experimental data are reported in the REACH dossier, only estimations by QSAR. This is not compliant with REACH requirements. Following REACH guidance documents, for ionisable or ionic compounds experimentally determined data on adsorption/desorption are required. This holds also true for the mobility evaluation scheme. Correspondingly, using KOCWIN for calculation as recommended for non-ionisable compounds, a warning is issued that  $K_{OC}$  may be sensitive to pH. The value calculated (MCI-method) is  $\log K_{OC}$  1.83. This is far below the cut-off for mobility of  $\log K_{OC}$  4.5

While QSAR normally cannot be used for ionisable compounds, the substance bears at least one negative charge, is soluble in water (g/L range), and precipitation or complexation within soil is unlikely. Due to the net negative charge of most soils adsorption will be rather lower than estimated by calculation. Therefore, the compound is assessed to be *mobile*, being in line with available monitoring data. By default, however, no assessment would be possible without experimental data.

### Toxicity assessment

The compound does not fulfil T criteria – neither due to classification & labelling, nor because of a low DNEL (833  $\mu\text{g}/\text{kg}$  bw/day).

### Conclusion

The compound could not be evaluated following the default assessment scheme for PMT properties because of missing experimental values for both, degradability and mobility.

By expert assessment, the compound is concluded to be **relevant but not critical in raw water** (based on monitoring data on behalf of missing data on P):

- E1/E2 fulfilled
- P questionable: approximately 50% removal in STPs reported, and based on QSAR alone the compound would be regarded as not *persistent* in water. But obviously biodegradation is not sufficiently high to cope with exposure according to monitoring data.
- M fulfilled (based on QSAR supported by further considerations)
- T not fulfilled

While a thorough PMT assessment was not possible due to missing experimental data, these tentative assessment results are not in contradiction to reported monitoring data.

### 4.3.2 Tri(chloropropyl) phosphate, TCPP, CAS: 13674-84-5

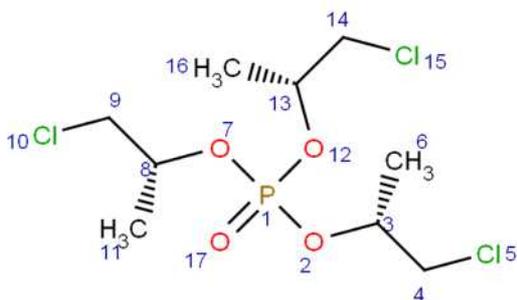
The compound is used as a flame retardant and was selected due to high concentrations in STP effluents with a high frequency of detection and no or insignificant STP removal (Loos, et al., 2013; Reemtsma, et al., 2006; Rodil, et al., 2012). TCPP was detected in drinking water samples in Spain (more than 60% of samples) with a median concentration of 40 mg/L (Rodil, et al., 2012). Further, high water cycle spreading index (see section 2.6.1) was determined for this compound, confirming its relevance (Reemtsma, et al., 2006). Altogether, 3 independent reports confirm high STP effluent concentrations (see Table 28).

#### Exposure

As the substance is fully REACH registered, E1 (exposure tier 1) is fulfilled. Due to a high tonnage band of 10,000 to 100,000 tons per year the substance is relevant independently of specified ERCs. However, specified ERCs indicate considerable environmental release: From the high category, ERCs 4, 5, 8a are reported, from the medium to high category ERCs 8c and 8F. From the medium category, ERCs 8B, 8E, and 10A apply. Combined with tonnage this points to a high environmental exposure level. Therefore, the plausibility assessment for exposure based on REACH registration data is in agreement with observed environmental exposure from monitoring programs.

#### Substance characterisation

The substance has the following structure:



The substance is in the applicability domain, soluble (ca. 1 g/L) and characterized to be non-ionisable in the environmentally relevant pH range based on predicted values (JChem). The compound will therefore be neutral in the environment.

#### Persistence assessment

The substance is not readily biodegradable (14% DOC within 28 days in OECD 301E). However, an enhanced biodegradation screening test is available. A closed bottle test (OECD 301D) was prolonged to 60 days and 60% mineralisation (based on O<sub>2</sub>-consumption) was reached (RL2). Based on this test, the compound is evaluated as not persistent in water according to the persistence evaluation scheme.

However, this is in contradiction to the negligible removal in STPs, the P assessment within REACH PBT (characterized as P based on the experimental screening test data mentioned above) as well as QSAR prediction using BIOWIN: BIOWIN 6: <<0.5; BIOWIN 3: 2.11, i.e. < 2.25). The latter would lead to P according to QSAR, in spite of a fast biodegradability prediction by BIOWIN 2 (p= 1.0). According to the persistence evaluation scheme, QSAR is however not applicable because available experimental data are assumed to be of higher relevance and sufficient for P assessment.

While the enhanced biodegradation screening test data point to non-persistence, obviously, relative removal in STPs is negligible.

### Mobility assessment

Due to the applied methodology, assessment of mobility is per default restricted to *persistent* compounds. However, according to monitoring results the compound turned out to be not or only marginally degraded both, in STPs and in environmental waters (judging from the concentrations quantified). The substance is therefore assumed to be sufficiently *persistent* to allow for application of mobility criteria.

No reliable experimental data are reported in the REACH dossier. Because TCPP is non-ionisable, estimation by QSAR is applicable. Correspondingly, using KOCWIN for calculation as recommended for non-ionisable compounds, the value calculated (MCI-method) is  $\log K_{OC}$  3.21. This is considerably below the cut-off for mobility of  $\log K_{OC}$  4.5. The substance is therefore characterized to be *mobile* (M).

### Toxicity assessment

The compound does not fulfil T criteria – neither due to classification & labelling, nor because of a low DNEL (520  $\mu\text{g}/\text{kg}$  bw/day).

### Conclusion

Following the default assessment scheme for PMT properties the compound would have been evaluated as not *persistent* (not P) in water due to the pass level reached in an enhanced biodegradation screening test. This is in line with REACH guidance documents R. 11 (ECHA, European Chemicals Agency, 2012c) and R.7b (ECHA, European Chemicals Agency, 2012a). In consequence, the compound is assessed by default as not PMT and not relevant in raw water, because one decisive criterion – persistence – is not fulfilled. However, a more thorough analysis of available data leads to the following conclusions:

- E1/E2 fulfilled
- P fulfilled, as concluded from expert assessment. Opposing results from the enhanced biodegradation screening test reflect a true borderline case: a closed bottle test (OECD 301D) was prolonged to 60 days, the maximum allowed for prolongation according to REACH guidance document R.7B (ECHA, European Chemicals Agency, 2012a); and 60% mineralisation achieved (based on  $\text{O}_2$ -consumption) is the minimum to fulfil pass levels according to the OECD 301 tests. Consistently, the negative test on ready biodegradability, no or insignificant reported relative removal in STPs (Reemtsma, et al., 2006) as well as QSAR results (BIOWIN 6:  $\ll 0.5$ ; BIOWIN 3: 2.11, i.e.  $< 2.25 \rightarrow$  P) indicate P.
- M fulfilled
- T not fulfilled

By expert assessment, the compound is concluded to be **relevant but not critical in raw water**.

#### 4.3.3 Benzotriazole, 1H-, CAS: 95-14-7

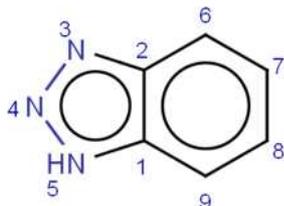
The compound is used as a corrosion inhibitor and was selected due to relevant concentrations detected in river water (median 226 ng/L) and groundwater, and extremely high concentrations in STP effluents (median 2.7  $\mu\text{g}/\text{L}$ , see Table 28) (Loos, et al., 2013; Loos, et al., 2009; Loos, et al., 2010).

## Exposure

As the substance is fully REACH registered, E1 (exposure tier 1) is fulfilled. A tonnage band of 1,000 to 10,000 tons per year and relevant ERCs indicate relevant environmental release: from the high category, ERCs 4, 8a and 8d are reported. Therefore, the plausibility assessment for exposure based on REACH registration data is in agreement with observed environmental exposure from monitoring programs.

## Substance characterisation

The substance has the following structure:



The substance is in the applicability domain, highly soluble (around 20 g/L) and characterized to be non-ionisable in the environmentally most relevant pH range 6 to 8 due to the following predicted value (JChem):

$pK_a$  (lowest): 8.6

The compound will therefore be regarded to be neutral under most prevalent environmental conditions. However, the predicted  $pK_a$  of 8.6 for acidic functionality is very close to the cut-off of  $pK_a < 8.5$  for relevant acidic functionality in the environment.

## Persistence assessment

The substance is hydrolytically stable and not readily biodegradable (0% ThOD within 28 days in OECD 301D). However, a test on inherent biodegradability is available (OECD 302B). While 83% degradation were reached within 28 days (DOC removal), the 3-hour value was too high (19%) and after 7 days only 50% degradation was reached. Based on these data, the compound is evaluated as *persistent* (P) according to the persistence evaluation scheme. This corresponds well with a high median effluent concentration reported for STPs of 2.7  $\mu\text{g/L}$  (Loos, et al., 2013) as well as monitoring results for river water and groundwater (Loos, et al., 2009; Loos, et al., 2010).

## Mobility assessment

Experimental data from a test following the batch equilibrium method with different soil types are available. The geometric mean value for  $K_{OC}$  is 51.7, i.e.  $\log K_{OC} = 1.71$ . This is far below the cut-off for mobility of  $\log K_{OC} 4.5$ . The compound is therefore assessed to be *mobile* (M).

## Toxicity assessment

The compound does not fulfil T criteria – neither due to classification & labelling, nor because of a low DNEL (540  $\mu\text{g/kg bw/day}$ ).

## Conclusion

According to the methodology for PMT assessment, the substance is evaluated to be **relevant in raw water (P, M, E1, E2 fulfilled), but not critical in raw water (T not fulfilled)**.

#### 4.3.4 Diuron, CAS: 330-54-1

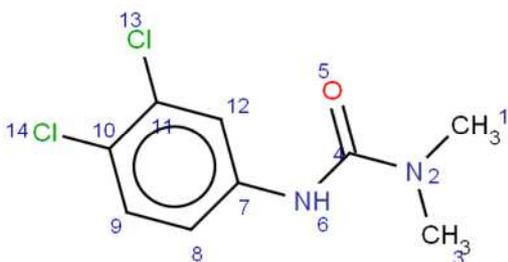
The compound is used as a broad band herbicide and biocide and was selected because it was detected in river water and groundwater in occasionally relevant concentrations (Loos, et al., 2009; Loos, et al., 2010) and identified by IOW/INERIS (IOW/INERIS, 2009) as a compound difficult to remove in drinking water treatment. The PEC2 for surface water derived by IOW/INERIS including measurements blow their respective LOD with ½ of this value is 0.168 µg/L. It is further reported in occasionally relevant concentrations in STP effluents (90<sup>th</sup> percentile: 83 ng/L) (Loos, et al., 2013).

#### Exposure

As the substance is fully REACH registered, E1 (exposure tier 1) is fulfilled. A tonnage band of 100 to 1,000 tons per year and relevant ERCs indicate relevant environmental release: from the high category, ERCs 5 and 10B are reported, from the medium release category ERC 10A. Therefore, the plausibility assessment for exposure based on REACH registration data is in agreement with observed environmental exposure from monitoring programs.

#### Substance characterisation

The substance has the following structure:



The substance is in the applicability domain, soluble (around 29 mg/L) and characterized to be non-ionisable at environmental conditions based on predicted values (JChem). The compound is therefore regarded to be neutral in the environment.

#### Persistence assessment

The substance is hydrolytically stable and not readily biodegradable (0% ThOD within 28 days in OECD 301F). No further relevant test results are reported. No PBT assessment is published within the REACH dossier. Under these conditions the persistence evaluation scheme foresees to apply QSAR to decide upon P. BIOWIN-results were the following: BIOWIN 2 0.013; BIOWIN 6: 0.014; BIOWIN 3: 2.27. Thus, while there is clearly no indication for fast biodegradability, the BIOWIN 3 result is slightly above the threshold for persistence (2.25 and lower). Based on these data, the compound is evaluated as not *persistent* (not P) in water according to the persistence evaluation scheme. This is, however, a questionable result. Monitoring data point to no or slow biodegradation in STPs and the environment. And the decisive result of BIOWIN 3 is very close to the cut-off. Deviating from the default, the compound will be regarded to be *persistent* (P) for the further assessment.

### Mobility assessment

Experimental data from a test following the batch equilibrium method with different soil types are available. The geometric mean value for  $K_{OC}$  is 384.3, i.e.  $\log K_{OC} = 2.59$ . This is far below the cut-off for mobility of  $\log K_{OC}$  4.5. The compound is therefore assessed to be mobile (M).

### Toxicity assessment

The compound is *toxic* due to classification and labelling: STOT RE2 (H373). Further, it is classified as Carc. Cat.2 (H351) which – without further information on possible thresholds – would lead to  $T_{screen}$  (i.e. *toxic* at the screening level). No DNEL (general population, oral, long term) is published in the REACH dossier. According to Cramer, the compound is high class, which would also correspond to  $T_{screen}$ .

### Conclusion

According to the PMT decision logic, the substance is evaluated to be **critical in raw water (P, M, E1, E2 and T fulfilled)**. However, as pointed out above, following the default assessment scheme for P, the substance would be evaluated as being not PMT, i.e. neither *pervious*, nor *relevant* or *critical* in raw water. This is because of the border-line QSAR result, leading to not P in water. This borderline case may be taken as an indication that our methodology is not overly conservative.

#### 4.3.5 Bisphenol A, CAS: 80-05-7

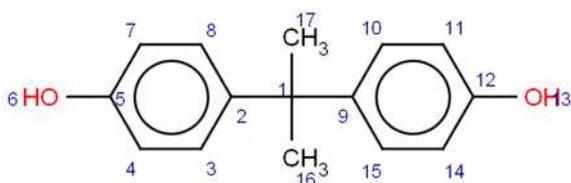
The compound was selected because it was detected in river water and groundwater in occasionally relevant concentrations (Loos, et al., 2009; Loos, et al., 2010). Further, a relevant PEC2 of 0.143  $\mu\text{g/L}$  for surface water was derived by IOW/INERIS (IOW/INERIS, 2009) based on a frequency of detection of 51%, including measurements below their respective LOD with  $\frac{1}{2}$  of this value. Kumar & Xagorarakis (Kumar and Xagorarakis, 2010) gave this compound a high priority for US stream water/source water with a high overall score (rank 2 of 100 compounds).

### Exposure

As the substance is fully REACH registered, E1 (exposure tier 1) is fulfilled. A tonnage band of 1,000,000 tonnes and more per year and relevant ERCs indicate relevant environmental release: From the high category, ERCs 4 and 5 are reported, from the medium to high category ERCs 8c and 8F. From the medium category, ERC 10A applies. Combined with the very high tonnage this indicates a high environmental exposure level. Therefore, the plausibility assessment for exposure based on REACH registration data is in agreement with observed environmental exposure from monitoring programs.

### Substance characterisation

The substance has the following structure:



The substance is in the applicability domain, soluble (around 300 mg/L) and characterized to be non-ionisable at environmental conditions based on predicted values (JChem). The compound is therefore regarded to be neutral in the environment.

### Persistence assessment

The substance is hydrolytically stable, but readily biodegradable (e.g. 89% ThOD within 28 days in OECD 301F). Also higher tier data are available which seem to demonstrate rapid degradation in surface waters, however no in depth assessment was possible within the scope of this project. Based on these data, the compound is evaluated to be not *persistent* (not P) in water according to the persistence evaluation scheme.

### Mobility assessment

In a strict sense, mobility criteria do only apply to *persistent* compounds. Nonetheless, data are analysed here for mobility based on criteria developed under the assumption of persistence.

Several reliable experimental data from tests following the batch equilibrium method with different soil types are available. The geometric mean value for  $K_{OC}$  is about 759 L/kg, i.e.  $\log K_{OC} = 2.88$ . This is far below the cut-off for mobility of  $\log K_{OC} 4.5$ . The compound is therefore assessed to be *mobile* (M).

### Toxicity assessment

The compound is *toxic* due to classification and labelling: Repr. Cat. 2 (H361f). The DNEL (general population, oral, long term) published in the REACH dossier is 50  $\mu\text{g}/\text{kg bw}/\text{d}$  and thus above the cut-off for T.

### Conclusion

According to the PMT decision logic, the substance is evaluated to be **neither PMT, nor *pervious*, *relevant* or *critical* in raw water**, because one decisive criterion – persistence – is not fulfilled. However, as pointed out above, the substance was assessed to

- have a *relevant* exposure potential (E1/E2 fulfilled),
- be *mobile* in regard to raw water (M)
- fulfill criteria for *toxic* (T)

and was in fact found in environmental monitoring studies. Thus, Bisphenol A is an example for compounds quantified in environmental waters in occasionally relevant amounts in spite of definitely not fulfilling PMT properties. This is explained by the fact that the higher the level of exposure (assumed to be very high, see subsection on exposure potential) the higher the biodegradation rate necessary to keep environmental concentrations low.

#### 4.3.6 Nitritotriacetic acid (NTA), CAS: 139-13-9

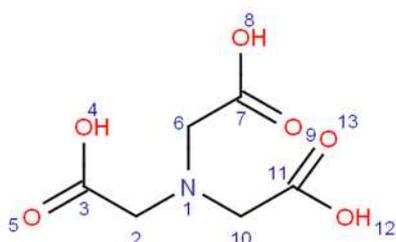
The compound is used as a complexing agent and was selected because it was detected with high frequency (77%) and relevant to high concentrations (maximum 10  $\mu\text{g}/\text{L}$ , LOQ 0.1-0.5  $\mu\text{g}/\text{L}$ ) in river water (Schäfer, et al., 2011).

## Exposure

As the substance is fully REACH registered, E1 (exposure tier 1) is fulfilled. A tonnage band of 100 to 1,000 tons per year and relevant ERCs indicate relevant environmental release: from the high category, ERCs 4, 5, 8A, 8D, 10B and 11B are reported, from the medium to high release category ERCs 8C and 8F, and from the medium release category ERC 10A. Further, the complexing agent NTA is used extensively in washing agents. Substantial and repeated discharge into the environment must be assumed for this use. Therefore, considerable environmental exposure may be anticipated and the plausibility assessment for exposure based on REACH registration data is in agreement with observed environmental exposure from monitoring programs.

## Substance characterisation

The substance has the following structure:



The substance is in the applicability domain, highly soluble (around 1 g/L) and characterized to be ionisable at environmental conditions based on predicted values (JChem):  $pK_a$  for carboxylic acid groups 3.5. The compound is therefore negatively charged in the environment (3 negative charges anticipated).

## Persistence assessment

The substance is readily biodegradable (e.g. 89% CO<sub>2</sub> within 14 days in OECD 301B). Also higher tier data are available which seem to demonstrate rapid (primary) degradation in a river sediment system, however, no in depth assessment was possible within the scope of this project. Based on these data, the compound is evaluated to be not *persistent* (not P) in water according to the persistence evaluation scheme.

## Mobility assessment

In a strict sense, mobility criteria do only apply to *persistent* compounds. Nonetheless, data are analysed here for mobility based on criteria developed under the assumption of persistence.

No experimental data are available. This is not compliant with REACH requirements. Following REACH guidance documents, for ionisable or ionic compounds experimentally determined data on adsorption/desorption are required. This holds also true for the mobility evaluation scheme. Correspondingly, using KOCWIN for calculation as recommended for non-ionisable compounds, a warning is issued that  $K_{OC}$  may be sensitive to pH. The value calculated (MCI-method) is  $\log K_{OC}$  1.42. This is far below the cut-off for mobility of  $\log K_{OC}$  4.5

While QSAR normally cannot be used for ionisable compounds, the substance bears three negative charges, is soluble in water (g/L range), and as a complexing agent precipitation upon binding of cations is not probable. Due to the net negative charge of most soils adsorption will be rather lower than estimated by

calculation. Therefore, the compound is assessed to be *mobile*, being in line with available monitoring data. By default, however, no assessment would be possible without experimental data.

### Toxicity assessment

The compound is *toxic* at the screening level ( $T_{\text{screen}}$ ) due to classification and labelling: Carc. Cat.2 (H351). The DNEL (general population, oral, long term) published in the REACH dossier is far above the threshold for toxicity (400  $\mu\text{g}/\text{kg}$  bw/d).

### Conclusion

According to the PMT decision logic, the substance is evaluated to be **neither PMT, nor *pervious, relevant* or *critical* in raw water**, because one decisive criterion – persistence – is not fulfilled. However, as pointed out above, the substance was assessed to

- have a *relevant* exposure potential (E1/E2 fulfilled),
- be *mobile* in regard to raw water (M)
- fulfill criteria for *toxic* at the screening level ( $T_{\text{screen}}$ )

and was in fact detected with high frequency and relevant concentrations in river water. NTA is therefore yet another example for compounds present in environmental waters while definitely not fulfilling PMT properties. This is explained by the fact that the higher the level of exposure (assumed to be considerably, especially due to the use as complexing agent in washing agents) the higher the biodegradation rate necessary to keep environmental concentrations low.

#### 4.3.7 2,4,6-Trinitrotoluene, CAS: 118-96-7

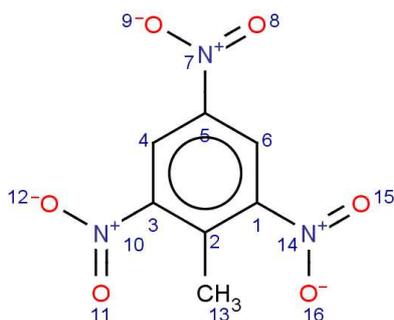
The compound was selected because it was detected with relevant frequency (52%) and high maximum concentration (3.5  $\mu\text{g}/\text{L}$ , LOQ: 0.09 – 20 ng/L) in river water (Schäfer, et al., 2011).

### Exposure

As the substance is fully REACH registered, E1 (exposure tier 1) is fulfilled. A tonnage band of 10,000 to 100,000 tons per year and relevant ERCs indicate relevant environmental release: from the high category, ERCs 4, 8A and 8D are reported, from the medium release category ERC 8E. Therefore, considerable environmental exposure may be anticipated and the plausibility assessment for exposure based on REACH registration data is in agreement with observed environmental exposure from monitoring programs.

### Substance characterisation

The substance has the following structure:



The substance is in the applicability domain, moderately soluble (127 mg/L) and characterized to be non-ionisable at environmental conditions based on predicted values (JChem). The compound is therefore regarded to be neutral in the environment.

### Persistence assessment

No valid data on hydrolysis are available. The compound is not readily biodegradable (1.27% ThOD corresponding to 18% primary degradation within 28 days). No further relevant test results are reported. A PBT assessment is published within the REACH dossier, however the justification for considering the compound as not *persistent* (fish metabolism) is not relevant in the scope of PMT assessment. Under these conditions the persistence evaluation scheme foresees to apply QSAR to decide upon P. BIOWIN-results were the following: BIOWIN 2 0.00; BIOWIN 6: 0.00; BIOWIN 3: 2.11. Thus, QSAR predicts the compound to be *persistent*.

Based on these data, the compound is evaluated to be *persistent* (P) according to the persistence evaluation scheme. This is in agreement with monitoring results.

### Mobility assessment

Experimental data from a test following the batch equilibrium method with different soil types are available. The geometric mean value for  $K_{OC}$  is 4080 assuming 2% OC on average, i.e.  $\log K_{OC} = 3.61$ . This is below the cut-off for mobility of  $\log K_{OC} 4.5$ . The compound is therefore assessed to be *mobile* (M).

### Toxicity assessment

The compound is *toxic* due to classification and labelling: STOT RE2 (H373). The DNEL (general population, oral, long term) published in the REACH dossier is 5  $\mu\text{g}/\text{kg bw}/\text{d}$ . This is below the threshold for toxicity of 9  $\mu\text{g}/\text{kg bw}/\text{d}$ . Therefore, also according to DNEL the compound is assessed to fulfil T.

### Conclusion

According to the PMT decision logic, the substance is evaluated to be **critical in raw water (P, M, E1, E2 and T fulfilled)**. The assessment is in line with monitoring data regarding E2, P, and M.

#### 4.3.8 4-/5-Tolyltriazole, CAS: 29385-43-1

The compound is used as a corrosion inhibitor in de-icing fluids and dishwashing agents. It was selected due to extremely high concentrations in STP effluents (median concentrations between 1 and 10  $\mu\text{g}/\text{L}$ ) with high frequency of detection (Loos, et al., 2013; Reemtsma, et al., 2006). Further, a low relative removal in STPs (ca. 10%) is reported for this compound and a high water cycle spreading index (see section 2.6.1) was determined (between 10 and 100) (Reemtsma, et al., 2006).

## Exposure

As the substance is fully REACH registered, E1 (exposure tier 1) is fulfilled. A tonnage band of 1,000 to 10,000 tons per year and relevant ERCs indicate relevant environmental release: from the high category, ERCs 4, 8a and 8d are reported. Therefore, the plausibility assessment for exposure based on REACH registration data is in agreement with observed environmental exposure from monitoring programs.

## Substance characterisation

The substance has the following structure (left: 4-tolyltriazole; right: 5-tolyltriazole):



Actually, multi-constituent substances are not in the applicability domain of the PMT assessment. However, constituents of the substance are restricted to only two structural isomers of high similarity. Therefore, an assessment is possible. Otherwise, the substance is in the applicability domain, highly soluble (around 4 g/L) and characterized to be non-ionisable in the environmentally most relevant pH range 6 to 8 due to the following predicted value (JChem, both isomers):

$pK_a$  (lowest): 8.8 (both isomers)

The substance will therefore be regarded to be neutral under most prevalent environmental conditions. However, the predicted  $pK_a$  of 8.8 for acidic functionality is very close to the cut-off of  $pK_a < 8.5$  for relevant acidic functionality in the environment.

## Persistence assessment

The substance is hydrolytically stable and not readily biodegradable (4% ThOD within 28 days in OECD 301D). Further, a test on inherent biodegradability for the 4-tolyltriazole is available (OECD 302B). No biodegradation was observed within 28 days while the test was valid.

Based on these data, the compound is evaluated as *persistent (P)* according to the persistence evaluation scheme. This is in agreement with reported high median effluent concentration for STPs as well as the associated low relative removal in STPs (see above).

## Mobility assessment

Experimental data from a test following the batch equilibrium method with different soil types are available. The geometric mean value for  $K_{OC}$  is 78.9, i.e.  $\log K_{OC} = 1.90$ . This is far below the cut-off for mobility of  $\log K_{OC} 4.5$ . The compound is therefore assessed to be *mobile (M)*.

## Toxicity assessment

The compound does not fulfil T criteria – neither due to classification & labelling, nor because of a low DNEL (250  $\mu\text{g}/\text{kg bw}/\text{day}$ ).

## Conclusion

Using the PMT assessment scheme implemented in KnowSEC, the substance is evaluated to be **relevant in raw water (P, M, E1, E2 fulfilled), but not critical in raw water (T not fulfilled)**.

### 4.3.9 Acesulfame K, CAS: 55589-62-3

6-methyl-1,2,3-oxathiazin-4(3H)-one 2,2-dioxide, potassium salt (Acesulfame K) is used as an artificial sweetener. It was selected due to extremely high concentrations in STP effluents (median concentration 14.3 µg/L) with high frequency of detection (Loos, et al., 2013).

## Exposure

As the substance is fully REACH registered, E1 (exposure tier 1) is fulfilled. A tonnage band of 1,000 to 10,000 tons per year and ERC 1 (manufacture) indicate relevant environmental release. No further ERCs are specified, while use as a sweetener implies widespread release during food production as well as by consumers. As a consequence, considerable environmental release would be anticipated from this use pattern. This is in agreement with observed environmental exposure from monitoring programs.

## Substance characterisation

The substance has the following structure:



The substance is in the applicability domain of the PMT assessment, is highly soluble (around 237 g/L) and characterized to be ionisable in the environmentally most relevant pH range 6 to 8 due to the following predicted value (JChem, both isomers):

$pK_a$  (lowest): 3.0

The substance will therefore be regarded to be negatively charged under environmental conditions.

## Persistence assessment

The substance is hydrolytically stable and not readily biodegradable (2% DOC within 28 days in OECD 301A). Further, a test on inherent biodegradability for Acesulfame K is available (OECD 302B). No relevant biodegradation was observed within 28 days (10%) while the test was valid.

Based on these data, the compound is evaluated as *persistent (P)* according to the persistence evaluation scheme. This is in agreement with the reported high median effluent concentration for STPs.

## Mobility assessment

No experimental data are available. This is not compliant with REACH requirements. Following REACH guidance documents, for ionisable or ionic compounds experimentally determined data on

adsorption/desorption are required. This holds also true for the mobility evaluation scheme. Using KOCWIN for calculation as recommended for non-ionisable compounds using the structure for the neutral form, the value calculated (MCI-method) is  $\log K_{OC} 0.33$ . This is far below the cut-off for mobility of  $\log K_{OC} 4.5$

While QSAR normally cannot be used for ionisable compounds, the substance bears a negative charge and is highly soluble in water (g/L range). Due to the net negative charge of most soils adsorption is anticipated to be rather lower than estimated by calculation. Further, high STP effluent concentrations do also point to a very low adsorption potential. Therefore, the compound is assessed to be *mobile (M)*, being in line with available monitoring data. By default, however, no assessment would be possible without experimental data.

### Toxicity assessment

The compound does not fulfil T criteria – neither due to classification & labelling (not classified), nor because of a low DNEL (64.3 mg/kg bw/day).

### Conclusion

Using the PMT decision rules, the substance is evaluated to be **relevant in raw water (P, M, E1, E2 fulfilled), but not critical in raw water (T not fulfilled)**. However, according to the default assessment scheme, mobility could not have been evaluated due to missing experimental data (ionizable compound).

## 4.4 Summary and discussion

By selection of REACH registered compounds based on criteria set to enlarge the probability to capture compounds fulfilling one or more of the properties P, M and T, 84 substances resulted. All of these were evaluated according to the PMT assessment scheme developed beforehand.

From the 84 monoconstituent substances,

- 8 were judged to be *pervious* to raw water (P, M, but not E2),
- 16 were concluded to be *relevant* in raw water (P, M, E2 but not T/T<sub>screen</sub>),
- 5 were assessed to be *critical* in raw water (P, M, E2, T) and
- 4 were evaluated to be *critical* in raw water at the screening level (P, M, E2, T<sub>screen</sub>).

Further, from the 8 compounds determined to be *pervious* to raw water, 2 and 1 substances fulfilled in addition criteria for T and T<sub>screen</sub>, respectively. However, these are not expected to be relevant because of low exposure potentials deduced from disclosed tonnages and environmental release categories (ERCs).

For validation of the PMT assessment rules, available literature data on environmental exposure and/or monitoring were retrieved for the 9 compounds determined to be critical in raw water (+/- screening level) and those 3 compounds *pervious* to raw water but at the same time evaluated as T or T<sub>screen</sub> (i.e. for altogether 12 compounds). As far as literature data could be retrieved, PMT assessment results were largely confirmed or were not in contradiction to these data:

1-methyl-4-(methylsulfonyl)-2-nitrobenzene and triethyl phosphonoacetate were assessed to meet the characteristics of PMT and PMT<sub>screen</sub> compounds, respectively. Because E2 is not fulfilled, they are regarded to be *pervious* but not *critical* in raw water. In both cases, no indications for environmental exposure could be identified, corroborating E2-results for these compounds.

Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate was concluded to meet PMT criteria. Because E2 is fulfilled, it is regarded to be critical in raw water. There are indeed indications from the USA that environmental exposure may be relevant.

4-aminophenol was assessed be a PMT compound. E2 is fulfilled, thus it is regarded to be critical in raw water. Available information on environmental exposure together with monitoring data corroborate results of the E2 module as well as the PM assessment.

The transition metal complex tricarbonyl(methylcyclopentadienyl)manganese (MMT) was concluded to meet the characteristics of a PMT compound. Because E2 is not fulfilled, it is regarded to be *pervious* but not *critical* in raw water. Available literature data essentially corroborate assessment results for P and M and are not in contradiction to E2 (no monitoring data).

Cyanide, 1,2-dichloroethane and trichloroethene were assessed to be PMT compounds, tetrachloroethene and naphthalene were determined to be PMT<sub>screen</sub> (i.e. T only screening level). Because E2 is fulfilled, these compounds are regarded to be critical in raw water (screening level for the latter two compounds) according PMT assessment rules. Available information on release (E-PRTR) and monitoring (Water Framework Directive) for these compounds corroborate both, the E2-assessment result as well as the PMT conclusion.

Dibutyl hydrogen phosphate was determined to meet the characteristics of a PMT<sub>screen</sub> compound. Because E2 is fulfilled, it is regarded to be critical in raw water (screening level for T). Concluding from the scarce monitoring data, E2-assessment in principle was correct but may be somewhat too precautionous. Controversial data on biodegradation in STP mirror the borderline state regarding P. In this case, a slightly conservative prediction for P by the PMT assessment scheme is intended.

Triclosan fulfilled the characteristics of a PMT<sub>screen</sub> compound. Because E2 was met, it is regarded to be probably critical in raw water (screening level for T). Concluding from available monitoring data, PMT assessment produced reasonable results considering that Triclosan is a borderline case with regard to both, mobility (high adsorption) as well as persistence.

Naphthalene as a compound critical in raw water (screening level for T) is interesting, as it is a low molecular PAH and thus of relatively high solubility. Thus, higher molecular weight PAH with heteroatoms (especially nitrogen, possibly also oxygen and sulphur) as substituents or within the aromatic ring system (so called semipolar polycyclic aromatic compounds, sPAC) could also be of relevance regarding raw water contamination. Results of an UBA project on the importance of sPAC under REACH were published recently (Schwarz, et al., 2014).

Experience gathered by the assessment of PMT properties for 82 from 84 compounds fulfilling E1 lead to amendment of the PMT assessment rules in some respects:

- The applicability domain was further specified, in that transition metal complexes are in principle within the applicability domain with the restriction that only experimentally derived values for  $K_{OC}$  and biodegradation may be used for the assessment (QSAR is not applicable). Further, biodegradation is confined to the organic part of the substance.
- The substance characterisation was amended by explicitly accounting for salts with at least one organic constituent: Each constituent has to be assessed separately. Only organic ions are relevant for assessment.

- To include also biodegradation data difficult to interpret from non-guideline tests, the conclusion on P from PBT assessment is used under special conditions and in a very constricted way, only, but in priority over QSAR derived data.

Table 29 gives an overview on the selection process applying the PMT methodology on the initial set of 84 mono-constituent compounds. Compounds are differentiated according to their origin (eChemPortal; drinking water directive, DWD; selection based on screening-type information).

It is interesting to note, that 64% of the identified PM compounds are ionisable. Therefore, it is important, indeed, that ionisable compounds are assessed for mobility considering this property explicitly. However, the percentage of ionisable compounds may be somewhat distorted in the present selection of compounds (to a higher value): According to the selection scheme used with eChemPortal, some data for  $K_{OC}$  had to be reported (experimental or calculated). Especially for non-ionisable compounds, however, the endpoint adsorption-desorption may not have been considered (i.e. empty) within the REACH registration dossier; such that those compounds would have been excluded by our assessment right from the start.

A further interesting aspect is the difficulty of selecting *persistent* compounds by simple screening. While eChemPortal was used to preselect for *persistent* compounds, only 49% of the initial set turned out to actually fulfil this property (see section 4.2.3 for an analysis of reasons for this). Similarly, from the 8 compounds originating from the selection based on screening-type information (8 of 10 fulfilling E1), only 1 turned out to be *persistent* (12.5%). This indicates an even lower significance for QSAR based screening.

Another important aspect is that relevant DNELs (oral, long-term, general population) occasionally were not derived even for compounds for which this would obviously be important. For 8 out of 33 PM compounds, no relevant DNELs were published (ECHA) (24%). Notably, 4 of these 8 compounds are (based on classification and labelling) critical in raw water (PMT) or critical at the screening level (PMT<sub>screen</sub>). A further of 3 compounds without DNELs was assessed to be *relevant* in raw water (PM and E2 fulfilled), making environmental exposure highly probable.

To validate the PMT assessment methodology developed in this project, a second analysis was performed. Monitoring data published in the recent literature were analysed for compounds frequently detected and quantified in relevant amounts in environmental waters or sewage treatment plant (STP) effluents. In effect, 20 compounds resulted, summarized together with their monitoring results in Table 28. Further selection according to monitoring data led to 9 compounds with high priority to be evaluated ex post for PMT properties using our assessment scheme. Ideally, those compounds would be classified at least as *relevant in raw water* - that is, fulfilling P, M and E2 - to confirm our PMT assessment methodology. Table 30 summarises the corresponding assessment results.

Following the default assessment scheme for PMT properties produced the following results:

All compounds fulfil E2: in most cases several high release category ERCs apply, often combined with high tonnage levels. Thus, E2 assessment is in full agreement with observed concentrations in STP effluents and / or environmental waters.

1 of 9 compounds (BP-4, ionisable) is dismissed because of lacking experimental data for both, persistence and mobility. One ionisable compound is dismissed because of lacking experimental data for mobility. Therefore, only 7 compounds fulfil minimum data requirements for assessment.

Table 29: Overview on the selection process applying the PMT methodology on the initial set of 84 mono-constituent compounds<sup>1)</sup>

	eChem-Portal	comment	DWD	Comment	SCR	comment	n total	n ionisable	% ionisable
N start	65		9		10		84		
Fulfil-ling E1	65		9		8	n= 2 interme-diates	82		
Suffici-ently soluble	63	n= 2 solubility <= 150 µg/L	9		8		80		
Organic	62	n= 1 inorganic compound	9		8		79		
No Hydroly-sis (degT50 >40 d)	52	10 compounds readily hydrolysable	7	2 compounds readily hydroly-sable	4	4 compounds readily hydrolysa-ble	63		
Not disquali-fied for P by QSAR	39	22 compounds with negative Ready test only ==> QSAR: 13 not P, 9 P	7		2	2 compounds with negative Ready test only ==> QSAR: 2 not P	48		
P	32	7 compounds with redundant test results or "not readily b.", but inherently from ready-Test	5	n= 2 not P	1	1 not P (inherent-ly biodegrad-able)	38	25	66%
PM	28	4 ionisable compounds without appropriate adsorption data for assessment of M	4	n=1 not M	1		33	21	64%
PM-E2	20		4		1		25	18	72%
PMT	4		3		0		7	1	14%
<b>PMT-E2</b>	<b>2</b>		<b>3</b>		<b>0</b>		<b>5</b>	<b>1</b>	<b>20%</b>
PMT <sub>screen</sub>	3	n= 2 Cramer-III; n=1 Carc. Cat. 2	1	Carc. Cat. 2	1	Carc. Cat. 2	5	2	40%
<b>PMT<sub>screen</sub>-E2</b>	<b>2</b>		<b>1</b>		<b>1</b>		<b>4</b>	<b>2</b>	<b>50%</b>
PM, not T	21		0		0		21		
<b>PM-E2, not T</b>	<b>16</b>		<b>0</b>		<b>0</b>		<b>16</b>	<b>15</b>	<b>94%</b>

1): Persistence assessment restricted on water phase: not P = not P in water.

Explanations: DWD = drinking water directive; SCR = selection based on screening-type information; E2 = exposure module 2: fulfilment indicates relevant environmental exposure.

Table 30: 9 compounds given high priority based on monitoring data: results of the ex-post PMT assessment performed to validate the PMT assessment methodology<sup>1)</sup>.

CAS	Name	E1/E2	P	M	T	Overall conclusion <sup>2)</sup>
4065-45-6	Benzophenone-4, BP-4 (UV screen)	<b>Yes</b> , high category ERC, 100 - 1,000 t/a	<b>Questionable</b> : no exp. data → <b>formally not assessable</b> ; QSAR: not P (BIO3: 2.66); ca. 50% removal in STPs	No exp. data for ionisable compound: formally not assessable; Expert assessment: <b>M</b>	<b>Not T</b>	<u>default</u> : not assessable Preliminary assessment: <i>Relevant</i> in raw water (however, P uncertain)
13674-84-5	tri(chloropropyl) phosphate, TCPP (flame retardant)	<b>Yes</b> , several high & medium category ERCs, 10,000 - 100,000 t/a	<u>Not P</u> (default, due to enhanced screening test result); <b>actually P</b> : negligible STP removal, QSAR indicates P (BIO3: 2.11)	<b>M</b>	<b>Not T</b>	PM - relevant, but not critical in raw water <u>default</u> : not PMT, not <i>pervious</i> to raw water
95-14-7	Benzotriazole, 1H- (corrosion inhibitor)	<b>Yes</b> , several high category ERCs, 1,000 - 10,000 t/a	<b>P</b>	<b>M</b>	<b>Not T</b>	PM - relevant, but not <i>critical</i> in raw water
330-54-1	Diuron (herbicide, biocide)	<b>Yes</b> , high and medium category ERCs, 100 - 1,000 t/a	<u>Not P</u> (default, due to QSAR Bio3: 2.27); expert assessment: P (QSAR borderline, high STP effluent concentrations)	<b>M</b>	<b>T</b> (C&L); no DNEL published	<b>PMT - critical in raw water</b> <u>default</u> : not PMT, not <i>pervious</i> to raw water
80-05-7	Bisphenol A	<b>Yes</b> , several high to medium category ERCs, >1,000,000 t/a	<b>Not P</b> (readily biodegradable)	<b>M</b>	<b>T</b> (C&L)	Not PMT, neither <i>pervious</i> , nor <i>relevant</i> or <i>critical</i> in raw water

CAS	Name	E1/E2	P	M	T	Overall conclusion <sup>2)</sup>
139-13-9	nitrilotriacetic acid (NTA) (complexing agent)	<b>Yes</b> , 6 high and 2 medium to high release category ERCs, 100 - 1,000 t/a	<b>Not P</b> (readily biodegradable)	No exp. data for ionisable compound: formally not assessable; Expert assessment: <b>M</b>	<b>T<sub>screen</sub></b> (C&L)	Not PMT, neither <i>pervious</i> , nor <i>relevant</i> or <i>critical</i> in raw water
118-96-7	2,4,6-trinitrotoluene	<b>Yes</b> , 3 high and 1 medium release category ERCs, 10,000 - 100,000 t/a	<b>P</b>	<b>M</b>	<b>T</b> (DNEL)	<b>PMT - critical in raw water</b>
29385-43-1	4-/5-tolyltriazole (corrosion inhibitor: deicing fluids, dishwashing agents)	<b>Yes</b> , 3 high release category ERCs, 1,000 - 10,000 t/a	<b>P</b>	<b>M</b>	<b>Not T</b>	PM - <i>relevant</i> , but not <i>critical</i> in raw water
55589-62-3	Acesulfame K (Sweetener)	<b>Yes</b> , ERC1, 1,000 - 10,000 t/a	<b>P</b>	No exp. data for ionisable compound: formally not assessable; Expert assessment: <b>M</b>	<b>Not T</b>	PM - <i>relevant</i> , but not <i>critical</i> in raw water <u>default</u> : no PMT assessment possible (missing experimental data for K <sub>OC</sub> )

1): Persistence assessment restricted on water phase: not P = not P in water.

2): Conclusions, occasionally considering expert assessments or reported relative efficiencies of removal in sewage treatment plants (STPs). In case one property by default was not assessable, no overall conclusion would result in the default assessment. Deviations from default assessment are indicated.

From these 7 compounds,

- 4 (57%) are by default evaluated not to fulfil all PMT properties and to be *not pervious to raw water* because of being regarded as not *persistent* in water.
- 2 are assessed to be *relevant in raw water* (P, M and E2 fulfilled)
- 1 is identified as *critical in raw water* (P, M, E2 and T fulfilled)

In other words, the PMT assessment methodology developed in this project was successful in predicting

- environmental exposure for all 9 compounds (100%)
- persistence for 6 from 8 compounds with minimum data set (75%; TCPP & Diuron borderline cases, obviously misclassified as not P in water)
- mobility for 6 from 6 compounds with minimum data set (100%)

By expert assessment, further compounds could be included in the assessment or found to actually fulfil P properties:

Regarding biodegradability evaluation, TCPP and Diuron – while formally assessed to be not P in water (borderline), actually were evaluated to most probably fulfil P. Both are borderline cases which may always occur if cut-offs are applied. To avoid as far as possible misclassifications in those instances, particular attention is afforded. While dismissed by default due to lacking experimental data on P and M, the UV screen BP-4 is tentatively assessed to possibly fulfil P (P questionable, but certainly not rapidly biodegradable) based on relative elimination rates in STPs (Rodil, et al., 2012) and most probably also M. Further, the ionisable compound Acesulfam K could be included by expert assessment of M, in spite of missing experimental data for mobility.

Reviewing the monitoring based PMT assessment amended by those expert evaluations as outlined above, leads to the following results:

- 4 (to 5, BP-4 uncertain) further compounds were identified to be *relevant* in raw water (P, M, E2 fulfilled):
  - TCPP (flame retardant)
  - Benzotriazole (corrosion inhibitor)
  - Tolyltriazole (corrosion inhibitor)
  - Acesulfam K (artificial sweetener)
  - BP-4 (UV screen) (however, P uncertain)
- 2 further compounds were identified to be *critical* in raw water (P, M, E2, T fulfilled):
  - Diuron (broad band herbicide – algae growth inhibitor construction sector)
  - 2,4,6-trinitrotoluene (explosive)

This extends the list of compounds identified from the assessment of the 84 compounds from the initial substance pool to

- a total of 7 PMT compounds *critical in raw water*
- a total of 4 PMT<sub>screen</sub> compounds *critical in raw water (screening level)* (no new compounds from monitoring data)
- a total of 20 (to 21, BP-4 uncertain regarding P) PM compounds *relevant in raw water*.

From both validation approaches it is concluded that the PMT assessment methodology results in overall valuable prospective results regarding potential raw water relevance of substances registered under REACH.

With these data at hand, it would be interesting to have an even closer look on data gathered within REACH from chemical safety reports, e.g. for the selection of 7 identified PMT compounds. It would be interesting if the risk assessment performed under REACH accounts for the potential for raw water contamination identified here for these compounds. Further, detailed data from respective CSRs could possibly help to resolve  $T_{\text{screen}}$  for the 4  $\text{PMT}_{\text{screen}}$  compounds to T or not T.

Moreover, Bisphenol A and nitrilotriacetic acid (NTA) were assessed to be *mobile* and to fulfil criteria for T (Bisphenol A) and  $T_{\text{screen}}$  (NTA), respectively. Both are found frequently and in relevant concentrations in surface waters. However, they were clearly identified as readily biodegradable. Therefore they are assessed as being no PMT compounds, i.e. neither *pervious* nor *relevant* or *critical* in raw water. Both are examples for compounds frequently found in environmental waters while definitely not fulfilling PMT properties. This is explained by their high level of exposure (very high annual tonnage level for Bisphenol A; considerable exposure for NTA, especially due to the use as complexing agent in washing agents), leading to quantifiable environmental concentrations in spite of reliable data demonstrating rapid biodegradability.

## 5 Glossary

B	Bioaccumulative (see REACH guidance R.11 for further definition)
Critical in raw water	Substance fulfilling criteria E2, P, M, and T
DegT <sub>50</sub>	Time taken for a 50% decline in mass or concentration of a substance in the environment / an environmental compartment due to degradation. Half-life – specified for different media and degradation processes
DNEL	Derived no effect level
ECETOC	European centre for ecotoxicology and toxicology of chemicals
ECHA	European Chemicals Agency
ERC	Environmental Release Category
ESD	Emission Scenario Document
EUSES	European Union system for the evaluation of chemicals (software)
Half-life	Time interval corresponding to a concentration decrease by a factor of 2 and characterising the rate of a first or pseudo-first order reaction. the half-life and the degradation rate constant are related by the equation $t_{1/2} = \ln(2)/k$
HLC	Henry's Law Constant: a measure for volatility of chemicals from water, temperature dependent
K <sub>d</sub>	Distribution coefficient for adsorption [L/kg]
KnowSEC	Extension of KnowWE, used for documentation and decision support of substance related tasks at UBA
KnowWE	Semantic wiki for the development of diagnostic knowledge bases and OWL/RDF(S) ontologies.
K <sub>OC</sub>	Organic carbon normalized adsorption coefficient [L/kg]
K <sub>OW</sub>	Octanol water partition coefficient
M	Mobile, as defined in section 2.2
OECD	Organisation for Economic Co-Operation and Development
Ontology	A data model to represent information resources and their interconnections
OWL	Web Ontology Language endorsed by the W3C for authoring ontologies or knowledge bases

P	Persistent, as defined in section 2.1
PBT	Persistent, bioaccumulative and toxic (see REACH guidance R.11 for further definition)
Pervious to raw water	Substance fulfilling criteria for P and M (only analysed if E1 fulfilled)
$pK_a$	Acid dissociation constant
$pK_b$	Association constant for protonation of the base; $pK_b \sim 14 - pK_a$ [25°C]
PMT	Persistent, mobile and toxic, as defined in section 2 groundwater
POP	Persistent organic pollutant
PPOP	Polar persistent organic pollutants
PPP	Polar persistent pollutant
QSARs	Quantitative structure activity relationships
Raw water	Water used for drinking water production (before drinking water treatment)
RDF	Resource Description Framework specified by the W3C for modeling of information in web resources.
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals. REACH regulation entered into force on 1 June 2007 (REGULATION (EC) No 1907/2006)
Relevant in raw water	Substance fulfilling criteria for E2, P and M
spERC	Specific environmental release category
STP	Sewage Treatment Plant
SVHC	Substances of very high concern
T	Toxic, as defined in section 2.3
$t_{1/2}$	Half-life
TGD	Technical guidance documents
TRA	Targeted risk assessment (software), developed by ECETOC (= ECETOC TRA)
TTC	Threshold of toxicological concern (Barlow, 2005)

UVCB	Substance of unknown or variable composition, complex reaction products or biological materials
vPvB	Very persistent, very bioaccumulative
W3C	World Wide Web Consortium, the main international standards organisation for the World Wide Web.

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